(s, CH, 4 H), 4.0 (q, CH_2CH_3, 16 H), 1.93 (t, CH_2CH_3, 24 H), −6.61 (d, CH_3, 3 H), $J_{^{103}Rh-CH}$ = 3.0 Hz. LR FABMS (C_5H_5N): OEPRh–CH_3 *m/e* = 650. ^1H NMR (C_6D_6): δ 10.21 (s, CH, 4 H), 3.97 (q, CH_2CH_3, 16 H), 1.92 (t, CH_2CH_3, 24 H), −6.01 (d, CH_3, 3 H), $J_{^{103}Rh-CH}$ = 3.0 Hz).

(OEP)Rh–C(O)CH$_3$. (Octaethylporphyrin)rhodium acyl was prepared by literature procedures.[11b] ^1H NMR (C_5D_5N): δ 10.43 (s, CH, 4 H), 4.07 (m, CH_2CH_3, 16 H), 1.91 (t, CH_2CH_3, 24 H), −3.14 (s, C(O)CH_3, 3 H). LR FABMS (C_5H_5N): (OEP)Rh–C(O)CH_3 *m/e* = 678. ^1H NMR (C_6D_6): δ 10.30 (s, CH, 4 H), 3.98 (m, CH_2CH_3, 16 H), 1.90 (t, CH_2CH_3, 24 H), −3.16 (s, C(O)CH_3, 3 H).

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Registry No. **1**, 63439-10-1; **2**, 63372-77-0; (OEP)Rh–CHO, 79666-16-3; [(OEP)Rh(py)$_2$]ClO$_4$, 118977-41-6; (OEP)Rh–I, 69509-36-0; Na[(OEP)Rh], 118977-42-7; (OEP)Rh–CH(OH)CH$_3$, 83691-20-7; (OEP)Rh–CH$_3$, 36643-85-3; (OEP)Rh–C(O)CH$_3$, 83691-22-9; CO, 110-86-1; H_2, 1333-74-0; $CH_2{=}CH_2$, 74-85-1; CH_3I, 74-88-4; $CH_3C(O)Cl$, 75-36-5; CH_3CHO, 75-07-0; pyridine, 110-86-1.

Synthesis, Optical, Photophysical, and Redox Properties of a Ligand-Bridged Heteronuclear (OC)$_5$W(pyz)Re(CO)$_4$Cl (pyz = Pyrazine) Complex

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The heteronuclear ligand-bridged complex $(OC)_5W(pyz)Re(CO)_4Cl$ (pyz = pyrazine) has been prepared by thermal reaction of $ClRe(CO)_4(pyz)$ with photochemically generated $W(CO)_5(THF)$ (THF = tetrahydrofuran). Infrared, electronic absorption, photophysical, and redox data have been obtained from this complex, the corresponding mononuclear derivatives, and the homonuclear dimer complexes $(OC)_5W(pyz)W(CO)_5$ and $Cl(OC)_4Re(pyz)Re(CO)_4Cl$. Infrared spectra illustrate that the carbonyl ligands in the $W(CO)_5$ and $ClRe(CO)_4$ groups of these compounds have approximately C_{4v} and C_s local symmetries, respectively. Electronic absorption spectra reveal the presence of $^1A_1 \rightarrow {}^1E$ ligand field (LF) and M → π^*(pyz) metal to ligand charge-transfer (MLCT) transitions for all species. In each case the MLCT bands are attributed to be at lowest energy; these transitions are substantially lowered in the binuclear molecules and reflect the perturbation of the pyz π^*-acceptor system. The absorption spectra indicate that the chromophores' LF transitions are relatively unaffected on binucleation, whereas the energy of the ligand π^*-system is influenced by both metals. Emission spectra, lifetimes, quantum yields, and excitation spectra recorded from the complexes in 283–298 K solution are consistent with the lowest lying MLCT excited state model. No evidence has been obtained from the electronic spectra for a metal to metal charge-transfer (MMCT) transition in the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex. Cyclic voltammetry data have been obtained from each complex; oxidation potentials are in accordance with the $^1A_1$ HOMO assignment, and first reduction potentials are further illustrative of the energy stabilization of the pyz π^*-acceptor system. Comparisons of redox potential differences with MLCT transition energies indicate appreciable Franck–Condon reorganization energies in the binuclear Re complexes. Calculated conproportionation constants are also representative of strong electronic perturbations of the binucleating pyz ligands in these complexes.

Introduction

In the past few years there has been great interest in the electronic spectra[1] and photochemical properties[2] of ligand-bridged zerovalent group 6 metal carbonyl dimer complexes. Extensive studies have been carried out on binuclear complexes that are linked between two $M(CO)_5$ groups with the formula $(OC)_5M{-}L{-}M'(CO)_5$ and between two $M(CO)_4$ fragments with the formula $(OC)_4M{-}L{-}M'(CO)_4$ (M, M′ = Cr, Mo, W). One aspect of research in our laboratory has been concerned with the excited-state properties of the $(OC)_5M{-}L{-}M'(CO)_5$ system. In particular, we have sought to understand the substantial photophysical and photochemical changes that occur to these molecules on forming dimers and on varying the binucleating ligand.[3] Additionally, the extraordinary solvent dependence exhibited by several of these binuclear complexes has been rationalized in terms of the bridging ligands' electronic characteristics and the nature of the lowest energy excited states in these molecules.[4]

This paper reports a further development in our investigation of this system with the now successful synthesis

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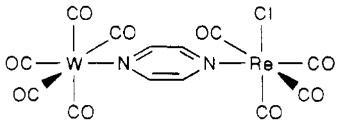
Table I. Infrared Carbonyl Stretching Frequencies and Assignments for the Mononuclear and Binuclear Metal Carbonyl Complexes[a]

complex	ν_{CO}, cm^{-1}				
	$A_1{}^1$	B_1	E	$A_1{}^2$	
$(OC)_5W(pyz)W(CO)_5$	2070 (m)	1968 (vw)	1946 (s), 1915 (s)	1892 (s)	
$W(CO)_5(pyz)$	2066 (m)	1987 (sh)	1928 (br)	1890 (s)	
	ν_{CO}, cm^{-1}				
	A′(3)	A′(2)	A″	A′(1)	
$Cl(OC)_4Re(pyz)Re(CO)_4Cl$	2114 (m)	2012 (s)	1998 (m)	1935 (s)	
$ClRe(CO)_4(pyz)$	2119 (m)	2010 (s)	1985 (m)	1930 (s)	
	ν_{CO}, cm^{-1}				
	A′(3)	$A_1{}^1$/A′(2)	B_1/A″	E/A′(1)	$A_1{}^2$
$(OC)_5W(pyz)Re(CO)_4Cl$	2118 (w)	2028 (vs)	1989 (m)	1944 (s)	1898 (m)

[a] Recorded in methylene chloride. Band intensities: s, strong; m, moderate; br, broad; vw, very weak; sh, shoulder.

of the heteronuclear complex $(OC)_5W(pyz)Re(CO)_4Cl$ (pyz = pyrazine).



A detailed spectroscopic and electrochemical study of this unsymmetrical organometallic binuclear species has been undertaken with the primary objective being to learn about the nature and extent of electronic interaction that exists across the pyz ligand binding these two different metals. To make the necessary comparisons we have also studied the physical properties of the mononuclear derivatives and the corresponding homonuclear ligand-bridged complexes.

Results and Discussion

The heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex was obtained by thermally reacting $ClRe(CO)_4(pyz)$ with prior photogenerated $W(CO)_5(THF)$ in a hexanes solution (see eq 1 and 2). In this relatively nonpolar solution the

$$W(CO)_6 \xrightarrow[0.1\ M\ THF/hexanes]{h\nu,\ \lambda = 313\ nm} W(CO)_5(THF) + CO \quad (1)$$

$$W(CO)_5(THF) + ClRe(CO)_4(pyz) \rightarrow (OC)_5W(pyz)Re(CO)_4Cl + THF \quad (2)$$

product complex does not suffer thermal decomposition, and, in fact, it is virtually insoluble and precipitates readily. Alternative efforts to prepare the heteronuclear product via the $ClRe(CO)_4(THF)$ adduct were unsuccessful because $W(CO)_5(pyz)$ is thermally unstable in the 0.1 M THF/hexanes solution.

Infrared carbonyl stretching frequencies recorded from the series of mononuclear and binuclear complexes studied are shown in Table I. The $W(CO)_5(pyz)$ and $(OC)_5W(pyz)W(CO)_5$ complexes exhibit three moderate/strong bands; these are assigned to $A_1{}^1$, E, and $A_1{}^2$ modes, in accordance with the local C_{4v} symmetry of the carbonyl ligands.[5] The predicted infrared-inactive B_1 mode is also observed as a weak spectral feature, indicating that the carbonyl ligands are somewhat distorted from ideal C_{4v} symmetry in these molecules. The four moderate/strong bands of the $ClRe(CO)_4(pyz)$ and $Cl(OC)_4Re(pyz)Re(CO)_4Cl$ complexes are assigned to 3A′ and A″ modes, concordant with the local C_s symmetry of the carbonyl ligands in the cis configuration.[6] Significantly, the unsymmetrical ligand-bridged $(OC)_5W(pyz)Re(CO)_4Cl$ complex displays five infrared bands; these are attributed to the carbonyl stretching frequencies of both the $W(CO)_5$ (C_{4v}) and $ClRe(CO)_4$ (C_s) moieties. Between 1940 and 2030 cm^{-1} some of these bands are overlapping (see Table I).

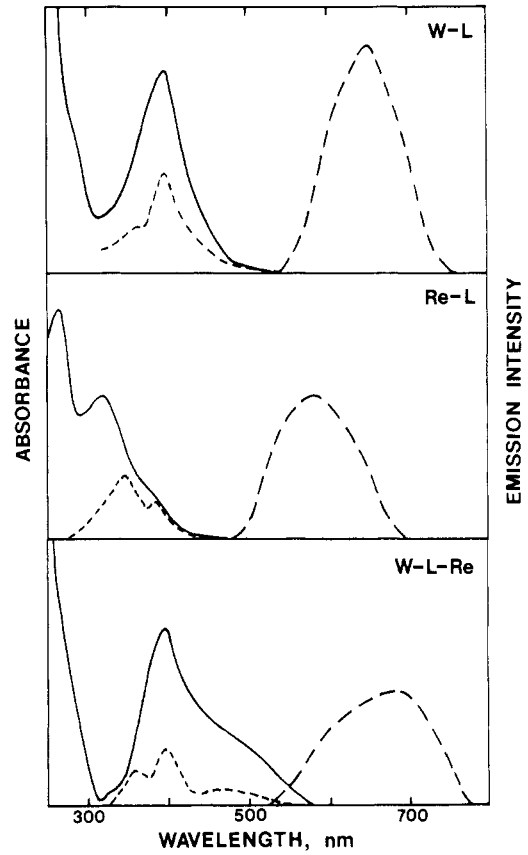


Figure 1. Electronic absorption (—), emission (– –), and excitation (- - -) spectra of $W(CO)_5(pyz)$ (W–L), $ClRe(CO)_4(pyz)$ (Re–L), and $(OC)_5W(pyz)Re(CO)_4Cl$ (W–L–Re) in deoxygenated methylene chloride. Emission spectra were recorded following excitation at 400 nm, and they are fully corrected for variations in detector response as a function of wavelength. Excitation spectra were recorded with the emission monitored at the uncorrected emission maxima, and they are fully corrected for wavelength variations in exciting lamp intensity.

Figure 1 illustrates electronic absorption spectra recorded from the mononuclear $W(CO)_5(pyz)$ and $ClRe(CO)_4(pyz)$ complexes and the ligand-bridged heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex in methylene chloride. Absorption data obtained from all of the compounds studied are summarized in Table II. Previously, it has been shown that the low-energy absorption region of these d^6 W(0) complexes consists of $^1A_1(e^4b_2{}^2) \rightarrow {}^1E(e^3b_2{}^2a_1{}^1)$ ligand field (LF) and W → π^*(pyz) metal to ligand charge-transfer (MLCT) transitions.[1d,2c,3] The spectra of the d^6 Re(I) derivatives are assigned analogously to $^1A_1 \rightarrow {}^1E$ LF and Re → π^*(pyz) MLCT bands, but these transitions are noticeably at higher energies. Charge-transfer W → π^*(CO) and Re → π^*(CO) transitions are also observed at wavelengths below 300 nm. A full assignment of all the absorption bands is included in Table II.

In accordance with these electronic assignments the $^1A_1 \rightarrow {}^1E$ LF transitions are relatively unshifted in the binu-

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Table II. Electronic Absorption and Emission Data for the Mononuclear and Binuclear Metal Carbonyl Complexes in Deoxygenated Methylene Chloride at 298 K

complex	absorption λ_{max}, nm (ϵ, M^{-1} cm^{-1}) M → π^*(CO)	$^1A_1 \rightarrow {}^1E$	M → π^*(pyz)	emission[a] λ_{max}, nm	$\Delta\nu_{1/2}$, cm^{-1}	$10^4\phi_e$[b]	τ_e,[c] ns
$(OC)_5W(pyz)W(CO)_5$	282 (7200)	395 (6000)	521 (12800)	730	2.70	1.60	103
$Cl(CO)_4Re(pyz)Re(CO)_4Cl$	267 (1980)	318 (sh)	400 (1100), 466 (sh)	688	2.68	3.03	137
$(OC)_5W(pyz)Re(CO)_4Cl$	280 (sh)	323 (sh), 397 (1580)	486 (sh)	688	3.24	1.59	196
$W(CO)_5(pyz)$	285 (sh)	398 (8700)	*d*	649	2.60	0.29	42
$ClRe(CO)_4(pyz)$	263 (1930)	323 (1220)	371 (sh)	583	3.47	1.85	153

[a] Exciting wavelength is 380 nm. Emission data recorded at 283 K for the Re complexes. [b] Absolute quantum yields measured relative to the emission of $Ru(bpy)_3^{2+}$; accurate to within ±10%. [c] Lifetimes accurate to within ±5 ns except for $W(CO)_5(pyz)$ which has errors of ±2 ns. [d] Overlaps substantially with LF transition; sh = shoulder.

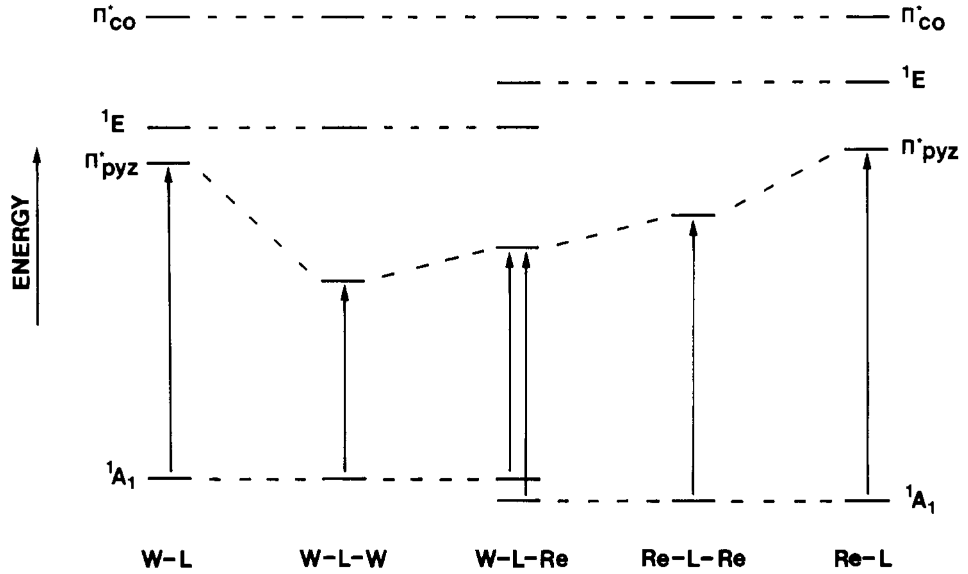

Figure 2. Qualitative energy level scheme based on the absorption spectra of the $W(CO)_5(pyz)$ (W–L), $ClRe(CO)_4(pyz)$ (Re–L), $(OC)_5W(pyz)W(CO)_5$ (W–L–W), $Cl(OC)_4Re(pyz)Re(CO)_4Cl$ (Re–L–Re), and $(OC)_5W(pyz)Re(CO)_4Cl$ (W–L–Re) complexes. For clarity only the MLCT transitions are shown.

clear complexes from those of their corresponding mononuclear derivatives; this illustrates that the d orbital symmetries and ligand field characters of the $W(CO)_5$ and $ClRe(CO)_4$ fragments are largely preserved on binucleation. Contrastingly, the M → π^*(pyz) MLCT transitions are substantially red-shifted in the binuclear complexes compared to their mononuclear derivatives, reflecting perturbation of the ligand π^*-acceptor orbitals on forming the bridged species. As noted previously for a series of ligand-bridged W binuclear compounds, this effect is particularly striking for molecules that are linked via the conjugated pyz ligand.[3,4]

Significantly, the absorption spectrum of heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ is not an aggregate of the individual mononuclear components (see Figure 1). The low-lying MLCT feature indicates a strongly perturbed pyz ligand π^*-system in this complex. It is important to note that although the MLCT band in the unsymmetrical complex lies in between those of the $(OC)_5W(pyz)W(CO)_5$ and $Cl(OC)_4Re(pyz)Re(CO)_4Cl$ complexes, its spectrum is not simply the sum of the spectra from the homonuclear ligand-bridged species. Indeed, the ligand π^* orbital energy is clearly different for each of these metal carbonyl complexes. These results demonstrate that the energy of the pyz π^*-system is strongly influenced by *both* organometallic substituents, whereas the LF absorptions are virtually unaltered; thus, the metal d orbitals are essentially unperturbed by the coordination of the second metal. Fitting with this rationale the spectrum of the heteronuclear complex (see Figure 1) exhibits LF $^1A_1 \rightarrow {}^1E$ transitions at energies of both the Re and W mononuclear components. The broad MLCT band of $(OC)_5W(pyz)Re(CO)_4Cl$ must comprise transitions from both the Re- and W-filled d levels ($^1A_1$) to the delocalized pyz π^*-acceptor systems, although these individual bands are apparently too close in energy to be resolved. Attempts to separate these MLCT transitions via solvent and temperature dependence studies have been unsuccessful because of the limited solubility of the heteronuclear complex in nonpolar media and its thermal instability in polar solvents. From the observed extinction coefficients (see Table II) it appears that there is significant orbital mixing between the $^1A_1 \rightarrow {}^1E$ and M → π^*(pyz) states, especially when these levels are close in energy. Consequently, the MLCT band of the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex is much weaker than the corresponding band of the symmetrical $(OC)_5W(pyz)W(CO)_5$ species. Figure 2 portrays a qualitative orbital energy level diagram consistent with these absorption interpretations.

Photophysical measurements illustrate that all the metal complexes exhibit emission in 283–298 K fluid solution (see Figure 1 and Table II), and these strongly support the lowest energy MLCT absorption assignments. The emission spectra, lifetimes, and quantum yields are, in fact, typical of metal carbonyls emitting from MLCT states.[7] Each complex displays a broad emission band; in each molecule the emission spectral distribution was unaffected

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Table III. Excitation Spectral Data for the Mononuclear and Binuclear Metal Carbonyl Complexes in Deoxygenated Methylene Chloride at 298 K[a]

complex	λ_{max}, nm
$(OC)_5W(pyz)W(CO)_5$	396, 532
$Cl(OC)_4Re(pyz)Re(CO)_4Cl$	364, 396, 466 (sh)
$(OC)_5W(pyz)Re(CO)_4Cl$	354, 398, 460
$W(CO)_5(pyz)$	362, 396
$ClRe(CO)_4(pyz)$	352, 392

[a] Excitation spectra recorded while monitoring at the uncorrected emission maxima; sh = shoulder. Data was obtained at 283 K for the Re complexes.

on varying the exciting wavelength between 300 and 400 nm, and the observed emission decay was strictly single exponential with a lifetime that was constant at any wavelength under the emission band. These results illustrate that in each complex the MLCT manifold is thermally equilibrated in solution at room temperature.[4b] Excitation spectra have been recorded from all of the complexes while monitoring the emission at the MLCT band maxima, and these are summarized in Table III. Illustrative spectra are depicted in Figure 1. In each case the excitation spectra confirm the origin of the emission from the lowest energy MLCT absorption band. Higher energy band maxima are also observed which correspond to the LF $^1A_1 \rightarrow {}^1E$ transitions, and this demonstrates that the LF levels are able to effectively decay, via nonradiative processes, to the emitting MLCT states. These spectra also illustrate that there is little emission on exciting at even shorter wavelengths ($\lambda < 300$ nm); this is believed to be a result of efficient photodissociation from higher lying LF states and efficient nonradiative depopulation of the $M \rightarrow \pi^*(CO)$ levels.[3]

The possibility of a metal to metal charge-transfer (MMCT), analogous to an intervalence transition (IT)[8] as predicted by the Hush model,[9] has been explored because the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex formally has mixed valence W(0) and Re(I) sites. However, we have not found any indication of a MMCT transition in either the absorption or emission studies. In the absorption spectra of $(OC)_5W(pyz)Re(CO)_4Cl$ there is no band that can be identified solely to the heteronuclear complex (apart from the aforementioned MLCT absorptions), even in spectra recorded out to 2100 nm. Moreover, the emission quantum yield and lifetime data show absolutely no evidence for intramolecular quenching of the MLCT level, as may be expected for a lowest lying MMCT band.[10] Nevertheless, a MMCT band cannot be excluded just because it is not observed; it could, for instance, be hidden by one of the intense MLCT absorption or exist at higher energies. Indeed, the probability of electron transfer between these W and Re chromophores is expected to be very small because the metals each have a low-spin filled $(t_{2g})^6$ electronic configuration, and, therefore, it necessitates a symmetry-forbidden transition to a $d(\sigma^*)$ orbital on the acceptor metal. Such a transition would be anticipated to be of higher energy than the MLCT bands.

Cyclic voltammetry data have been recorded from all the complexes in deoxygenerated methylene chloride solution, and some representative voltammograms are shown in Figure 3. A list of all the redox data obtained is summarized in Table IV. The oxidation potentials measured are indicative of oxidation from the HOMO ($^1A_1$) levels of these complexes, and, in accordance with the absorption observations, they are not significantly altered on forming the ligand-bridged dimers from their mononuclear derivatives. Additionally, the electrochemical data illustrate that the W(0) complexes ($E_{ox.} \sim +1.25$ V) are substantially easier to oxidize than the Re(I) complexes ($E_{ox.} \sim +1.75$ V). However, the observed reversibility of the oxidation peaks indicate that the Re complexes, but not the W derivatives, are stable on oxidation. Importantly, it is noted that the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ species exhibits two oxidation potentials that correspond to the oxidations of both the W and Re $^1A_1$ HOMO levels, supporting the LF absorption interpretation shown in Figure 2.

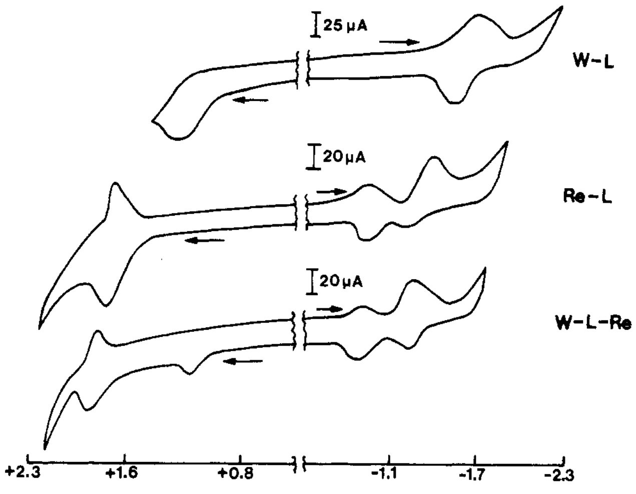

Figure 3. Cyclic voltammograms of $W(CO)_5(pyz)$ (W–L), $ClRe(CO)_4(pyz)$ (Re–L), and $(OC)_5W(pyz)Re(CO)_4Cl$ (W–L–Re) complexes in deoxygenated methylene chloride. Solutions contain 0.1 M TBAP as supporting electrolyte. All potentials are in volts vs SCE; scan rate is 80 mV s^{-1}.

Reduction potentials obtained represent ligand centered one-electron processes for the LUMO (pyz π^*) levels of the complexes. Both reversible $E_{pc} - E_{pa} \approx 0.058/n$ V (E_{pc} = cathodic peak potential, E_{pa} = anodic peak potential, n = number of electrons transferred per molecule) and irreversible ($E_{pc} - E_{pa} \gg 0.058$ V) potentials are observed.[1k,11] Cyclic voltammetry data recorded on scanning reversible waves following irreversible ones were identical with those obtained on scanning vice versa. This ensures that the observed data can indeed be attributed to the complexes and not to possible decomposition products. The first reduction potentials are consistent with the energy stabilization of the ligand π^*-acceptor orbital, following the order binuclear < mononuclear < free ligand (see Table IV). The data also illustrate that the Re(I) complexes tend to be easier to reduce than the W(0) complexes. Significantly, the observed first reduction potential of the heteronuclear $(OC)_5W(pyz)Re(CO)_4Cl$ complex at −0.90 V lies in between the values for the homonuclear dimer species, confirming the influence of both metal centers on the energy stabilization of the pyz ligand π^*-system.

A further qualitative relationship can be established for these binuclear molecules based on the redox potential difference, $\Delta E_{ox./red.}$ (see eq 3), and the MLCT transition

$$\Delta E_{ox./red.} = E_{ox.} - E_{red.}(0/1-) \text{ [in V]} \qquad (3)$$

energy (see Table II).[12] The calculated $\Delta E_{ox./red.}$ value for

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Table IV. Redox Potentials Obtained from the Free Pyrazine Ligand and the Mononuclear and Binuclear Metal Carbonyl Complexes in Methylene Chloride at 298 K[a]

complex	$E_{ox.}$	$E_{red.}$ (0/1−)	$E_{red.}$ (1−/2−)	$E_{red.}$ (2−/3−)
$(OC)_5W(pyz)W(CO)_5$	+1.26 (i)	−1.21	>−2.3	
$Cl(CO)_4Re(pyz)Re(CO)_4Cl$	+1.73	−0.47 (i)	−0.89	−1.23
$(OC)_5W(pyz)Re(CO)_4Cl$	+1.82, +1.16 (i)	−0.90	−1.24	
$W(CO)_5(pyz)$	+1.25 (i)	−1.70 (i)		
$ClRe(CO)_4(pyz)$	+1.76	−0.93	−1.40 (i)	
pyz		>−2.30		

[a] Electrochemical measurements performed in deoxygenated solutions containing 0.1 M TBAP. All potentials in volts vs SCE; scan rate 80 mV/s; scan range +2.3 to −2.3 V; i = irreversible process. All potentials were reproducible to ±0.02 V.

$(OC)_5W(pyz)W(CO)_5$ is 2.47 eV (for a one-electron process) which is close to the MLCT transition energy of 2.38 eV. In contrast, the calculated values for $(OC)_5W(pyz)Re(CO)_4Cl$ and $Cl(OC)_4Re(pyz)Re(CO)_4Cl$ are 2.06 and 2.20 eV, apparently displaying no correlation with the MLCT energies of 2.55 and 2.66 eV, respectively. This suggests that an additional energy term (χ) must be incorporated to rationalize the MLCT transition energies of the Re complexes (see eq 4). Here, E_{op} is the optical transition

$$\Delta E_{ox./red.}\ [\text{in V}] = E_{op}\ [\text{in eV}] - \chi \qquad (4)$$

energy and χ represents the Franck–Condon reorganization energy from intermolecular and intramolecular vibrations. There is good agreement for the $(OC)_5W(pyz)W(CO)_5$ molecule whereas the χ values obtained for both the binuclear Re complexes imply much more distortion; this may be due to additional twisting arising from the cis coordination of the large Cl ligand in the $ClRe(CO)_4$ groups.

Each of the ligand-bridged complexes exhibit two or three reduction potentials associated with the pyz ligand. The difference (Δ) between the first two reduction potentials may be related to the conproportionation constant (K_{con}), represented by eq 5;[1j,3,13] these processes are shown for the heteronuclear complex in eq 6–8. The K_{con} value

$$\Delta = E_{red.}(0/-) - E_{red.}(1-/2-) = 0.0591 \log K_{con}\ (\text{at } 25\ ^\circ\text{C}) \qquad (5)$$

$$(OC)_5W(pyz)Re(CO)_4Cl + e^- \overset{E_{red.}(0/1-)}{\rightleftharpoons} [(OC)_5W(pyz)Re(CO)_4Cl]^- \qquad (6)$$

$$[(CO)_5W(pyz)Re(CO)_4Cl]^- + e^- \overset{E_{red.}(1-/2-)}{\rightleftharpoons} [(CO)_5W(pyz)Re(CO)_4Cl]^{2-} \qquad (7)$$

$$[(CO)_5W(pyz)Re(CO)_4Cl]^{2-} + (OC)_5W(pyz)Re(CO)_4Cl \overset{K_{con}}{\rightleftharpoons} 2[(OC)_5W(pyz)Re(CO)_4Cl]^- \qquad (8)$$

calculated for $(OC)_5W(pyz)W(CO)_5$ is 3×10^{18}, and the Re dimers both have $K_{con} \sim 10^7$; these large K_{con} values provide further evidence for the electronic characteristics of the ligand π^*-acceptor systems in these binuclear complexes. Differences in the above values may be due to varying energy repulsions between the two electrons in the HOMO orbital and/or the lowering of electron density in the Re complexes because of its bond to the highly electronegative chlorine atom. The latter effect will tend to drain the electron density away from the Re center and consequently weaken the influence of the metals on the binucleating ligand.

Experimental Section

Materials. Tungsten hexacarbonyl (Strem) and rhenium pentacarbonyl chloride (Pressure) were purified by repeated sublimations prior to use. The pyz ligand (Aldrich) was recrystallized. Tetrahydrofuran (THF) used for syntheses was distilled from $LiAlH_4$ and stored under Ar. Methylene chloride used in the spectroscopic and electrochemical experiments was obtained as HPLC grade (J. T. Baker) and was dried over 4-Å molecular sieves and distilled prior to use. Other solvents used were of Photrex grade (J. T. Baker) and were distilled under N_2 to ensure removal of emitting impurities. Tetrabutylammonium perchlorate (TBAP) was rigorously dried in vacuo before using as a supporting electrolyte. Nitrogen used in the purging experiments was purified to remove O_2 and H_2O according to a previously reported procedure.[14]

Synthesis of $ClRe(CO)_4(pyz)$. This complex was obtained by refluxing $ClRe(CO)_5$ (1.0 mmol) and pyz (1.25 mmol) in toluene (100 mL) under a N_2 atmosphere. The $ClRe(CO)_4(pyz)$ crude product precipitated during this reflux, and it was collected by vacuum filtration and subsequently washed several times with hexanes to remove unreacted starting materials. The compound was further purified by recrystallization from a 9:1 (v/v) hexane/methylene chloride solution and then sublimed at reduced pressure.

Synthesis of $W(CO)_5(pyz)$ and $(OC)_5W(pyz)W(CO)_5$. These complexes were prepared according to previously described procedures.[3,15]

Synthesis of $Cl(OC)_4Re(pyz)Re(CO)_4Cl$. This binuclear complex was obtained by refluxing $ClRe(CO)_5$ (2.0 mmol) and pyz (1.0 mmol) in toluene (100 mL) under N_2, similar to the above $ClRe(CO)_4(pyz)$ preparation. The product was collected by vacuum filtration and then purified by sublimation under reduced pressure.

Synthesis of $(OC)_5W(pyz)Re(CO)_4Cl$. This heteronuclear ligand-bridged complex was obtained by thermally reacting approximately equimolar amounts of $ClRe(CO)_4(pyz)$ with prior photogenerated $W(CO)_5(THF)$ in deoxygenated hexanes containing 0.1 M THF. In this relatively nonpolar solvent mixture the heteronuclear complex precipitated out of solution; it was subsequently vacuum filtered and purified by repeated washings with hexanes and then sublimed at reduced pressure.

The purified products were typically obtained in 50–55% yields and satisfactory analytic data (±0.4%, C, H, N) were obtained from all the complexes.

Spectral and Photophysical Measurements. Infrared spectra were obtained on a Perkin-Elmer 283B spectrometer from the complexes in methylene chloride solution by using a 1-mm path length NaCl cell; reported band maxima are considered accurate to ±2 cm^{-1}. Electronic absorption spectra were recorded on a Hewlett-Packard 8450A diode-array spectrometer, and the reported absorption maxima are believed accurate to ±2 nm. Emission and excitation spectra were recorded on an SLM Instruments Model 8000/8000S spectrometer which incorporates

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a photomultiplier-based photon-counting detector. A red-sensitive Hamamatsu R928 photomultiplier tube was used for these measurements.

The obtained emission and excitation spectra were fully corrected for variations in the detector response and exciting lamp intensity as a function of wavelength; the band maxima were reproducible to ±4 nm. Excitation data were recorded from solutions that were optically dilute ($A < 0.1$) throughout the spectral region; under these conditions excellent agreements were observed between the absorption and excitation data for known standards such as quinine sulfate and 1,2-benzanthracene.[16] Emission quantum yields (ϕ_e) were determined by the Parker-Rees method[17] with dilute $Ru(bpy)_3^{2+}$ in deoxygenated aqueous solution at 283 K ($\phi_e = 0.046$)[18] as a calibrant. These values were corrected for the differing refractive indices of the solvents,[19] and they are believed to be accurate to ±10%. In all the emission and excitation experiments the sample solutions were filtered through 0.22-μm Millipore filters and deoxygenated prior to taking readings. The solution temperature was controlled to ±0.1 K. Solvent blanks were also run to check for possible emitting impurities.

Emission lifetimes (τ_e) were determined on a PRA System 3000 time-correlated pulsed single-photon apparatus that is described more fully in an earlier paper.[3] Solutions were excited in the 300–400 nm region with monochromatic light from a PRA Model 510 nitrogen flash lamp, typically using a lamp pulse width of 1 ns. Single exponential decays were observed for each sample, and the lifetime errors were estimated to be ±5 ns. The reported values represent the average of at least three readings.

Electrochemical Studies. Cyclic voltammetry data were recorded on a BioAnalytical Systems Corrosion Model CV-47 voltammograph connected to a Houston Instruments Model 200 X-Y recorder. The electrochemical cell contained a glassy-carbon working electrode, a platinum-wire auxiliary electrode, and a saturated calomel reference electrode (SCE). The concentrations of the metal carbonyl complexes in these experiments were in the 10^{-3}–10^{-4} M range, and 0.1 M tetrabutylammonium perchlorate (TBAP) was present as the supporting electrolyte. The measurements were uncorrected for the liquid-junction potentials, but these are estimated to be less than 0.01 V. The ferrocene–ferrocenium ($F_c/F_c^+ = 0.466$ V) oxidation was used as an internal standard,[13c,20] and the reported potentials are calibrated to this value. The scan rate used in these experiments was 80 mV s^{-1}. In all cases absorption spectra recorded following electrochemical measurements were unchanged, indicating negligible complex decomposition.

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Registry No. $ClRe(CO)_4(pyz)$, 119325-59-6; $ClRe(CO)_4(pyz)^-$, 119325-64-3; $ClRe(CO)_4(pyz)^{2-}$, 119325-67-6; $(OC)_5W(pyz)W(CO)_5$, 70738-71-5; $(OC)_5W(pyz)W(CO)_5^-$, 79070-32-9; $(OC)_5W(pyz)W(CO)_5^{2-}$, 119325-65-4; $Cl(OC)_4Re(pyz)Re(CO)_4Cl$, 119325-60-9; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^-$, 119325-68-7; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^{2-}$, 119325-69-8; $Cl(OC)_4Re(pyz)Re(CO)_4Cl^{3-}$, 119325-70-1; $(OC)_5W(pyz)Re(CO)_4Cl$, 119325-61-0; $(OC)_5W(pyz)Re(CO)_4Cl^-$, 119325-62-1; $(OC)_5W(pyz)Re(CO)_4Cl^{2-}$, 119325-66-5; $W(CO)_5(pyz)$, 65761-19-5; $W(CO)_5(pyz)^-$, 119325-63-2; $ClRe(CO)_5$, 14099-01-5; $W(CO)_5(THF)$, 36477-75-5; pyz, 290-37-9; pyz^-, 34512-20-4.

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(Cyclopentadienyl)ruthenium Complexes of 3-Methoxyestrone: A High-Field NMR and X-ray Crystallographic Study

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The α- and β-stereoisomers of (η^6-estrone 3-methyl ether)(η^5-cyclopentadienyl)ruthenium(II) hexafluorophosphate have been synthesized by thermal ligand exchange between (cyclopentadienyl)tris(acetonitrile)ruthenium hexafluorophosphate and estrone 3-methyl ether. The initial 7:3 α:β mixture was fractionally crystallized to yield each pure stereoisomer. ^1H and ^{13}C NMR spectra were analyzed in detail for each stereoisomer, and an X-ray structure for the β-isomer of $(C_{19}H_{24}O_2)Ru(C_5H_5)^+PF_6^-$ was carried out: monoclinic; $P2_1$; $a = 8.0717$ (7) Å, $b = 14.813$ (1) Å, $c = 10.597$ (1) Å; $\beta = 109.93$ (1)°; $Z = 2$. The structure was refined to R and R_w values of 0.0251 and 0.0325, respectively, by using 1989 reflections.

Introduction

In recent years, there has been burgeoning interest in the use of organometallic moieties to modify the chemistry of steroidal systems.[1] Typically, the $Fe(CO)_3$ fragment has been used to protect the diene unit in the B ring of ergosterol and related plant steroids; this permitted the facile manipulation of the C(22)–C(23) double bond.[2] Likewise, (η^3-allyl)palladium and η^6-$Cr(CO)_3$ groups have

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