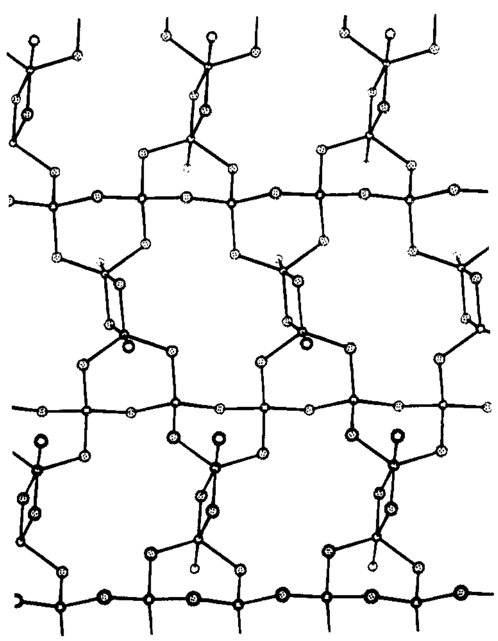

Figure 4. Two-dimensionally nonmolecular pattern of Cd (small open circles) and S (stipled circles) atoms in crystalline $^{2}_{\infty}\{\mathrm{Cd(SCH_2CH_2OH)_2}\}$ (**6**). The open circles linked to Cd represent coordinated alcohol functions.

$\mathrm{Cd_2}$-*spiro*-$\mathrm{Cd_2}$-$\mathrm{Cd_3}$-$\mathrm{Cd_2}$-$\mathrm{Cd_3}$-*spiro*-$\mathrm{Cd_2}$-*spiro*-$\mathrm{Cd_2}$}. Around the macrocycle, the pathway with the smallest number of connections involves 24 cadmium atoms bridged by 24 thiolate ligands (each $\mathrm{Cd_3}$ cycle contributes one thiolate bridge in this pathway).

The macrocycles form a pseudoherringbone pattern, shown in two dimensions in Figure 2, but which is actually three-dimensional as a consequence of the tetragonal symmetry of the lattice and the 4-fold screw axes parallel to *c*. The $\mathrm{Cd_3}$ cycles on the edges of the macrocycle provide the linkages to other macrocycles that are approximately perpendicular to those shown in Figure 2 and are translated by *c*/4. Thus each macrocycle is externally connected to other macrocycles at ten points, generating a rather complex three-dimensional network. It is possible to describe this structure in different ways and to trace connections and chains of the small cycles other than those emphasized by the macrocycles in Figure 2.

Figure 3 shows the ligand 2-methylphenyl groups associated with one macrocycle. The major feature to notice is that the aryl groups are directed away from the chain and away from the DMF ligands.

Discussion

The DMF molecule tripodally located over the face of the $\mathrm{Cd_3}$ cycle is an unusual but rationalizable feature. All Ar substituents on a $\mathrm{Cd_3(\mu\text{-}SAr)_3}$ cycle, whether axial or equatorial, must be located on one side of the plane of the cycle, leaving the opposite face vacant. Because the Ar substituents on the adjoining $\mathrm{Cd_2}$ cycles cannot intrude over this vacant face, there is space for a small molecule such as DMF.

The crystal structure of **5** contains features similar to those in the crystal structure of the cadmium alkanethiolate $^{2}_{\infty}\{\mathrm{Cd(SCH_2CH_2OH)_2}\}$ (**6**),[21] which is outlined in Figure 4. There exist in **6** $\mathrm{Cd_3(\mu\text{-}SR)_3}$ cycles and $\mathrm{Cd_2(\mu\text{-}SR)_2}$ cycles, spiro-linked at cadmium, as in **5**, but in **6** they occur in a two- rather than a three-dimensionally nonmolecular network. Some of the ligand hydroxy functions in **6** provide secondary coordination at one of the two types of Cd atoms, while there is extensive intra- and interlayer hydrogen bonding of the ligands. In **6**, the proportion of the crystal volume occupied by the ligands is smaller than in the $\mathrm{Cd(SAr)_2}$ compounds.

Why are there no adamantanoid cages in the crystal structure of **5**? We presume that the 2-methyl substituent on the ligand aryl group causes steric interference. Although the adamantanoid cage is paradigmatic in molecular cadmium arenethiolate compounds,[22-25] it has not yet been confirmed for any arenethiolate ligand with a substituent in the 2-position, and it is now well established that bulkier 2-aryl substitution disrupts molecular structures of metal thiolates even further.[26-28] Our preliminary results on the ^{113}Cd NMR spectra of **5** in DMF solution show appreciable differences from the behavior of **1**-**4**.

Acknowledgment. Funding by the Australian Research Council is gratefully acknowledged. We thank Dr. A. D. Rae for assistance with the program RAELS.

Supplementary Material Available: Table S1, listing atomic coordinates, thermal parameters, and distances and angles for **5**, and Table S2, giving crystallographic details pertaining to data collection, processing, and refinement of the structures of **5** (10 pages); a listing of structure factors for **5** (19 pages). Ordering information is given on any current masthead page.

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Notes

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Synthesis and Characterization of Rhenium(I) Complexes Bound to the Bridging Ligand 2,3-Bis(2-pyridyl)pyrazine

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Received June 12, 1989

Our research group has been interested in the design and characterization of mono- and bimetallic low-spin d^6 transition-metal complexes bound through nitrogen aromatic heterocyclic ligands such as 2,3-bis(2-pyridyl)pyrazine (dpp) and 2,3,5,6-tetrakis(2-pyridyl)pyrazine (tppz), for potential use in photon-capture/excited-state energy-transfer processes.[1] Several studies have recently demonstrated that rhenium carbonyl centers bound with 2,2′-bipyrimidine (bpm) and other pyridyl ligands have highly abosrbing MLCT bands in the visible spectrum and are emissive and electrochemically stable, making them ideal fragments in photon-capture energy-transfer processes.[2-7] Thus, a relatively

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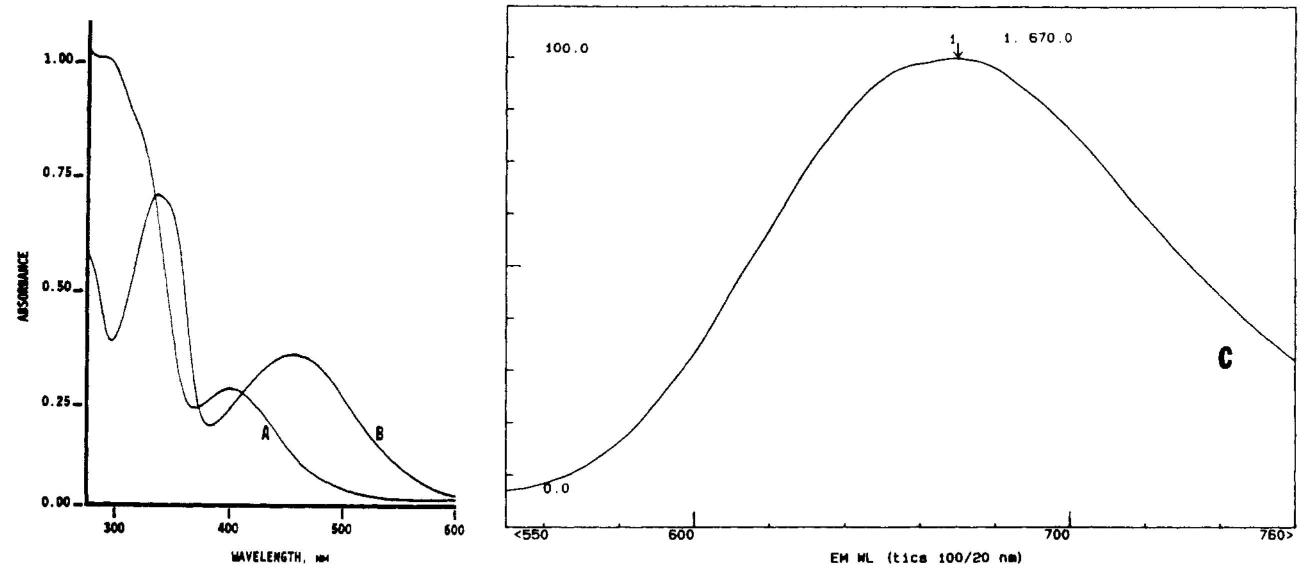

Figure 1. Electronic absorption spectra for (A) $[Re(CO)_3Cl]dpp$ (7.1×10^{-5} M) and (B) $[Re(CO)_3Cl]_2dpp$ (7.4×10^{-5} M) recorded in CH_3CN and emission spectrum for (C) $[Re(CO)_3Cl]dpp$ in deoxygenated room-temperature CH_3CN.

few $[Re(CO)_3Cl]L$ complexes with absorption and electrochemical characteristics similar to those of the well-studied Ru(II) family have been prepared and studied with possible application in light-induced electron-transfer reactions. We wish to contribute to this field the preparation and UV-visible, electrochemical, emission, solvatochromic, and infrared characterization of the newly prepared $[Re(CO)_3Cl]dpp$ and $[Re(CO)_3Cl]_2dpp$ complexes.

Experimental Section

Materials. $Re(CO)_5Cl$ was obtained from Pressure Chemical Co., Pittsburgh, PA, and used without purification. The ligand 2,3-bis(2-pyridyl)pyrazine (dpp) and DMSO-d_6 for ^{13}C NMR spectroscopy were obtained from Aldrich Chemical Co. Other solvents were obtained from Fisher and used without redistillation. Elemental analyses were performed by Atlantic Microlab Inc., Atlanta, GA.

Instrumentation. Electronic absorption spectra were recorded on a Varian DMS 300 spectrophotometer with matching quartz cells. Cyclic voltammograms were recorded on an EG&G Princeton Applied Research Co. Model 264A polarographic analyzer with a Princeton Applied Research Model 0074 X-Y recorder. The Pt working electrode (3.0-mm diameter) was polished prior to each scan. A Ag/AgCl (nominally −0.04 V vs SCE) reference electrode was used. All potentials are reported vs SCE and are uncorrected for junction potentials. The potentials reported for oxidation couples $E_{1/2}$ are estimates obtained by averaging anodic and cathodic peak potentials, unless otherwise noted. Cyclic voltammograms were recorded in CH_3CN with 0.1 M tetrabutylammonium perchlorate as an electrolyte. Infrared spectra were recorded as solids in KBr pellets on a Nicolet DX-20 FTIR with 1-cm^{-1} resolution. Emission spectra were recorded at both Clemson University, on a Spex Fluorescence (II) spectrometer controlled by a Spex DM 1B Labcoordinator with a Houston DMP40 digital plotter, and the U.S. Air Force Academy, on an SLM Aminco C 4800 emission spectrometer.

Synthesis. The monometallic rhenium complex $[Re(CO)_3Cl]dpp$ was prepared by mixing 0.144 g (0.398 mmol) of $Re(CO)_5Cl$ and 0.305 g (1.302 mmol) of dpp in 75 mL of anhydrous methanol contained in a 100-mL round-bottom flask. The mixture was brought to reflux under Ar, and the initially yellow solution turned orange within 1 h. The mixture was heated at reflux for a total of 40 h under a continuous stream of Ar. After the mixture was allowed to cool to room temperature, petroleum ether was added and the resulting mixture cooled to 0 °C. The yellow product was collected by filtration, dissolved through the filter with a minimum of CH_2Cl_2, and loaded onto a freshly prepared alumina column (2-cm diameter × 8-cm length). The yellow band was eluted with CH_2Cl_2, collected, and rotary-evaporated to 25 mL. Addition of 200 mL of petroleum ether induced precipitation. The yellow precipitate turned orange when dried at 40 °C under vacuum (less than 0.5 Torr). Yield: 0.123 g (0.228 mmol), 57%. Anal. Calcd for $ReC_{17}H_{10}N_4O_3Cl$: C, 37.81; H, 1.87; N, 10.38. Found: C, 37.82; H, 1.88; N, 10.32. ν_{CO}: 2025, 1916, 1902 (sh) cm^{-1}.

Table I. Electronic Absorption Data for Rhenium(I) Complexes[a]

complex	solvent	λ_{max},[c] nm ($10^{-3}\epsilon$, $M^{-1}\,cm^{-1}$)	assgnt	ref
$[Re(CO)_3Cl]dpp$	CH_3CN	399 (3.5)	MLCT	*b*
		315 sh (12.3)	$\pi \rightarrow \pi^*$	
		285 (14.0)	$\pi \rightarrow \pi^*$	
	CH_2Cl_2	415	MLCT	*b*
		315 sh	$\pi \rightarrow \pi^*$	
		285	$\pi \rightarrow \pi^*$	
	$CHCl_3$	422	MLCT	*b*
		320 sh	$\pi \rightarrow \pi^*$	
		290 sh	$\pi \rightarrow \pi^*$	
$[Re(CO)_3Cl]_2dpp$	CH_3CN	455 (9.5)	MLCT	*b*
		350 sh	$\pi \rightarrow \pi^*$	
		335 (20.0)	$\pi \rightarrow \pi^*$	
	CH_2Cl_2	481	MLCT	*b*
		350 sh	$\pi \rightarrow \pi^*$	
		334	$\pi \rightarrow \pi$	
	$CHCl_3$	495	MLCT	*b*
		350 sh	$\pi \rightarrow \pi^*$	
		334	$\pi \rightarrow \pi^*$	
$[Re(CO)_3Cl]bpm$	CH_3CN	384 (2.7)	MLCT	2
		310 sh	MLCT	
		232 (23)	$\pi \rightarrow \pi^*$	
$[Re(CO)_3Cl]phen$	CH_2Cl_2	410 sh	MLCT	6
		377 (4.0)	MLCT	
$[Re(CO)_3Cl]_2bpm$	CH_3CN	465	MLCT	4

[a] Various solvents noted in Table. [b] This work. [c] sh = shoulder.

The bimetallic complex $[Re(CO)_3Cl]dpp[Re(CO)_3Cl]$ was prepared by mixing 0.146 g (0.43 mmol) of $Re(CO)_5Cl$ and 0.038 g (0.16 mmol) of dpp in 75 mL of anhydrous methanol contained in a 100-mL round-bottom flask. The mixture was brought to reflux under Ar, and the initially yellow solution produced a red precipitate within 1 h. The mixture was heated at reflux for a total of 48 h under a continuous stream of Ar. The precipitate was collected by filtration of the hot solution, washed with 400 mL of boiling methanol, and dried under vacuum. Yield: 0.098 g (0.12 mmol), 75%. Anal. Calcd for $Re_2C_{20}H_{10}N_4O_6Cl_2$: C, 28.40; H, 1.19; N, 6.63. Found: C, 28.50; H, 1.20; N, 6.57. ν_{CO}: 2026, 1940 (sh), 1914 cm^{-1}.

Results and Discussion

The $[Re(CO)_3Cl]dpp$ complex exhibits an intense solvent-dependent transition in the visible spectrum (Tables I and II, Figure 1A). The intensity and position of the transition in CH_3CN are similar to those previously reported for $[Re(CO)_3Cl]bpm$ and other $[Re(CO)_3Cl]L$ complexes (where L = a nitrogen aromatic heterocyclic ligand). Due to the solvent-dependent wavelength

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Table II. MLCT Absorption ν_{max} Values (cm^{-1}) of $[Re(CO)_3Cl]_{1,2}$dpp Complexes in Different Solvents and Linear Correlation Parameters[a] with E^*_{MLCT}[b]

solvent	E^*_{MLCT}	ν_{MLCT}-{$[Re(CO)_3Cl]$dpp}	ν_{MLCT}-{$[Re(CO)_3Cl]_2$dpp}
DMSO	1.00	25295	22557
CH_3CN	0.98	25063	21978
acetone	0.82	24712	21898
pyridine	0.77	24331	21645
CH_2Cl_2	0.67	24096	20790
1,2-$Cl_2C_2H_4$	0.64	24040	20620
THF	0.59	23995	21398[c]
$CHCl_3$	0.42	23697	20202
toluene	0.30	23310	insol
		$A = 22440$ $B = 2678$ $r = 0.981$	$A = 18351$ $B = 4007$ $r = 0.951$

[a] Parameters for the equation $\nu_{max} = A + BE^*_{MLCT}$ and the correlation coefficient r. Wavelengths were recorded to ±1 nm and are the average of three scans. [b] Solvent parameter taken from ref 21. [c] Value for THF excluded from calculation of A, B, and r; inclusion of that value yields A, B, and r values of 18706, 3640, and 0.907, respectively.

maxima of the peak and large molar absorptivities, this is assigned as a MLCT Re ($d\pi$) → dpp ($p\pi^*$) transition. The absorption shoulders at 315 and 285 nm are solvent independent (Table I). Owing to the fact that higher energy MLCT transitions exhibit solvatochromic dependence comparable to that of the lowest MLCT, these are most likely intraligand $\pi \rightarrow \pi^*$ transitions of the bound (315 nm) and unbound (285 nm) pyridine dpp rings rather than higher energy MLCT transitions. The $[Re(CO)_3Cl]_2$dpp complex also displays an intense solvent-dependent peak in the visible spectrum (Tables I and II, Figure 1B). Again, on the basis of the intensity and solvent-dependent wavelength maximum of the absorption and similarity to that of the previously reported bimetallic $[Re(CO)_3Cl]_2$bpm complex, the lowest energy absorption for $[Re(CO)_3Cl]_2$dpp is assigned as a MLCT transition. The absorption shoulder at 350 nm and the peak maximum at 335 nm for $[Re(CO)_3Cl]_2$dpp are also solvent-independent (Table I) and are assigned as $\pi \rightarrow \pi^*$ transitions to the bound dpp ligand rings. Of note for the bimetallic complex is the absence of a peak near 285 nm, which is consistent with the fact that both pyridine rings of dpp are coordinated. The shift to lower energy for the bimetallic vs monometallic lowest energy MLCT transition has previously been observed with a variety of nitrogen aromatic heterocyclic bridging ligands including pz,[8] bpm,[9] and dpp.[10] The lower energy bimetallic vs monometallic MLCT transition has been interpreted as being due to a combination of lowering of the bridging ligand $p\pi^*$ LUMO and formation of a metal ($d\pi$)–bridging ligand ($p\pi^*$)–metal ($d\pi$) nonbonding molecular orbital.[8-10] The lowering of the dpp ($p\pi^*$) LUMO of the $[Re(CO)_3Cl]_2$dpp vs $[Re(CO)_3Cl]$dpp complex is electrochemically measured (Table III) as 0.43 V (3468 cm^{-1}) compared with the MLCT shift (3085 cm^{-1}) in the visible spectrum. This result suggests that the metal HOMO of the bimetallic complex must also be stabilized vs the monometallic complex, and this is also verified electrochemically as an increased oxidation potential of the Re in the bi- vs monometallic complex.

Table III. Electrochemical[a] Data for $[Re(CO)_3Cl]_{1,2}$L and $[Ru(bpy)_2]_{1,2}$L (L = dpp and bpm) Complexes

complex	oxidn $E_{1/2}$,[b] V	redn $E_{1/2}$,[c] V	E_{an-cat}, mV	ref
$[Re(CO)_3Cl]$dpp	+1.45 (irrev)	−1.03	80	*d*
$[Re(CO)_3Cl]_2$dpp	+1.55 (irrev)	−0.60	80	*d*
$[Re(CO)_3Cl]$bpm	+1.43 (irrev)	−1.03		5
$[Re(CO)_3Cl]$bpm	+1.47 (irrev)	−1.00		*d*
$[Re(CO)_3Cl]_2$bpm	+1.48 (irrev)	−0.51		4
$[Ru(bpy)_2]dpp^{2+}$	+1.30			12
$[Ru(bpy)_2]_2dpp^{4+}$	+1.30, +1.50			12
$[Ru(bpy)_2]bpm^{2+}$	+1.40			13
$[Ru(bpy)_2]_2bpm^{4+}$	+1.53, +1.69			13

[a] Cyclic voltammograms were recorded in CH_3CN/0.10 M tetrabutylammonium perchlorate at a scan rate of 200 mV/s. E values were recorded vs a Ag/AgCl electrode (nominally −0.04 V vs SCE) and are reported vs SCE for comparison with complexes listed in refs 2 and 5. [b] Rhenium oxidations were irreversible, and E_{ox} is reported. [c] Average of anodic and cathodic waves of the ligand reduction. [d] This work.

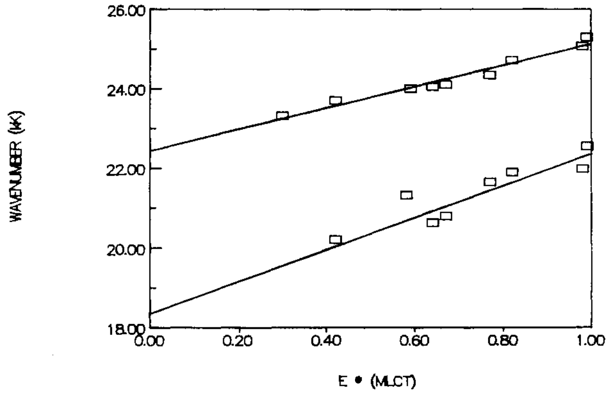

Figure 2. Plots of ν_{max}(MLCT) energies (10^3 cm^{-1}) vs E^*_{MLCT} for $[Re(CO)_3Cl]$dpp (top) and $[Re(CO)_3Cl]_2$dpp (bottom).

The emission spectrum of $[Re(CO)_3Cl]$dpp was obtained in room-temperature deoxygenated acetonitrile solution (Figure 1C). The monometallic complex emits at a maximum of 670 nm. An excitation profile shows the maximum emission at 670 nm occurs upon irradiation at 408 nm. The position and shape of the emission are consistent with those previously reported for other rhenium carbonyl MLCT-emitting complexes.[4] The bimetallic $[Re(CO)_3]_2$dpp complex was found to be nonemissive, and this result is identical with that for the $[Re(CO)_3Cl]_2$bpm complex.[3] The absence of emission for the bimetallic bpm complex was attributed to a nonobservable excited state, such as an intervalence or ^{3}CT state.

Cyclic voltammetry of the $[Re(CO)_3Cl]_{1,2}$dpp complexes toward negative potential shows reversible waves (Table III) corresponding to a reduction localized on the pyrazine ring of the dpp ligand.[11] The shift to less negative reduction potential for $[Re(CO)_3Cl]_2$dpp (−0.60 V) with respect to $[Re(CO)_3Cl]$dpp (−1.03 V) demonstrates the electron-withdrawing capability of the $[Re(CO)_3Cl]$ fragment in the bimetallic complex. Cyclic voltammetry of the $[Re(CO)_3Cl]_{1,2}$dpp complexes toward positive potential shows an irreversible oxidation at +1.45 V for the monometallic complex and an irreversible oxidation at +1.55 V for the bimetallic complex. The observed irreversible metal oxidation, the reversible ligand reduction, and the shift to less negative reduction potential for bimetallic complexes are in agreement with previous observations for $[Re(CO)_3Cl]$L complexes.[2-7] A sample of $[Re(CO)_3Cl]$bpm was prepared according to the literature,[5] and side by side comparison of Re(bpm) vs Re(dpp) shows Re(dpp) potentials to be less positive than the Re(bpm) potentials. The decrease in oxidation potential of $[Re(CO)_3Cl]_{1,2}$dpp vs $[Re(CO)_3Cl]_{1,2}$bpm complexes is similar to a comparison (Table III) of $[Ru(bpy)_2]_{1,2}dpp^{2+,4+}$ and $[Ru(bpy)_2]_{1,2}bpm^{2+,4+}$ complexes.[12,13] For the Ru(II) species, the bpm-ligated species exhibit more positive redox couples than the dpp complexes. Comparison of $[M(CO)_4]$dpp vs $[M(CO)_4]$bpm (M = Cr, Mo, W) electrochemical data is not available in the literature.[14-16,21]

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Negative solvatochromism has been well established for group 6 metal carbonyl species.[14–24] The energy (ν_{max} (10^3 cm^{-1})) of the MLCT transition of the mono- and bimetallic [Re(CO)$_3$Cl]$_{1,2}$dpp complexes was obtained from the absorption spectra of the complexes in several solvents (Table II) and plotted vs the E^*_{MLCT} parameter for the solvent in which the spectrum was acquired (Figure 2). The solvent sensitivity has previously been defined as $B = \nu_{max}/E^*_{MLCT}$.[19–21] The generally observed shift to higher energy of the MLCT transition in solvents of higher polarity has been attributed to ground-state stabilization of noncentrosymmetric complexes in more polar solvents.[17,21] Several centrosymmetric bimetallic complexes that have no permanent dipoles, such as [(CO)$_5$W]$_2$pz[19] and [Mo(CO)$_4$]$_2$bpm,[21] display larger B values than their monometallic analogues, and thus additional factors including molecular polarizability and σ-donating and π-back-bonding ability of the ligand have been utilized in the interpretation of the solvatochromic behavior. For the bimetallic [Re(CO)$_3$Cl]$_2$dpp complex, $B = 4007$ is larger than $B = 2678$ for the monometallic [Re(CO)$_3$Cl]dpp complex. Due to the fact that both the [Re(CO)$_3$Cl]dpp and [Re(CO)$_3$Cl]$_2$dpp complexes are noncentrosymmetric, and most likely contain permanent dipoles, the magnitude of B (increased solvatochromic sensitivity) of the bi- vs monometallic complexes can be attributed to a combination of increased molecular polarizability and dipole interactions. While exclusion of chlorinated solvents does not significantly alter solvatochromatic parameter values, THF causes an extreme deviation from linear behavior for the [Re(CO)$_3$Cl]$_2$dpp complex (Table II, Figure 2). The magnitude of B for the [Re(CO)$_3$Cl]$_{1,2}$dpp complexes is approximately equal to those reported for [Mo(CO)$_4$]$_{1,2}$bpm[21] (B = 3110, 4110) and [Mo(CO)$_4$]$_{1,2}$dpp[1b] complexes (B = 3060, 3257). Replacement of the CO group on a metal center by the electronegative Cl atom appears to have little effect on the B value, in comparison with previously noted replacements by electron-donating groups such as 2-pyridine or η^5-C$_5$R$_5$.[21] Solvatochromic values for [Re(CO)$_3$Cl]$_{1,2}$bpm and similar Re complexes were not reported.

Acknowledgment. We acknowledge the generous financial support of this work through a Bristol-Myers Co. Grant of the Research Corp. R.R.R. thanks Professor J. D. Petersen and Brent MacQueen, Department of Chemistry, Clemson University, and Lt. Col. Dennis Fife, Department of Chemistry, U.S. Air Force Academy, for emission data.

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Strategy for the Synthesis of Mixed Phosphine–Phosphine, Phosphine–Arsine, and Phosphine–Stibine Complexes of the Types Re$_2$H$_8$(PR$_2$Ph)$_2$(EPh$_3$)$_2$ and Re$_2$H$_8$(PRPh$_2$)$_3$(EPh$_3$) (R = Me, Et; E = P, As, Sb)

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Received August 15, 1989

The dirhenium octahydride complexes of stoichiometry Re$_2$H$_8$(PR$_3$)$_4$ constitute an important class of transition-metal polyhydride complexes whose structures,[1–4] redox characteristics,[5] and chemical reactivities[6–11] are of much current interest. Studies of their reactivity behavior have included protonation,[5,6] reactions with nucleophiles,[5,7,8] and reactions with copper(I),[9] gold(I),[10] and tin(II)[11] reagents. Many of these investigations have paralleled related studies on mononuclear rhenium polyhydrides, especially the very familiar heptahydrides ReH$_7$(PR$_3$)$_2$,[12] which also display a wide range of chemical reactivities[12–16] and interesting structural characteristics.[17] Of special note is the conversion of certain ReH$_7$(PR$_3$)$_2$ complexes to Re$_2$H$_8$(PR$_3$)$_4$ under thermal and photochemical conditions.[12,18]

While several different methods have been used in the past to generate the dirhenium octahydrides,[12,18–23] none were adapted to cover a wide range of phosphine ligands until we developed a synthetic strategy that we found was suitable for use with monodentate and bidentate phosphine ligands.[3,24] This utilized the dirhenium(II) complexes Re$_2$Cl$_4$(PR$_3$)$_4$[25–28] as starting materials and involved reaction with LiAlH$_4$ in glyme or THF. These one-pot reactions were dependent only upon the availability of the Re$_2$Cl$_4$(PR$_3$)$_4$ starting materials. In developing this procedure, we had reasoned that, with the use of starting materials that already contained the desired (R$_3$P)$_2$ReRe(PR$_3$)$_2$ architecture, i.e., (PR$_3$)$_2$Cl$_2$ReReCl$_2$(PR$_3$)$_2$, the strategy would be simplified and the yields optimized. This methodology requires that the phosphine ligands that are already bound to the dirhenium core not be labile, a condition that seems to be met. As a further development of this chemistry, we have examined how the dirhenium complexes Re$_2$Cl$_6$(PR$_3$)$_2$ and Re$_2$Cl$_5$(PR$_3$)$_3$,[25,29] which contain fewer than *four* phosphines, might be used to prepare mixed-phosphine complexes of stoichiometry Re$_2$H$_8$(PR$_3$)$_{4-n}$(PR'$_3$)$_n$ (n = 1 or 2), and closely related derivatives that contain

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