Synthesis and Characterization of Tetracarbonylmolybdenum(0) Complexes Bound to the Novel Bridging Ligand Dipyrido[2,3-*a*:2',3'-*h*]phenazine (DPOP)

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There have been many articles detailing the synthesis and characterization of metal complexes bound through novel nitrogen aromatic heterocyclic ligands.[1] Ligands with multiple nitrogen sites that are μ coordinating are utilized in the formation of bi- and polymetallic metal–ligand complexes, with applications as oligomer metal complexes,[2,3] as intramolecular energy transfer centers,[4–12] or in solvatochromic studies.[13–20] Bidentate coordination of ligands is desirable because of the chelate effect on complex stability and enhanced metal dπ–bridging ligand pπ–metal dπ electronic interaction. Many bidentate ligands such as bppz, dpp, bptz, or abpy (Chart I), utilize a 2-pyridyl ring σ bonded to either a central ring such as pyrazine, triazine, or tetrazine, or the azo linkage, such that the metal dπ coordination to the 2-pyridyl ring may not contribute to the metal dπ–bridging ligand pπ–metal dπ electronic communication. Our research interest is in the preparation and evaluation of metal complexes bound to novel bridging ligands that might serve in polymetallic energy transfer processes and the maximization of parameters that increase metal–bridging ligand–metal communciation. We have prepared the mono and bimetallic $(Mo(CO)_4)_{1,2}$(dpop) complexes with the bridging ligand dipyrido[2,3-*a*:2',3'-*h*]phenazine (dpop) (Figure 1), that is the cyclized form of the μ-chelating bis-bidentate bridging ligand 2,5-bis(2-pyridyl)pyrazine (bppz) containing the σ-bonded 2-pyridyl groups. The novel dpop ligand is a planar bis-bidentate bridging ligand with a delocalized π network that allows metal coordination to each nitrogen directly in the π system. We wish to report solvatochromic, electrochemical, IR, and ^{1}H NMR characterization of the ligand and complexes and assess the effect of cyclization of the bridging ligand as compared with previously reported bis(α-diimine) type ligands.

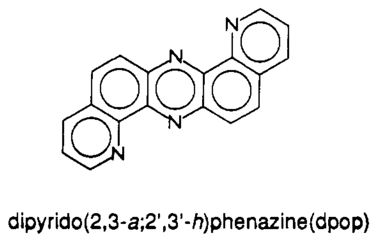
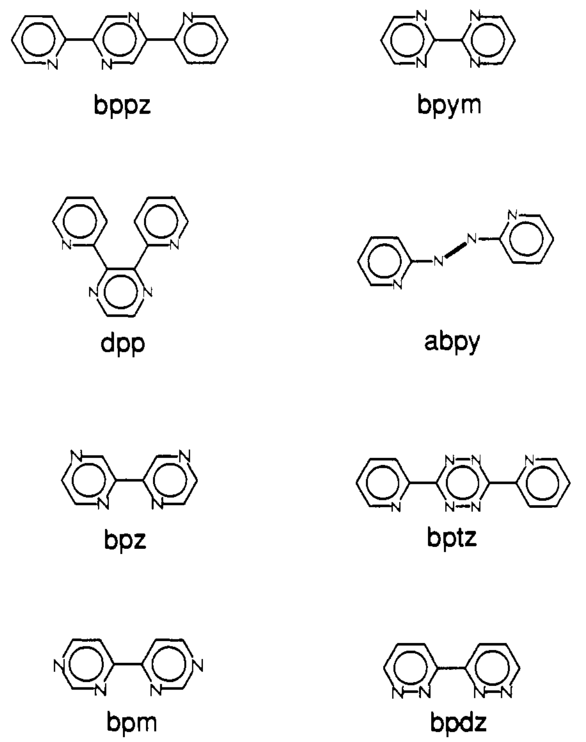


Figure 1. Dipyrido[2,3-*a*:2',3'-*h*]phenazine (dpop).

Chart I



Experimental Section

Materials. Analytical reagent grade solvents and compounds were used for preparations and experiments described in this work. Deuterated THF-d_8 used in NMR experiments was obtained from MSD Isotopes, Merck Frosst Canada, Inc. 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 Bio Analytic Systems CV-1B cyclic voltammograph with a Princeton Applied Research Model 0074 X-Y recorder. Cyclic voltammograms were recorded in CH_3CN with 0.010 M tetrabutylammonium perchlorate as the supporting electrolyte. A Ag/AgCl (3 M KCl, nominally −0.04 V vs SCE) reference electrode was used and calibrated with a $Fe(CN)_6^{4-}$ (1.0 M H_2SO_4) solution at +0.69 V vs NHE. All potentials are reported vs SCE, and are uncorrected for junction potentials. The $E_{1/2}$ values reported for redox couples are obtained by averaging anodic and cathodic peak potentials. Emission experiments were conducted on a Hitachi Model F-3210 fluorescence spectrophotometer, fitted with an extended range detector sensitive to 800 nm, and samples were degassed with Ar. ^{1}H NMR spectra were recorded in THF-d_8 on a Varian Gemini 200 MHz FT-NMR instrument using a 5-mm probe and a 10-s pulse delay. Samples were freeze–thaw degassed and sealed prior to data collection. Infrared spectra were recorded as solid KBr samples on a Perkin-Elmer Model 1420 IR spectrometer from 4000 to 600 cm^{-1}.

Synthesis. The dpop ligand was prepared according to the literature with minor modifications.[21] The nitration of phenazine was achieved at

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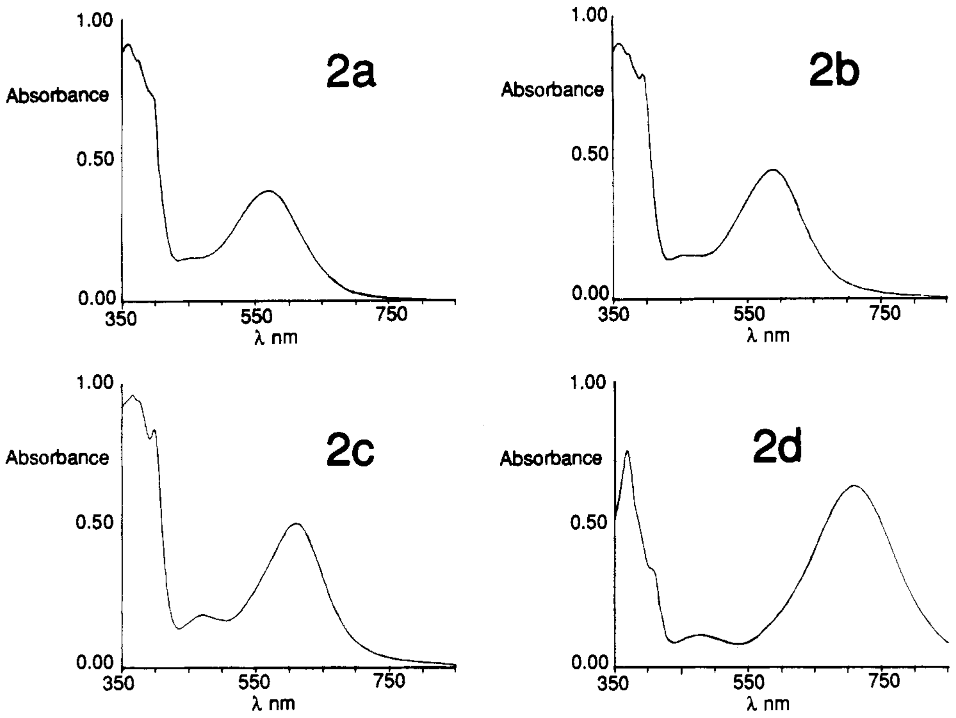

Figure 2. Electronic absorption spectra of $(Mo(CO)_4)(dpop)$ in (a) acetone, (b) THF, and (c) toluene and (d) $(Mo(CO)_4)_2(dpop)$ in acetone.

80 °C rather than at 100 °C to avoid excessive oxidation of phenazine, and cyclization of the 1,6 dihydrophenazine was achieved at 120 °C rather than 145 °C. Anal. Calcd 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. Average yield from 10.0 g of phenazine: 0.85 g (5%) [lit. 6%].

$(Mo(CO)_4)_2$(dpop). The bimetallic $(Mo(CO)_4)_2$(dpop) complex was prepared by mixing 0.100 g (3.54×10^{-4} mol) of the bis-bidentate ligand dpop and 0.440 g (1.67×10^{-3} mol) of $Mo(CO)_6$ in 0.10 dm^3 of toluene in a round bottom flask fitted with a condenser (top closed with a septum and an Ar inlet needle). After being degassed for 1 h, the mixture was heated at reflux for 6 h. After the mixture was cooled to room temperature, diethyl ether was added to a total volume of 0.50 dm^3 and cooled below 0 °C overnight. The solid was collected by filtration on a fine porosity filter funnel and air dried. The product was dissolved by washing the solid on the filter funnel with acetone, and the blue solution was collected and eluted down an alumina column (2.5 cm diameter × 20 cm length) with acetone. The blue-green liquid separated from traces of the purple monometallic complex and was collected and rotary evaporated to dryness. Yield $(Mo(CO)_4)_2$(dpop)·acetone (mol mass 756.4): 0.082 g (1.08×10^{-4} mol), 31%. Anal. Calcd for $C_{29}H_{16}N_4O_9Mo_2$: C, 46.05; H, 2.14; N, 7.40. Found: C, 46.03; H, 2.16; N, 7.39.

$(Mo(CO)_4)$(dpop). The $(Mo(CO)_4)$(dpop) complex was prepared by mixing 0.122 g (4.24×10^{-4} mol) of dpop and 0.110 g (4.17×10^{-4} mol) of $Mo(CO)_6$ in 0.075 dm^3 of toluene in a round bottom flask, which was fitted with a condenser (top closed with a septum and Ar inlet needle) and deoxygenated with Ar for 1 h before heating to reflux for 1.5 h. The solution was cooled to room temperature and rotary evaporated to dryness. The product was extracted from the solid in the round bottom flask by washing with acetone and filtering the mixture through a fine porosity funnel. The collected liquor was eluted down an alumina column as described above, collected in a round bottom flask, and rotary evaporated to a volume less than 0.005 dm^3. To the remaining purple liquor, 0.025 dm^3 of diethyl ether was added followed by 0.20 dm^3 of petroleum ether. The precipitate was collected by centrifuge and vacuum dried. Yield $(Mo(CO)_4)$(dpop) (mol mass 490.30): 0.0361 g (7.36×10^{-5} mol), 17%. Anal. Calcd for $C_{22}H_{10}N_4O_4Mo$: C, 53.9; H, 2.1; N, 11.4. Found: C, 54.6; H, 2.4; N, 11.6.

Results and Discussion

The syntheses of the mono- and bimetallic $(Mo(CO)_4)_{1,2}$(dpop) complexes are based on previously reported preparations of tetracarbonylmolybdenum(0) complexes with similar nitrogen aromatic heterocyclic ligands such as bpym[22] or dpp,[23] which allows heating of the dpop ligand and $Mo(CO)_6$ in an inert solvent, rather than through irradiation of the $Mo(CO)_6$ complex in the presence of ligand, reaction of the photogenerated $Mo(CO)_5$(THF), or other $Mo(CO)_4(C_7H_8)$ intermediates as previously described.[13–19,24] The mono- and bimetallic $(Mo(CO)_4)_{1,2}$(dpop) complexes were preferentially prepared by heating a 1:1 or 1:3 (excess) mixture of the dpop ligand with $Mo(CO)_6$ in an inert deoxygenated solvent. After isolation, chromatography, and washing, the products were identified as $(Mo(CO)_4)_{1,2}$(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 the characteristic solvatochromic behavior of MLCT transitions.

The $(Mo(CO)_4)_{1,2}$(dpop) complexes are sparingly soluble (5 mg/0.250 dm^3) in a variety of solvents, and exhibit intense solvent-dependent electronic transitions between 900 and 350 nm. The ν_{max} values reported were obtained within 10 min of sample preparation as both complexes are susceptible to dpop ligand loss in coordinating solvents such as DMSO. The monometallic $(Mo(CO)_4)$(dpop) complex in acetone has a lowest energy MLCT(I) transition at 569 nm (ϵ = 5600 M^{-1} cm^{-1}) and higher energy transitions at 395 nm (sh, ϵ = 10 000 M^{-1} cm^{-1}), 375 nm (sh, ϵ = 11 000 M^{-1} cm^{-1}) and 359 nm (ϵ = 12 500 M^{-1} cm^{-1}) (Figure 2a, Table I). The flat region of the spectrum in acetone near 450 nm contains a weaker intensity transition (ϵ = 2000 M^{-1} cm^{-1}) masked by the intense absorptions at 569 and 395 nm. The weaker intensity transition becomes visible as a solvatochromic MLCT(II) peak when the MLCT(I) transition is shifted to lower energy in solvents of lower polarity (Figure 2a–c). Plots of ν_{max} MLCT(I) and ν_{max} MLCT(II) vs the E^*_{MLCT} solvent parameter[13] for aliphatic and aromatic solvents with different polarity (Table II) give slopes of B = 2207 with an intercept A = 15 730 cm^{-1} for MLCT(I), and B = 1996 with an intercept of A = 20 612 cm^{-1} for MLCT(II). The higher energy transitions appear as shoulders in some solvents, and comparative ν_{max} are difficult to obtain;

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Table I. Electronic Absorption and Electrochemical Data[a] for the Dpop and $(Mo(CO)_4)_{1,2}$(dpop) Complexes

complex ion	solvent	λ_{max}, nm	$\epsilon \times 10^{-3}$, $M^{-1}\ cm^{-1}$	$E_{1/2}(0/-1)$, V
dpop	ethanol	402	10.1	−1.25
		380	9.2	
		301	92.0	
$(Mo(CO)_4)$(dpop)	acetone	568	5.6	−0.82
		450 (sh)	2.0	
		395 (sh)	10.0	
		375	11.0	
		359	12.5	
	THF	588		
		459		
		395 (sh)		
		375		
		359		
	toluene	611		
		474		
		395		
		380 (sh)		
		364		
$(Mo(CO)_4)_2$(dpop)	acetone	711	16.6	−0.46
		478	3.2	
		405	9.5	
		367	20.5	
	THF	740		
		488		
		410 (sh)		
		371		
	toluene	785		
		508		
		415 (sh)		
		372		

[a] Electrochemical potentials were recorded in CH_3CN containing 0.01 M TBAP and reported vs SCE.

Table II. MLCT Absorption ν_{max} ($cm^{-1} \times 10^3$) for $(Mo(CO)_4)_{1,2}$(dpop) Complexes in Different Solvents[a]

		$(Mo(CO)_4)$(dpop)		$(Mo(CO)_4)_2$(dpop)	
solvent	E^*_{MLCT}	MLCT(I)	MLCT(II)	MLCT(I)	MLCT(II)
CH_3CN	0.98	17 889		14 306	21 142
acetone	0.82	17 575		14 065	20 921
methanol	0.73	16 750		insol	insol
CH_2Cl_2	0.67	16 667	471	13 123	19 881
THF	0.59	16 978	459	13 514	20 492
$CHCl_3$	0.43	16 000	480	12 563	19 417
benzene	0.34	16 475	469	12 853	19 881
toluene	0.30	16 420	472	12 740	19 685
A		15 730	20 612	12 065	19 137
B		2207	1996	2361	2125
r		0.999	0.996	0.996	0.992

[a] Parameters for the equation $\nu_{max} = A + BE^*_{MLCT}$ and the correlation coefficient r. The solvent parameter E^*_{MLCT} is from ref 13. Calculated A, B, and r values exlude data from alcohols and chlorinated solvents.

however, they do not appear to be solvent sensitive. 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.[14] Comparison of the MLCT(I) transition energies of $(Mo(CO)_4)(L_2)$ complexes shows the Mo dπ(HOMO) → dpop pπ*(LUMO) transition to be lower in energy when compared with L_2 = bpy, bpym, dpp, bpz, bpdz, and bpm[17-20] but higher in energy compared to L_2 = abpy.[14,20]

The bimetallic $(Mo(CO)_4)_2$(dpop) complex in acetone displays a lowest energy MLCT(I) transition in acetone at 711 nm (ϵ = 16 600 $M^{-1}\ cm^{-1}$) with higher energy transitions at 478 nm (ϵ = 3200 $M^{-1}\ cm^{-1}$), 405 nm (sh, ϵ = 9500 $M^{-1}\ cm^{-1}$) and 359 nm (ϵ = 20 500 $M^{-1}\ cm^{-1}$) (Table I, Figure 2d). The lower energy MLCT(I) transition for the bimetallic $(Mo(CO)_4)_2$(dpop) complex in comparison with the monometallic $(Mo(CO)_4)$(dpop) complex is consistent with similar comparisons of mono- and bimetallic $(Mo(CO)_4)_{1,2}(L_2)$ species. The lower bimetallic MLCT(I) energy is understood as being due to a stabilization of the dpop pπ* LUMO when bonded to a second π withdrawing $Mo(CO)_4$ fragment (also verified electrochemically), and formation of a Mo dπ-dpop pπ-Mo dπ (nonbonding) HOMO, resulting in a lower energy Mo dπ(nb)(HOMO) → dpop pπ*(LUMO). Plots of ν_{max} MLCT(I) and ν_{max} MLCT(II) vs E^*_{MLCT} give slopes of B = 2361 with an intercept A = 12065 cm^{-1} for MLCT(I), and B = 2125 with an intercept of A = 19 137 cm^{-1} for MLCT(II) (Table II). Following the pattern for C_{2h} ligands, solvent sensitivity (B) of MLCT(I) is about equal to that of MLCT(II), in contrast with results for the D_{2h} bpym bimetallic complex. It is surprising, however, that the MLCT(I) solvent sensitivity of the bimetallic $(Mo(CO)_4)_2$(dpop) complex (B = 2361) is close to that of the monometallic $(Mo(CO)_4)$(dpop) complex (B = 2207), in contrast with results for bpym, dpp, and abpy.[14,23] The result may be due to larger polar interactions of the planar noncentrosymmetric $(Mo(CO)_4)$(dpop) monometallic complex with solvent than found in similar bpym, dpp or abpy complexes, contributing to ground state stabilization. The MLCT(I) energy of the bimetallic $(Mo(CO)_4)_2$(dpop) is lower than that reported for $(Mo(CO)_4)_2$ (L = bpym and bppz[14,15,20,22] and dpp[23]) complexes, but larger than $(Mo(CO)_4)_2$ (L = bptz and abpy[14,15,22]). Considering centrosymmetric bimetallic complexes, this is consistent with the observation that the solvent sensitivity (B) of MLCT(I) decreases with decreasing absolute MLCT energies.[14] The observed MLCT(I) and solvent sensitivity ordering for L = μ nitrogen aromatic heterocyclic ligands in $(Mo(CO)_4)_2$(L) complexes is bpym > bppz > dpop > bptz > abpy. On the basis of the simple predictive model of Kaim[15a] that solvatochromic behavior of centrosymmetric bimetallic complexes arises from change in polarizability between the ground and excited state; this suggests that the dpop ligand is a relatively poor σ donor in the ground state and a better base in the excited state. The noted reactivity of the mono and bimetallic dpop complexes toward heterocyclic ligand substitution in coordinating solvents such as DMSO also supports the placement of dpop as a relatively weak σ donor ligand. It would be most valuable to verify this result with Huckel MO coefficients, and anion radical ESR measurements as previously reported for similar bridging ligands.[15a]

Although $(Mo(CO)_4)$(bpy) and similar complexes have been reported to undergo MLCT emission in room temperature solution between 600 and 800 nm,[16,25] the $(Mo(CO)_4)$(dpop) complex was found to be nonemissive in room-temperature Ar-degassed CH_3CN and C_6H_6 solutions with emission wavelength ($\lambda < 800$ nm) detection limits. It is possible that the uncomplexed dpop nitrogen atoms undergo solvent interactions that provide an efficient vibrational relaxation pathway, as has been noted for $(Mo(CO)_4)(NO_2\text{-phen})$ complexes.[16] Due to the fact that MLCT transition energies for the $(Mo(CO)_4)$(dpop) complexes are lower than for those previously reported, it is possible MLCT emission exceeds the red limit of the detection capabilities.

Cyclic voltammograms of the uncomplexed dpop ligand and of the $(Mo(CO)_4)_{1,2}$(dpop) complexes were recorded in CH_3CN containing 0.01 M TBAP SCE toward negative potential and show reversible (ΔE = 60–80 mV) $E_{1/2}(0/-1)$ couples that are reported in Table I. Potentials of the metal complexes were recorded within 10 min of preparation to minimize dpop ligand substitution. The $E_{1/2}(0/-1)$ reduction couple of the uncomplexed dpop at −1.25 V is less negative (more easily reduced) than bpym (−1.9 V) and bppz (−1.7 V), but harder to reduce than bptz (−0.9 V).[15b] The $E_{1/2}(0/-1)$ dpop ligand-centered couples are −0.82 V for the $(Mo(CO)_4)$(dpop) monometallic and −0.46 V for the $(Mo(CO)_4)_2$(dpop) bimetallic complexes. The 0.43-V difference in ligand-centered $E_{1/2}(0/-1)$ couples for the uncomplexed dpop ligand and the $(Mo(CO)_4)$(dpop) complex and the

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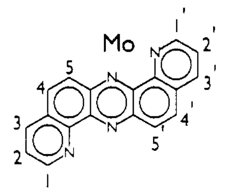
Table III. ^{1}H NMR Chemical Shifts (δ) of dpop and $(Mo(CO)_4)_{1,2}$(dpop) Complexes[a]



complex	H(1) H(1′)	H(2) H(2′)	H(3) H(3′)	H(4) H(4′)	H(5) H(5′)	$J_{1,2}$ $J_{1',2'}$	$J_{2,3}$ $J_{2',3'}$	$J_{1,3}$ $J_{1',3'}$	$J_{4,5}$ $J_{4',5'}$
dpop	9.19	7.76	8.43	8.20	8.37	4.4	8.0	1.8	9.2
$(Mo(CO)_4)$(dpop)	9.27	7.87	8.57	8.48	9.37	4.4	8.1	1.8	9.5
	9.70	8.03	8.77	8.40	8.58	5.1	8.1	1.4	9.1
$(Mo(CO)_4)_2$(dpop)	9.78	8.12	8.89	8.62	9.59	5.2	8.1	1.4	9.4

[a] Recorded in THF-d_8 and reported in ppm (δ) vs TMS; J coupling constants in Hz.

0.36-V difference between the monometallic $(Mo(CO)_4)$(dpop) and bimetallic $(Mo(CO)_4)_2$(dpop) are consistent with previous studies that demonstrate the effect of the second metal fragment on a bimetallic coordinating ligand is smaller than effect of the first metal for planar ligands. The $E_{1/2}(0/-1)$ electrochemical couple at −0.46 V for the bimetallic $(Mo(CO)_4)_2$(dpop) complex is less negative than that for bpym (−0.8 V) and that for bppz (−0.8 V) in the analogous complexes. This follows the electronic absorption MLCT results that show a lower energy to Mo $d\pi \rightarrow$ dpop $p\pi^*$ MLCT transition. Positive potentials applied to the $(Mo(CO)_4)_{1,2}$(dpop) complexes produce irreversible (0/1+) oxidation of the metal center and metal–metal electrochemical interaction, as $\Delta E_{1/2}(2-1)$, could not be determined.

Infrared spectra of the mono- and bimetallic $(Mo(CO)_4)_{1,2}$(dpop) complexes were recorded in KBr between 2100 and 1800 cm^{-1}. Both mono- and bimetallic complexes show four CO absorptions, with ν_{CO} = 2005, 1905, 1850, and 1825 cm^{-1} for the monometallic complex and ν_{CO} = 2000, 1915, 1870, and 1822 cm^{-1} for the bimetallic complex. The pattern is as expected for the *cis*-tetracarbonylmolybdenum arrangement.

^{1}H NMR spectra of the uncomplexed dpop ligand and $(Mo(CO)_4)_{1,2}$(dpop) complexes were recorded in THF-d_8, and numerical data are presented in Table III. Spectra of the $(Mo(CO)_4)_{1,2}$(dpop) complexes recorded in deuterated DMSO showed evidence of monometallic ligand dissociation to give uncoordinated dpop ligand, and bimetallic cleavage to form monometallic product within 15 min. Freeze–thaw deoxygenated samples of $(Mo(CO)_4)_{1,2}$)(dpop) in THF were stable for up to 4 h without significant reactivity.

The ^{1}H resonances for the uncomplexed dpop ligand and $(Mo(CO)_4)_{1,2}$(dpop) complexes are assigned by positions, coupling constants, and integrations as referenced to previous literature reports.[26] The dpop ligand gives five sets of signals as expected which all integrate with a relative value of 1. The H(1) proton resonance is farthest downfield at 9.19 ppm and is split by protons H(2) and H(3), producing a doublet of doublets. Sets of doublets of doublets at 8.43 ppm are tentatively assigned as H(3) and those at 7.76 ppm as H(2), consistent with similar ligands.[26] Two sets of doublets are assigned as H(5) at 8.37 ppm, and H(4) at 8.20 ppm, again, consistent with assignments for protons in 1,5-phenanthroline.[26] The bimetallic $(Mo(CO)_4)_2$(dpop) complex also displays five proton signals which integrate to relative values of 1. Tentative assignments for the three sets of doublets of doublets are H(1)′ at 9.78, H(2′) at 8.12, and H(3′) at 8.89 ppm, and the two sets of doublets are H(4′) at 8.62 and H(5′) at 9.59 ppm. The downfield shift of H(5′) proton by 1.22 ppm from the free ligand to bimetallic complex is most likely due to that proton being held coplanar and in the deshielding region of the cis CO ligand. Such a shift has also been reported for the bimetallic abpy-bridged complex. The monometallic $(Mo(CO)_4)$(dpop) complex displays doublet of doublet proton splitting in the pyrido rings that is easily assignable with the complexed ring protons downfield as in the bimetallic complex and noncomplexed ring protons upfield near those observed for the free ligand. Four nonequivalent phenazine ring protons give four sets of doublets. The doublet farthest downfield at 9.37 ppm is assigned to H(5), which is in the uncomplexed ring, but held in the coplanar and deshielding region of the coordinated metal carbonyl. The doublet set at 8.48 ppm is assigned as H(4) based on coupling constants and coupled α–β proton signals. The doublets at 8.56 and 8.40 ppm are assigned to H(5′) and H(4′), respectively, based on coupling constants, shift additivity, and the coupled α–β proton signals.

Conclusions

Ring cyclization of the bppz σ bonded 2-pyridyl rings to give the dpop ligand stabilizes the ligand $p\pi^*$ LUMO. Effects are observed in the electronic absorption spectra, with lower energy MLCT transitions and lower solvatochromic sensitivity for the dpop complexes. The decreased σ-donor ability (basicity) of the dpop ligand reduces the stability of the zerovalent complexes in coordinating solvents. Metal–metal communication could not be electrochemically evaluated due to the oxidative instability of the metal complexes. The coplanarity of the coordinated tetracarbonylmolybdenum with H(5) in the monometallic complex and H(5′) in the bimetallic complex places it in the deshielding region of the carbonyl group, and it is observed farther downfield than H(3) and H(3′). Studies are underway to evaluate whether the reduced basicity of the dpop, as compared with the uncyclized form of the bidentate ligand bppz, affects coordination behavior on cationic metal centers such as Re(I) and Ru(II).

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Supplementary Material Available: Figures showing ν_{max} vs E^*_{MLCT} for the data in Table II and ^{1}H NMR chemical shifts for the data in Table III (2 pages). Ordering information is given on any current masthead page.

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(26) Memory, J. D.; Wilson, N. K. *NMR Spectra of Aromatic Compounds* Wiley: New York, 1982.