Synthesis and characterization of tricarbonylchlororhenium(I) complexes bound to the novel bridging ligand dipyrido(2,3-*a*;2′,3′-*h*)phenazine (dpop)

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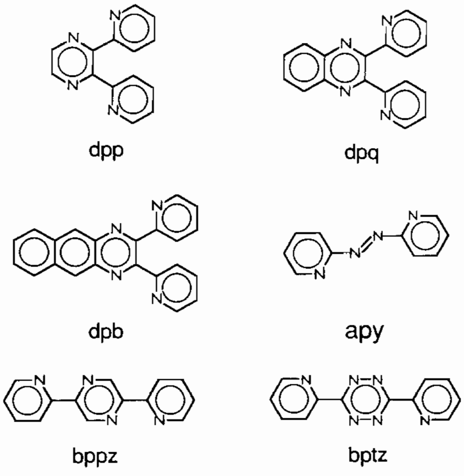
Abstract

Rhenium(I) tricarbonylchloride complexes with the novel planar bis-bidentate ligand dipyrido(2,3-*a*;2′,3′-*h*)-phenazine (dpop) have been prepared and characterized. Electronic absorption spectra show solvatochromic MLCT absorptions in the visible spectrum that are red shifted from tricarbonylchlororhenium(I) complexes with similar bis-bidentate ligands. Electrochemical results show dpop centered reversible reductions in the $[Re(CO)_3Cl]_{1,2}$(dpop) complexes to be at less negative potentials than for similar pyridyl ligands in tricarbonylchlororhenium(I) complexes. Both electronic absorption and electrochemical data suggest that the effects of the cyclized dpop bridging ligand, in comparison with bipyridyl coordinating type bridging ligands, are lower energy electronic absorptions and less negative reversible bridging ligand reduction potentials.

Introduction

The study of tricarbonylhalorhenium complexes bound to novel α-diimine bridging ligands (Scheme 1) has grown recently, due in part to favorable electronic absorption, emission and electrochemical properties for energy transfer processes [1–11]. The design of the bridging ligand directly effects the desired properties of the overall complex due to Re(dπ) → BL(pπ*) MLCT absorption and emission, and ligand centered reductions. Lower energy absorptions and more favorable reduction potentials have been demonstrated as a function of increasing π delocalization within the bridging ligand for the series $[Re(CO)_3Cl](L_2)$; L_2 = dpp > dpq > dpb [1, 3].



Scheme 1.

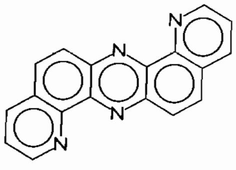


Fig. 1. Dipyrido(2,3-*a*;2′,3′-*h*)phenazine (dpop).

Our research group has been interested in the design of novel bridging ligand–metal systems which best enhance photon-induced energy transfer processes [5, 12–14]. The bis-bidentate ligand dipyrido(2,3-*a*;2′,3′-*h*)phenazine (dpop) (Fig. 1) is the cyclized analogue of bppz, and as such is unique in that it is a planar highly conjugated ligand which contains no σ connected coordinating rings. We wish to report the synthesis and characterization of the mono and bi-metallic $[Re(CO)_3Cl]_{1,2}$(dpop) complexes, and assess the effect of a completely aromatic bridging ligand on electronic properties.

Experimental

Materials

Reagent grade solvents and compounds were used for preparations and experiments described in this work.

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$Re(CO)_5Cl$ was obtained from Pressure Chemical Company, Pittsburgh, PA, and used without purification. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA.

Instrumentation

Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on a Bioanalytic Systems CV-1B cyclic voltammograph with a Hewlett Packard 7044A XY recorder. Cyclic voltammograms were recorded in CH_2Cl_2 using 0.1 M tetrabutylammonium perchlorate as an electrolyte. The platinum working electrode (1.0 mm diameter) was polished and the solutions were thoroughly deoxygenated prior to each scan. An Ag/AgCl (3 M KCl, -0.04 V versus SCE) reference electrode was used and the electrode potentials were verified with $Fe(CN)_6{}^{3-/4-}$ in 1.0 M H_2SO_4 at $+0.49$ V versus SCE. All potentials are reported versus SCE, and are uncorrected for junction potentials. The $E_{1/2}$ for reversible couples reported are estimates obtained by averaging anodic and cathodic peak potentials while E_{ox} or E_{red} values are reported for irreversible processes. IR spectra were recorded as solid KBr samples on a Perkin-Elmer 1420 spectrophotometer from 4000 to 600 cm^{-1}. NMR chemical shifts were obtained on a Varian model Gemini 200 in a 5 mm probe operating at 200 MHz using a 5 s pulse delay.

Synthesis

The dpop ligand was prepared according to the literature [15], with slight temperature modifications as previously described [16]. *Anal.* Calc. for $C_{18}H_{10}N_4$ (mol. mass 282.3): C, 76.58; H, 3.57; N, 19.85. Found: C, 76.33; H, 3.64; N, 19.76%.

[Re(CO)$_3$Cl](dpop)

The monometallic complex was prepared by heating at reflux under a continuous stream of Ar, a mixture of 0.050 g (0.177 mmol) dpop and 0.064 g (0.177 mmol) $Re(CO)_5Cl$ in 0.10 dm^3 CH_3OH, for a period of 14 h. After cooling to room temperature, the solid was collected by vacuum filtration and air dried. The red $[Re(CO)_3Cl](dpop)$ complex was re-dissolved on the fritted disc funnel with $CHCl_3$, and the liquor loaded in several aliquots on an alumina column (15 cm × 2.5 cm diameter) in $CHCl_3$, and eluted with $CHCl_3$. The red band from all aliquots was collected and rotary evaporated to dryness. The product was collected, washed with 0.05 dm^3 $CHCl_3$ to remove any remaining traces of dpop ligand, then with diethyl ether, and vacuum dried. Yield $[Re(CO)_3Cl](dpop)$ (mol. mass 587.99) 0.064 g (0.109 mmol) 61%. *Anal.* Calc. for $C_{21}H_{10}N_4O_3ReCl$: C, 42.89; H, 1.72; N 9.52. Found: C 42.73: H, 1.78; N, 9.41%. ν (cm^{-1}) 2020; 1905 (broad).

[Re(CO)$_3$Cl]$_2$(dpop)

The bimetallic $[Re(CO)_3Cl]_2(dpop)$ complex was prepared by heating at reflux under a continuous stream of Ar, a mixture of 0.050 g (0.177 mmol) dpop and 0.141 g (0.390 mmol slight excess) $Re(CO)_5Cl$ in 0.100 dm^3 CH_3OH, for a period of 14 h. After cooling to room temperature, the grey solid was collected by vacuum filtration, washed with 0.20 dm^3 of hot CH_3OH, then 0.10 dm^3 of $CHCl_3$. The product was finally washed with diethyl ether and vacuum dried. Yield $[Re(CO)_3Cl]_2(dpop)$ (mol. mass 893.68) 0.136 g (0.109 mmol) 86%. *Anal.* Calc. for $C_{24}H_{10}N_4O_6Re_2Cl_2$: C, 32.26; H, 1.13; N 6.27. Found: C 32.01: H, 1.18; N, 6.23%. ν (cm^{-1}) 2015; 1910 (broad).

Results and discussion

The syntheses of the mono and bi-metallic $[Re(CO)_3Cl]_{1,2}(dpop)$ complexes are based on previously reported preparations of halocarbonylrhenium(I) complexes with similar nitrogen aromatic heterocyclic ligands such as bpym [4, 6, 9], dpp [3, 5] or bppz [2] which prescribe heating the dpop ligand and $Re(CO)_5Cl$ in an inert deoxygenated solvent. The mono and bimetallic $[Re(CO)_3Cl]_{1,2}(dpop)$ complexes were preferentially prepared by heating a 1:1 or 1:2 (slight metal excess) mixture of the dpop ligand with $Re(CO)_5Cl$ in methanol at reflux. After isolation, chromatography and washing, the products were identified as $[Re(CO)_3Cl]_{1,2}(dpop)$ by percent C, H, and N analyses, and the C/N ratio. The purity of each complex was further verified by ^1H NMR characterization, IR spectra, clarity of cyclic voltammograms, and characteristic solvatochromic behavior of MLCT transitions.

The monometallic $[Re(CO)_3Cl](dpop)$ complex is slightly soluble in a number of organic solvents and displays a broad, intense ($\epsilon > 4 \times 10^3$ M^{-1} cm^{-1}) solvent-dependent absorption (440–470 nm) in the visible spectrum, with more intense solvent independent absorptions at 405, 345 and 310 nm (Fig. 2(a), Tables 1 and 2). The lowest energy absorption follows normal solvatochromic behavior with shorter wavelengths being observed in solvents of higher polarity as has been previously reported for similar Re(I) complexes with nitrogen aromatic heterocyclic ligands [3, 5, 16–18]. On the basis of intensity, absorption energy and solvatochromic behavior the lowest energy absorption for $[Re(CO)_3Cl](dpop)$ is assigned as an MLCT $Re(d\pi) \rightarrow dpop(p\pi^*)$ transition. Higher energy absorption shoulders at 405 and 345 nm and the absorption maxima at 310 nm for $[Re(CO)_3Cl](dpop)$ are solvent

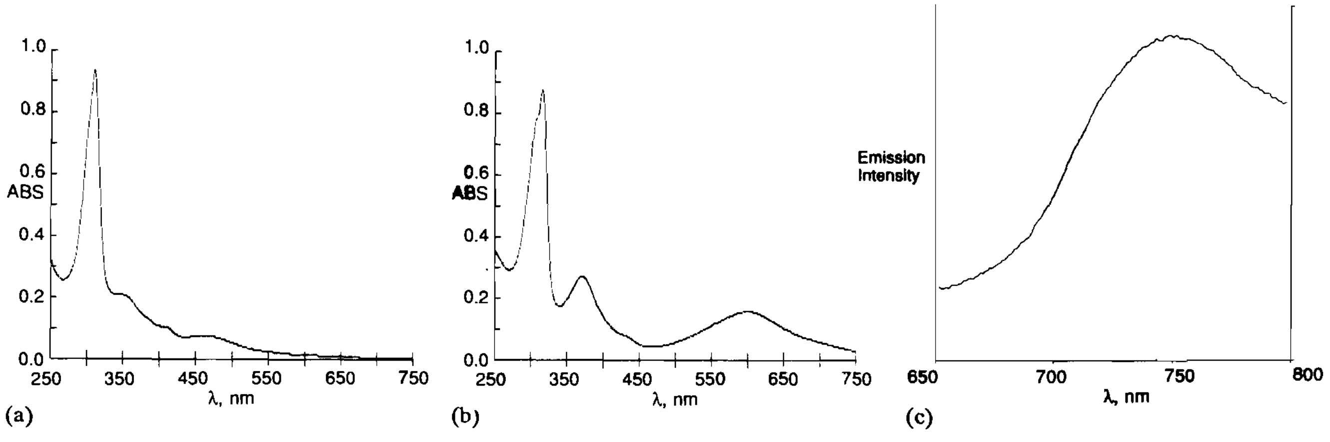


Fig. 2. UV–Vis electronic absorption spectra for (a) $[Re(CO)_3Cl](dpop)$ and (b) $[Re(CO)_3Cl]_2(dpop)$ recorded in CH_2Cl_2. (c) Emission spectrum of $[Re(CO)_3Cl](dpop)$ in de-oxygenated CH_2Cl_2.

TABLE 1. Electronic absorption and emission data for tricarbonylchlororhenium(I) complexes

Complex	λ_{max} (nm) $\epsilon \times 10^{-3}$	Assignment	Emission λ	Solvent	Reference
$[Re(CO)_3Cl]dpp$	404	MLCT	670; 679^{a}	CH_3COCH_3	3, 5
$[Re(CO)_3Cl]dpq$	438	MLCT	750^{a}	CH_3COCH_3	3
$[Re(CO)_3Cl]dpb$	462	MLCT		CH_3COCH_3	3
$[Re(CO)_3Cl]dpop$	449	MLCT		CH_3COCH_3	this work
	464 4.9	MLCT	750	CH_2Cl_2	this work
	405(sh) 7	IL			
	345(sh)13	IL			
	310 62	IL			
$[Re(CO)_3Cl]_2dpp$	457	MLCT		CH_3COCH_3	3, 5
$[Re(CO)_3Cl]_2bpym$	469	MLCT		CH_3COCH_3	2
$[Re(CO)_3Cl]_2bppz$	504	MLCT		CH_3COCH_3	2
$[Re(CO)_3Cl]_2dpq$	507	MLCT		CH_3COCH_3	3
$[Re(CO)_3Cl]_2dpb$	532	MLCT		CH_3COCH_3	3
$[Re(CO)_3Cl]_2dpop$	567	MLCT		CH_3COCH_3	this work
	597 8.8	MLCT		CH_2Cl_2	this work
	425(sh) 5	IL			
	370 15	MLCT			
	315 50	IL			
$[Re(CO)_3Cl]_2bptz$	697	MLCT		CH_3COCH_3	2
$[Re(CO)_3Cl]_2apy$	761	MLCT		CH_3COCH_3	2

[a] Emission data reported in CH_3CN.

independent and correspond with intensity and energy of dpop intraligand (IL) transitions at 402, 380, 360, 330(sh) and 302 nm. While the lowest energy LF transitions for similar Re(I) complexes have been calculated [3] to be at *c*. 340–350 nm, they are most likely obscured by IL transitions. On this basis and due to the lack of solvatochromism, higher energy absorptions for $[Re(CO)_3Cl](dpop)$ are tentatively assigned as dpop IL rather than LF or higher energy MLCT transitions.

The $[Re(CO)_3Cl]_2(dpop)$ complex in solution displays two intense ($\epsilon > 7 \times 10^3$ M^{-1} cm^{-1}) broad solvent-dependent peaks in the Vis–UV spectrum with a higher energy solvent independent absorption at 315 nm (Tables 1 and 2, Fig. 2(b)). Again, based on the intensity and solvent dependent wavelength maximum of the absorption, and similarity with the previously reported bimetallic $[Re(CO)_3Cl]_2(BL)$ complexes [3], the two lowest energy absorptions for $[Re(CO)_3Cl]_2(dpop)$ are assigned as MLCT(I) and MLCT(II) $Re(d\pi) \rightarrow dpop(p\pi^*)$ transitions. Solvent independent absorptions at 425(sh) nm and the peak maximum near 315 nm for $[Re(CO)_3Cl]_2(dpop)$ (Table 1) correlate with dpop IL transitions, and are tentatively assigned as dpop IL transitions. The shift to lower energy for the bimetallic versus monometallic lowest energy MLCT transition has previously been observed for many Ru(II) complexes [12–14, 18, 19] and with similar mono and bimetallic tricarbonylchlororhenium(I) complexes [2, 3,

TABLE 2. MLCT absorption ν_{max} (cm^{-1}) for (Re(CO)$_3$Cl)$_{1,2}$(dpop) complexes in different solvents^a

Solvent	E^*_{MLCT}	(Re(CO)$_3$Cl)(dpop) MLCT(I)	((CO)$_3$ClRe)$_2$(dpop) MLCT(I)
DMSO	1.00	22500	18100
CH_3CN	0.98	22600	17750
DMA	0.93	22400	17900
Acetone	0.82	22250	17625
Pyridine	0.77	22025	17175
Methanol	0.73	22450	18000
CH_2Cl_2	0.67	21600	16700
THF	0.59	21600	17250
$CHCl_3$	0.43	21260	16370
Toluene	0.30	21025	16450
A		20330	15837
B		2240	2112
r		0.994	0.953

^{a}Parameters for the equation ν_{max}MLCT $= A + BE^*_{MLCT}$, and the correlation coefficient r. The solvent parameter E^*_{MLCT} is from ref. 20. Data for methanol, CH_2Cl_2 and $CHCl_3$ are presented, but not figured in the calculation of A, B, r for reasons discussed in the text.

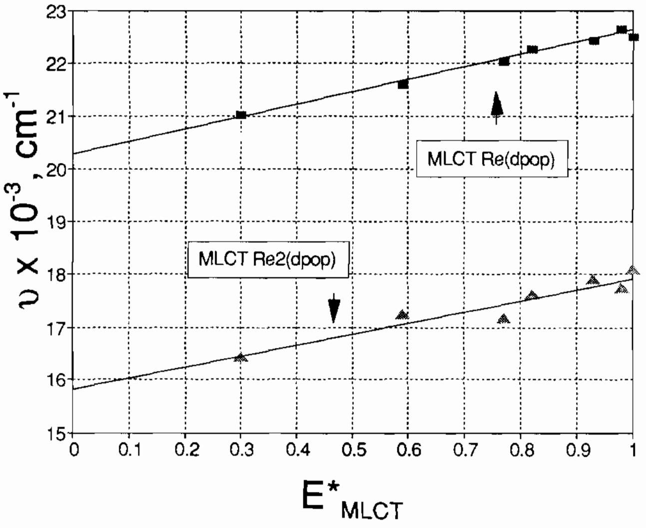


Fig. 3. Plots of the solvatochromic behavior of the [Re(CO)$_3$Cl]$_{1,2}$(dpop) complexes.

5] with nitrogen aromatic heterocyclic bridging ligands and has been interpreted as being due to a stabilization of the bridging ligand pπ^* LUMO upon coordination of a second electron withdrawing metal center. The effect of coordination of the Re(I) metal centers on the dpop (pπ^*) LUMO is also observed as a red shift of the dpop IL transitions in complexes.

Both the mono and bimetallic [Re(CO)$_3$Cl]$_{1,2}$(dpop) complexes were found to be inert ($t_{1/2} > 30$ days) in solution as opposed to the previously reported [(CO)$_4$Mo]$_{1,2}$(dpop) complexes [16] in which $t_{1/2}$ was found to be less than 4 h in solution.

One method for evaluation and comparison of the solvatochromism of complexes is based upon Lees solvent parameter E^*_{MLCT} [20]. While based upon studies for Group 6 carbonyl species, the equation $\nu_{max} = -A + BE^*_{MLCT}$ has been used to compare results for Re(I) complexes [5]. As in previous studies of similar Mo(CO)$_4$)(L) complexes, data for methanol, dichloromethane and chloroform were excluded from the plot for reasons of extensive hydrogen bonding or chloride polarizability [21]. Results for [Re(CO)$_3$Cl]$_{1,2}$(dpop) give values of $B = 2240$; 2112 (Fig. 3) and are lower than $B = 2678$; 4007 reported for the [Re(CO)$_3$Cl]$_{1,2}$(dpp) respective complexes [5]. The smaller B value observed for the Re(I)(dpop) versus Re(I)(dpp) complexes parallels the same result for [(CO)$_4$Mo]$_{1,2}$(dpop) versus [(CO)$_4$Mo]$_{1,2}$(dpp) [16, 22].

The MLCT energies of the [Re(CO)$_3$Cl]$_{1,2}$(dpop) complexes are lower than those reported for [Re(CO)$_3$Cl]$_{1,2}$(bppz) complexes [2]. As dpop is the cyclized analog of bppz, the lower energy MLCT transitions are understood as being due to a greater degree of π delocalization within the bridging ligand as has been interpreted for results for tricarbonylchlororhenium(I) dpp, dpq and dpb complexes with increasing π delocalization [3]. Of additional interest is the lateral comparison of MLCT energies of Re(I) complexes with the other highly delocalized bridging ligands dpb and dpq. While the bridging ligands dpq and dpb retain direct π Re–BL–Re interaction through the delocalized central ring, coordination also occurs to the σ linked 2-pyridyl rings, in contrast to dpop, in which all coordinating nitrogen atoms are within the delocalized π network. Thus the lower energy of Re(dπ)$\rightarrow$dpop(pπ^*) MLCT transitions is related to the expanded delocalized network and π connectivity of nitrogens within the bridging ligand.

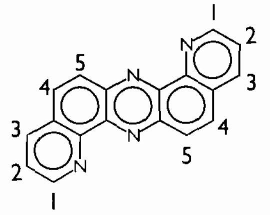
Utilizing the high PMT detector voltage and signal averaging, weak solvent dependent emission was observed for the [Re(CO)$_3$Cl](dpop) complex dissolved in de-oxygenated solvents. Excitation of the monometallic complex in 2 °C CH_2Cl_2 at 464 nm produced a broad emission maximum at 750 nm (Fig. 2(c)) without fine structure. The emission of the [Re(CO)$_3$Cl](dpop) complex is lower in energy than that reported for similar Re(I) complexes, but in the region expected for lower energy MLCT absorptions, and is consistent with a dpop(pπ^*)$\rightarrow$Re(dπ) emission [1, 3–5]. The weakness of the luminescence may be related to the detrimental effect of the energy gap law, which predicts an exponential increase in k_{nr} as a function of decreasing emission energy, as shown for a series of homologous Re(I) complexes [1, 23, 24]. Thus, the observed emission at 13334 cm^{-1} (750 nm) is consistent with weak intensity as the non-radiative path predominates. Luminescence experiments were not attempted with the

TABLE 3. Electrochemical potentials of some tricarbonylchlororhenium(I) complexes

Complex	E_p[a]	$E_{1/2}(0/-1)$	$E(-1/-2)$[b]	$E(\mathrm{Re}+1/0)$[c]	Solvent[d]	Reference
$[Re(CO)_3Cl]dpp$[d]	+1.44	−1.01		−1.62	CH_3CN	3
$[Re(CO)_3Cl]dpq$[d]	+1.51	−0.74		−1.36	CH_3CN	3
$[Re(CO)_3Cl]dpb$[d]	+1.52				CH_3CN	3
		−0.69	−1.41		CH_2Cl_2	3
$[Re(CO)_3Cl]dpop$	+1.58	−0.62	−1.35		CH_2Cl_2	this work
$[Re(CO)_3Cl]_2dpp$[d]	+1.50	−0.56	−1.17	−1.54	CH_3CN	3
$[Re(CO)_3Cl]_2bpym$		−0.34	−1.02		CH_3CN	2
$[Re(CO)_3Cl]_2bppz$		−0.36	−1.01		CH_3CN	2
$[Re(CO)_3Cl]_2dpq$[d]	+1.56	−0.29	−1.09	−1.46	CH_3CN	3
$[Re(CO)_3Cl]_2dpb$[d]	+1.57				CH_3CN	3
		−0.27	−0.95		CH_2Cl_2	3
$[Re(CO)_3Cl]_2dpop$	+1.62	−0.08	−0.91		CH_2Cl_2	this work
$[Re(CO)_3Cl]_2dptz$		−0.33	−1.0		1,2-$Cl_2C_2H_4$	2
$[Re(CO)_3Cl]_2apy$		+0.45	−0.35		1,2-$Cl_2C_2H_4$	2

[a] E_p values are anodic peak potentials for the irreversible Re(+1/+2) oxidation. [b] $E(-1/-2)$ values are reported for second ligand reduction. [c] E_{cat} are reported for irreversibly Re(+1/0) reductions. [d] E values from ref. 3 have been reduced by 0.04 V for comparison to SCE.

TABLE 4. ^1H NMR chemical shifts (δ) of dpop and the $[Re(CO)_3Cl]_2(dpop)$ complex[a]



Complex	H(1) (H1′)	H(2) H(2′)	H(3) H(3′)	H(4) H(4′)	H(5) H(5′)
dpop	9.19	7.76	8.43	8.20	8.37
$(Re(CO)_3Cl)_2(dpop)$	9.68	8.20(*cis*)	8.97	8.76(*cis*)	9.19(*cis*)
		8.22(*trans*)	8.98	8.78(*trans*)	9.20(*trans*)

[a] Recorded in d_8-THF and reported im ppm (δ) vs. TMS.

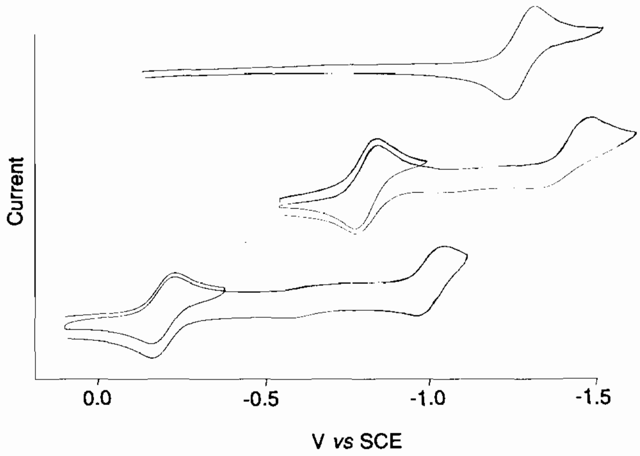


Fig. 4. Cyclic voltammograms of dpop (top); $[Re(CO)_3Cl](dpop)$ (middle) and $[Re(CO)_3Cl]_2(dpop)$ (bottom) vs. SCE.

$[Re(CO)_3Cl]_2(dpop)$ complex as the emission would be lower in energy and intensity than the detection limits.

IR spectra for the $[Re(CO)_3Cl]_{1,2}(dpop)$ complexes were obtained in KBr, and both show intense carbonyl stretches in the 2100–1900 cm^{-1} region (see 'Synthesis'). For both complexes, a sharp intense band is observed near 2015 cm^{-1}, with an equally intense but broad band near 1910 cm^{-1}. With the interpretation that the lower energy broad band is a non-resolved set with approximately equal intensities, the results are consistent with the facial orientation of carbonyl ligands.

Electrochemical results for the $[Re(CO)_3Cl]_{1,2}(dpop)$ complexes and uncomplexed dpop ligand are summarized in Table 3 and shown in Fig. 4. The application of positive potential on the mono and bimetallic complexes produces irreversible Re(I)/Re(II) oxidations with E_{ox} at +1.50 and +1.54 V versus SCE, respectively. Cyclic voltammograms of the uncomplexed dpop ligand

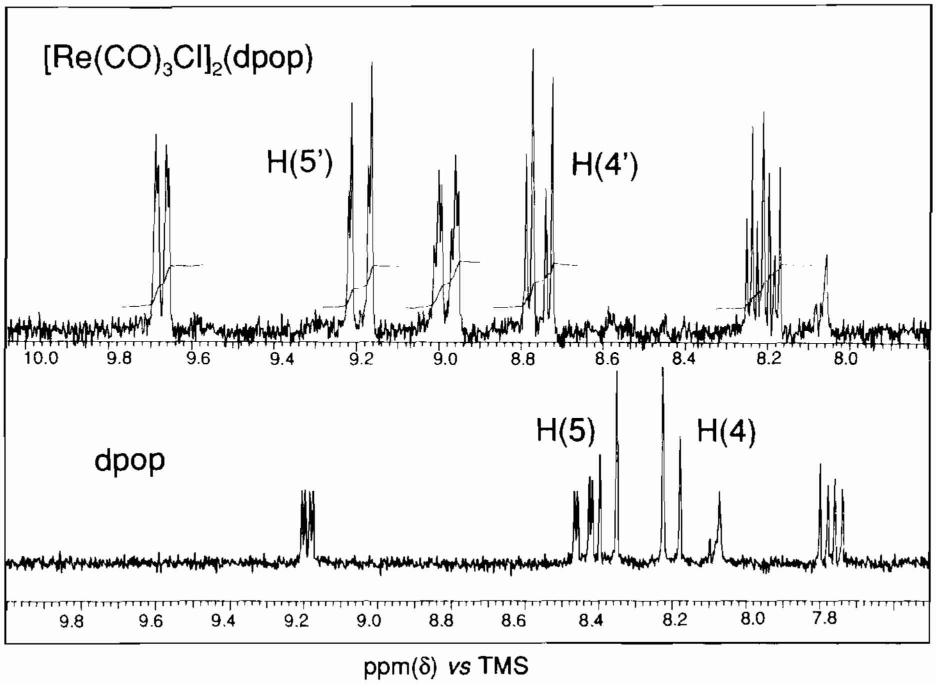


Fig. 5. NMR spectra for the $[Re(CO)_3Cl]_2$(dpop) and dpop in d_8-THF with chemical shifts reported in ppm (δ) vs. TMS.

toward negative potential produce a single reversible wave with $E_{1/2} = -1.29$ V versus SCE. Mono and bimetallic $[Re(CO)_3Cl]_{1,2}$(dpop) complexes also display ligand centered reversible potentials at $E_{1/2} = -0.71$ and -0.17 V, respectively. The shift toward less negative potential for bridging ligand centered reduction upon complexation is as expected for coordination of the electropositive $Re(CO)_3Cl$ fragment. In addition to the reversible waves, both mono and bimetallic $[Re(CO)_3Cl]_{1,2}$(dpop) complexes also show additional reduction waves. The second reduction for $[Re(CO)_3Cl]$(dpop) is irreversible (no return anodic wave) at $E_{red} = -1.45$, while the second for the $[Re(CO)_3Cl]_2$(dpop) complex is quasi-reversible ($E_{an} - E_{cat} = 100$ mV) at -1.02 V versus SCE. Second reversible, quasi-reversible and irreversible reduction waves have been reported for several similar Re(I) polypyridyl complexes, and have been attributed to the bridging ligand $(1-/2-)$ reduction or Re(I)/Re(0) reduction [3]. In the $[Re(CO)_3Cl]$(BL = dpq; dpb) complexes, second reduction potentials were independent of Cl^- replacement with a consistent ΔE difference from the first ligand reduction and therefore attributed to a bridging ligand centered process. Because the second reduction potential of $[Re(CO)_3Cl]$(dpop) is sufficiently negative to be attributed to either ligand $(1-/2-)$ or Re(1/0) based upon previous reports, the data are insufficient as to conclusively establish the nature of second reduction. Based on the relatively less negative potential of -1.02 V, quasi-reversibility and similarity of cathodic currents of the two reduction waves, the second reduction wave for $[Re(CO)_3Cl]_2$(dpop) is tentatively attributed to a dpop $(-1/-2)$ reduction.

^1H NMR chemical shifts were obtained for the uncomplexed dpop ligand, and the bimetallic $[Re(CO)_3Cl]_2$(dpop) obtained in d_8-THF and results are reported in Table 4 and presented in Fig. 5. The uncomplexed dpop ligand gives five sets of proton signals with relative integral of 1, and assignments are made by analogy to previously reported pyridyl ligands [25]. The bimetallic complex shows sets of proton resonances that suggest *cis* and *trans* structures being defined by the positions of the chloro ligand with respect to the Re(dpop)Re plane. Similar results have also been observed for the bimetallic $[Re(CO)_3Cl]_2$(bpym) complex [4]. Two structures for $[Re(CO)_3Cl]_2$(dpop) are most apparent for the H(4′) and H(5′) signals which appear as pairs of doublets. The chemical shift of H(5′) is downfield from the uncomplexed ligand and is a pair of doublets (9.20 ppm, integration 4; 9.19 ppm, integration 6), rather than a doublet. NMR data from $[Re(CO)_3Cl]$(dpop) in other solvents yields large chemical shift differences when comparing protons on complexed and uncomplexed rings that exclude the possibility that the observed $[Re(CO)_3Cl]_2$(dpop) signals might be due to some monometallic complex. The relative downfield shift of H(5′) is attributed to being held co-planar and in the deshielding region of the equatorial CO. The pair of doublets for H(5′) suggests one bimetallic structure slightly forces non-planarity, and in the absence of crystallographic data or isomeric separations, we tentatively attribute the doublet at 9.19 ppm to the *cis* structure. Chemical shifts for H(3′) are inconclusive for assignment as *cis* or *trans*.

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