energy compared to [II, II] and split into at least two components. In D_{4h} symmetry, the $e_u^2 e_g^1$ excited state of the mixed-valence ion will split into four states, and transitions between the E_u ground state and each of these are allowed. It is not surprising therefore that the UV absorption for the mixed-valence species shows more structure than for the [II, II] species where only one transition ($A_{2u} \leftarrow A_{1g}$) is allowed. The shift of the MBLCT bands to higher energy is indicative of valence delocalization. In analogous weakly interacting, valence-localized systems (e.g., $[(Ru(NH_3)_5)_2(pyrimidine)]^{5+}$),[29] usually no shift or a small shift to lower energy is observed when the [II, II] species is oxidized to the [III, II]. In the case of a valence-trapped system, when the [II, II] species is oxidized to [III, II], the charge is lost from a single center. The energy the πd donor orbital is little affected while that of the ligand π^* orbital is lowered because of the increase in charge at the oxidized metal center, and thus the energy of the MBLCT is lowered. In the case of delocalized complexes, the electron is removed from an orbital that is shared by both metal centers. Therefore, the oxidation to the mixed-valence state results in a more strongly bound πd level because there is an increase in charge at both metal sites. As a result the MBLCT is shifted to higher energy.

It is of interest to compare the properties of the three mixed-valence molecules $[(Ru(NH_3)_5)_2L]^{5+}$ where L = N_2, NCCN[30] and pyrazine.[7,8] The energy and width of the

near-IR transition decrease with increasing bridging-ligand size. The energy shifts are related to the splitting between $1e_g$ and $2e_u$ (Figure 5), which in turn depends on the interaction of the metals via the bridging ligands.[29,31] Qualitatively, the near-IR bands are similar in their degree of asymmetry.

In regard to the much debated question of the electronic structure and dynamics of the Creutz ion,[7,8] little can be said to clarify the description on the basis of the present work. It is to be noted, however, that the MBLCT band shifts to somewhat lower energy upon oxidation of $[(Ru(NH_3)_5)pyz]^{4+}$ to the mixed-valence ion.[8] This is in contrast to the shift to higher energy in the present μ-dinitrogen cases, which feature stronger metal–metal interaction. This observation is consistent with the view held by some[32,33] that the metal–metal interaction in the Creutz ion places it somewhere between the localized and completely delocalized regimes.

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(31) Lauher, J. *Inorg. Chim. Acta* **1980,** *39,* 119.
(32) Mayoh, B.; Day, P. *Inorg. Chem.* **1974,** *13,* 2273.
(33) Taube, H. *Ann. N.Y. Acad. Sci.* **1978,** *313,* 481.

Synthesis and Characterization of Mononuclear and Binuclear Ruthenium Complexes of 1,3-Bis(2-pyridylimino)isoindolines
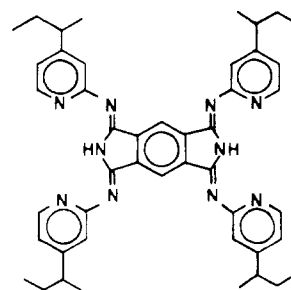
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Ruthenium complexes were prepared containing the ligand 4'-MeLH, resulting from the condensation of 1,2-dicyanobenzene and 2-amino-4-methylpyridine. The ligand functions as a tridentate chelate in its anionic or neutral form. Ruthenium complexes were prepared with metal to ligand ratios of 1:1 and 1:2. The 1:1 complex of Ru(III) also contains three chlorides as ligands, Ru(4'-MeLH)Cl$_3$, while in the 1:2 complex, Ru(4'-MeL)$_2$, the two deprotonated tridentate ligands provide a pseudooctahedral environment about the metal ion. Binuclear complexes were prepared in which the metals are bridged by the ligand made from the reaction of 1,2,4,5-tetracyanobenzene and 2-amino-4-*sec*-butylpyridine. The binucleating ligand binds two metal ions, providing three coordination sites for each, with the remaining coordination sites occupied by 4'-MeL$^-$. Binuclear Ru(II), Ru(III), and mixed-metal complexes were prepared. Spectral and electrochemical properties of these molecules were investigated.

Introduction

Binuclear transition-metal complexes, in which the two metals are bridged by the ligand **1**, 1,3,5,7-tetrakis(2-(4-*sec*-butylpyridyl)imino)benzodipyrrole, have been prepared and characterized.[2] The ligand **1**, HL–LH, binds two metal ions, functioning as a tridentate chelate for each metal. In the metal complexes the bridging ligand is normally present as a dianion

(1) (a) California Institute of Technology. (b) Ford Motor Co.
(2) Gagné, R. R.; Marritt, W. A.; Marks, D. N.; Siegl, W. O. *Inorg. Chem.* **1981,** *20,* 3260.
(3) The binucleating ligand with *sec*-butyl groups on the pyridine rings, **1**, is denoted as HL–LH. Mononucleating ligands, **2**, are denoted as RLH where substituents on the pyridine ring precede the abbreviation, e.g., 4'-MeLH. The organic molecule RLH (**2**) may function as a tridentate chelate in its neutral form or in its anionic form upon deprotonation of the pyrrole nitrogen.

1 ≡ HL–LH³

due to deprotonation of the two pyrrole nitrogens. Binuclear complexes were prepared in which the remaining metal coordination sites are occupied by the anion of the isoindoline ligand **2**, 1,3-bis(2-(4-methylpyridyl)imino)isoindoline, re-

sulting in two six-coordinate metal ions, (4′-MeL)ML–LM-(4′-MeL).

2

4′-MeLH, R = 4-CH$_3$[3]
5′-ClLH, R = 5-Cl

The bridging ligand **1** also made it possible to prepare polymeric metal species containing octahedral metal ions.[4] These oligomeric complexes were of interest because of their possible use as multielectron-transfer reagents. Adjacent metal ions in the complex are quite distant from one another, at approximately 11 Å.[5] The presence of the flat conjugated bridging ligand, however, suggested that electron transfer between the metal ions might be facile.

Mononuclear and binuclear complexes of first-row transition metals have previously been prepared and characterized.[2] Electrochemical and magnetic measurements of the binuclear species indicated little interaction between the metal ions.

Numerous studies involving ruthenium mixed-valent binuclear complexes have been made.[6,7] The results of these studies suggest that information concerning the rate of intramolecular electron transfer in polynuclear complexes containing the bridging ligand **1** might be obtainable by investigating the spectroscopic properties of the mixed-valent ruthenium binuclear complex. Mononuclear, binuclear, and trinuclear ruthenium complexes were prepared. The electrochemical and spectroscopic properties of these species are reported.

Results and Discussion

The syntheses of the ligands have been described elsewhere.[2,8]

Synthesis and Characterization of Mononuclear Ruthenium Complexes. The mononuclear bis(isoindoline)ruthenium(II) complex **3**, Ru(4′-MeL)$_2$, was prepared by reaction of the free ligand in a basic alcoholic solution with either tetrakis(dimethyl sulfoxide)dichlororuthenium(II), Ru(Me$_2$SO)$_4$Cl$_2$, or hydrated ruthenium trichloride (eq 1 and 2). The Ru(II) starting

$$Ru(Me_2SO)_4Cl_2 + 2(4'\text{-MeLH}) \xrightarrow{\text{base}} \underset{\textbf{3}}{Ru(4'\text{-MeL})_2} \quad (1)$$

$$RuCl_3{\cdot}xH_2O + 2(4'\text{-MeLH}) \xrightarrow{\text{base}} \underset{\textbf{3}}{Ru(4'\text{-MeL})_2} \quad (2)$$

material was preferred because the yield of the product was much improved. A greater than 60% yield was attained in this reaction, compared to approximately 15% yield when starting with hydrated ruthenium trichloride.

The preparation of Ru(4′-MeL)$_2$ from hydrated ruthenium trichloride is analogous to the synthesis of Ru(bpy)$_3^{2+}$.[9] In both these syntheses, ruthenium is reduced during the reaction

to Ru(II) with, presumably, the coincident oxidation of alcohol.

The mononuclear Ru(II) complex **3** is a dark blue crystalline solid, dissolving in nonpolar solvents such as methylene chloride and toluene to produce dark green solutions. Although air stable in the solid state, methylene chloride solutions of **3** are moderately air sensitive. The corresponding Ru(III) complex **4**, Ru(4′-MeL)$_2^+$, was isolated from a methylene chloride solution that had been exposed to air for several hours. The complex **3** was oxidized more conveniently with silver ion to the Ru(III) complex **4** and isolated as its ClO$_4^-$ salt (eq 3).

$$\underset{\textbf{3}}{Ru(4'\text{-MeL})_2} + AgClO_4 \rightarrow \underset{\textbf{4}}{Ru(4'\text{-MeL})_2ClO_4} + Ag \quad (3)$$

The dark red-brown Ru(III) complex **4** is paramagnetic with a magnetic moment of 1.85 μ_B, indicative of a d^5 low-spin complex having one unpaired electron. Attempts to prepare Ru(4′-MeL)$_2^+$ directly from the reaction of hydrated ruthenium trichloride and 4′-MeLH were unsuccessful.

The infrared spectra of the metal complexes exhibit strong bands due to the presence of the deprotonated isoindoline ligand.[2] The proton NMR spectra, electronic spectra, and electrochemistry are discussed in a later section.

Synthesis and Characterization of (RLH)RuCl$_3$. To avoid polymerization problems in the synthesis of the binuclear complex, it was necessary to isolate a ruthenium complex containing one chelated isoindoline ligand and several readily dissociable ligands. For the first-row transition metals, M(II) complexes of the type M(4′-MeL)OAc could be easily isolated, and they proved useful as intermediates in the synthesis of the binuclear species (eq 4). Attempts to prepare a monoiso-

$$2M(4'\text{-MeL})OAc + HL\text{-}LH \rightarrow$$
$$(4'\text{-MeL})ML\text{-}LM(4'\text{-MeL}) \quad (4)$$

indoline complex of Ru(II) were unsuccessful. Complexes containing Ru(III) of the type (RLH)RuCl$_3$ were prepared for various substituted isoindoline ligands. These complexes were utilized as the intermediate species necessary in the synthesis of the binuclear ruthenium complex.

The complexes (RLH)RuCl$_3$ (**5**) were made from the reaction of hydrated ruthenium trichloride and the isoindoline ligand in ethanol with no added base (eq 5). The Ru(III)

$$RuCl_3{\cdot}xH_2O + RLH \rightarrow \underset{\textbf{5}}{(RLH)RuCl_3} \quad (5)$$

complexes **5** were obtained as dark brown crystals which usually contained one molecule of ethanol per ruthenium as a solvate. The Ru(III) ions in these complexes are bound to a neutral isoindoline ligand, consistent with the analytical data, magnetic measurements, and the infrared spectrum of the complex. The infrared spectrum of (4′-MeLH)RuCl$_3$ has strong bands in the region 1600–1650 cm^{-1}, which are characteristic of a chelated nondeprotonated isoindoline ligand.[10] The proton, presumably, is not associated with the pyrrole nitrogen, since this would likely interfere with bonding to the metal. The proton may be associated with one of the imine nitrogens. Treatment of complex **5** with a second equivalent of ligand in the presence of a tertiary amine base led to the formation of the Ru(II) complex **3**, Ru(RL)$_2$.

Synthesis and Characterization of Binuclear Ruthenium Complexes. A binuclear Ru(II) complex, **6**, was prepared by treating the bridging ligand **1**, HL–LH, with 2 equiv of (4′-MeLH)RuCl$_3$ in basic ethanol, according to eq 6. The bi-

$$2(4'\text{-MeLH})RuCl_3 + HL\text{-}LH \xrightarrow{\text{base}}$$
$$\underset{\textbf{6}}{(4'\text{-MeL})RuL\text{-}LRu(4'\text{-MeL})} \quad (6)$$

nuclear complex **6** is intensely green and has high solubility

(4) Siegl, W. O. *Inorg. Chim. Acta* **1977**, *25*, L65.
(5) Estimated from data in: Gagné, R. R.; Gall, R. S.; Lisensky, G. C.; Marsh, R. E.; Speltz, L. M. *Inorg. Chem.* **1979**, *18*, 771. Stynes, H. C.; Ibers, J. A. *Ibid.* **1971**, *10*, 2304.
(6) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.
(7) Callahan, R. W.; Keene, F. R.; Meyer, T. J.; Salmon, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 1064.
(8) Siegl, W. O. *J. Org. Chem.* **1977**, *42*, 1872.
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(10) Gagné, R. R.; Marks, D. N., manuscript in preparation.

in organic solvents such as toluene. Although air stable in the solid state the complex is moderately air sensitive in solution. The binuclear Ru(II) complex **6** was successfully oxidized with silver ion to the corresponding Ru(III) binuclear species, which was isolated as its ClO_4^- salt, $(4'-MeL)RuL-LRu(4'-MeL)(ClO_4)_2$. Magnetic measurements indicate the presence of two isolated Ru(III) ions with a magnetic moment at ambient temperature of 1.83 μ_B/ruthenium in the complex. The infrared spectra of the binuclear Ru(II) and Ru(III) complexes are very similar to those of the mononuclear complexes containing deprotonated isoindoline ligands. Proton NMR spectra, electronic spectra, and electrochemical properties are discussed below.

A binuclear Ru(II) complex was prepared with the ligand **7**, $HL-O(CH_2)_3O-LH$, bridging the two metal ions. The
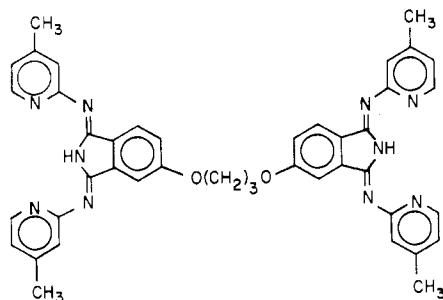
7

ligand was treated with 2 equiv of $(4'-MeLH)RuCl_3$ to prepare the binuclear complex **8** (eq 7). The binuclear complex **8** was

$$2(4'-MeLH)RuCl_3 + HL-O(CH_2)_3O-LH \rightarrow$$
$$(4'-MeL)RuL-O(CH_2)_3O-LRu(4'-MeL) \quad (7)$$
$$\mathbf{8}$$
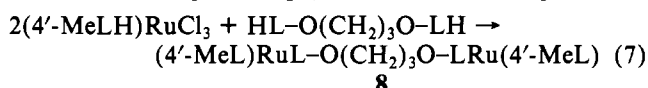
obtained as a dark green solid; the infrared spectrum indicated that both ends of the bridging ligand were complexed.

The preparation of heteronuclear bimetal complexes necessitated the addition of metal ions to the bridging ligand in a stepwise fashion. The ruthenium ion was added first, since both Ru(II) and Ru(III) are rather substitution inert. Ruthenium in either oxidation state was unlikely to undergo ligand exchange during the addition of the second metal ion. The reaction of the Ru(III) complex **5** with a large excess of bridging ligand (eq 8) afforded a mixture of products from

$$(4'-MeLH)RuCl_3 + excess\ HL-LH \xrightarrow{base}$$
$$\mathbf{5}$$
$$(4'-MeL)RuL-LH \quad (8)$$
$$\mathbf{9}$$
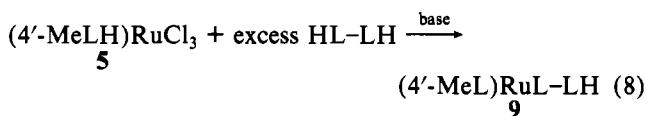
which the desired mononuclear complex **9**, in which one end of the bridging ligand remained unchelated, was isolated after chromatography. The complex **9** was obtained as a dark green powder that was quite soluble in nonpolar solvents including cyclohexane. The infrared spectrum exhibited a relatively strong band at approximately 1635 cm^{-1} characteristic of the unchelated end of the bridging ligand, in addition to bands at lower energy characteristic of the complexed end of the molecule.[2]

The characterization of complex **9** was further confirmed by its conversion to the previously isolated binuclear ruthenium complex **6**, $(4'-MeL)RuL-LRu(4'-MeL)$. Treatment of **9** with 1 equiv of $(4'-MeLH)RuCl_3$ converted it to the binuclear complex **6** in good yield. Alternatively, treatment of **9** with $(5'-ClLH)RuCl_3$ yielded a binuclear complex, **10**, in which the two ruthenium ions were in essentially identical coordination environments but in somewhat different electronic environments (eq 9).

The complex **9** was also readily converted to various heteronuclear bimetallic complexes with use of conditions de-

$$(4'-MeL)RuL-LH + (5'-ClLH)RuCl_3 \xrightarrow{base}$$
$$\mathbf{9}$$
$$(4'-MeL)RuL-LRu(5'-ClL) \quad (9)$$
$$\mathbf{10}$$
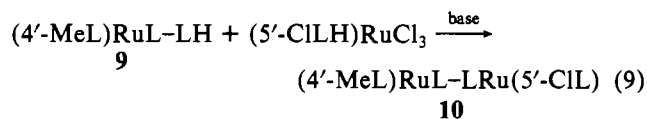
veloped earlier for mononuclear complexes. For example, complex **9** reacted with cupric acetate to form the Ru, Cu complex **11** and with dichlorobis(benzonitrile)palladium(II) to form the Ru, Pd complex **12** in good yield (eq 10 and 11). No evidence for metal ion exchange was observed in either reaction.

$$(4'-MeL)RuL-LH + Cu(OAc)_2 \rightarrow$$
$$\mathbf{9}$$
$$(4'-MeL)RuL-LCu(OAc) \quad (10)$$
$$\mathbf{11}$$

$$(4'-MeL)RuL-LH + PdCl_2(NCC_6H_5)_2 \rightarrow$$
$$\mathbf{9}$$
$$(4'-MeL)RuL-LPdCl \quad (11)$$
$$\mathbf{12}$$
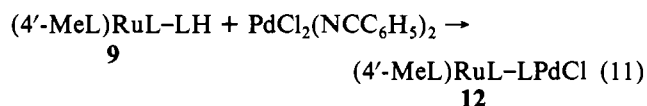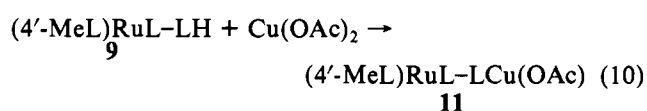
Synthesis and Characterization of a Trinuclear Ru(II) Complex. The first step in the synthesis of the trinuclear complex was the preparation of the mononuclear complex **13**. Tetrakis(dimethyl sulfoxide)dichlororuthenium(II) reacted with a large excess of bridging ligand to form a mixture of products from which the mononuclear complex **13** was isolated after chromatography (eq 12). The complex **13** is dark green

$$RuCl_2(Me_2SO)_4 + excess\ HL-LH \xrightarrow{base} HL-LRuL-LH$$
$$\mathbf{13}$$
$$(12)$$
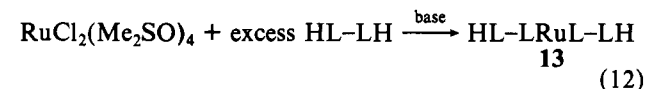
and exhibited a moderately strong band in the infrared spectrum at approximately 1635 cm^{-1} characteristic of the uncomplexed ends of the bridging ligands. The mononuclear complex **13** reacted with 2 equiv of $(4'-MeLH)RuCl_3$ according to eq 13 to afford the trinuclear Ru(II) complex **14**

$$HL-LRuL-LH + 2(4'-MeLH)RuCl_3 \xrightarrow{base}$$
$$\mathbf{13}$$
$$(4'-MeL)RuL-LRuL-LRu(4'-MeL) \quad (13)$$
$$\mathbf{14}$$
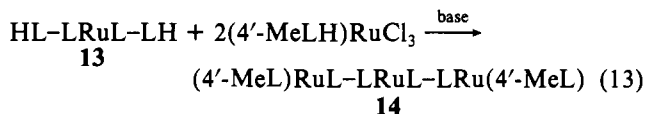
in good yield. The trinuclear complex was also dark green and gave an elemental analysis consistent with its formulation. In the infrared, the 1635-cm^{-1} band had disappeared, indicating that both ends of the bridging ligand were now complexed in the product. The infrared spectrum was otherwise quite similar to that of the binuclear Ru(II) complex **6**, $(4'-MeL)RuL-LRu(4'-MeL)$.

Proton NMR Spectra. The proton NMR spectra of the diamagnetic Ru(II) complexes were useful in identifying the complexes and testing their purity. Very broadened spectra were observed for the Ru(III) complexes and consequently were of no use in characterization.

The Ru(II) mononuclear complex **3**, $Ru(4'-MeL)_2$, gives a well-resolved spectrum, and peak assignments can be made from the integration and splitting pattern of the peaks (see Experimental Section). The spectrum of the binuclear Ru(II) complex **6**, $(4'-MeL)RuL-LRu(4'-MeL)$, provides evidence for its description as a discrete binuclear species. Integrations of peaks attributable to *sec*-butyl protons and to methyl protons gave the expected ratio for one binucleating ligand and two mononucleating ligands per complex, helping to substantiate that this complex is binuclear and not a higher order polymer. The aromatic protons were difficult to assign due to overlapping peaks in this region of the spectrum.

Electronic Absorption Spectra. The visible spectra of mononuclear and binuclear ruthenium complexes have intense ($\epsilon \approx 20000-50000$) ligand absorptions in the range 400–450 nm. These high-energy ligand absorptions are fairly broad, so that concentrated solutions (~10 mM) are very dark.

Table I. Electronic Spectral Data in Methylene Chloride (25 °C)

complex	λ_{max}, nm	ϵ
Ru(4′-MeL)$_2$	665	9800
(4′-MeL)RuL–LRu(4′-MeL)	710	21300
Ru(4′-MeL)$_2$ClO$_4$	770	400[a]
	847	400[a]
(4′-MeL)RuL–LRu(4′-MeL)(ClO$_4$)$_2$	770	1100[a]
	865	1100[a]

[a] These are maximum values of extinction coefficients. The bands observed appear as peaks on the tail of the visible absorption.
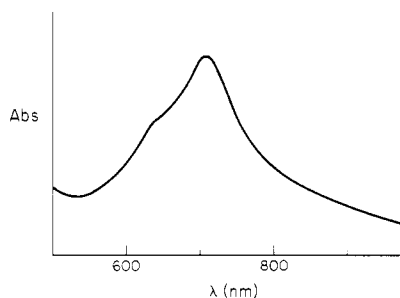

Figure 1. Visible–near-IR spectrum of (4′-MeL)RuL–LRu(4′-MeL) in methylene chloride.

In addition to the ligand absorptions, lower energy absorptions are observed in the complexes of Ru(II) and Ru(III) (Table I). An intense Ru(II) → L charge-transfer band is observed (Figure 1) at approximately 650–700 nm in the mononuclear and binuclear complexes Ru(4′-MeL)$_2$ and (4′-MeL)RuL–LRu(4′-MeL). The band is composed of overlapping absorptions, with a band shape quite similar to the Ru(II) → L charge-transfer band in tris(bipyridine)ruthenium(II), Ru(bpy)$_3$$^{2+}$.[11] The multiple absorption bands observed for Ru(bpy)$_3$$^{2+}$ have been ascribed to charge transfer into different antibonding ligand orbitals.

The Ru(III) complexes Ru(4′-MeL)$_2$ClO$_4$ and (4′-MeL)-RuL–LRu(4′-MeL)(ClO$_4$)$_2$ show absorptions in the near-infrared at approximately 770 and 860 nm. These absorptions may be assigned as L → Ru(III) charge transfer due to the similarity of the spectrum with that of Ru(bpy)$_3$$^{3+}$. Overlapping absorption bands are observed for Ru(bpy)$_3$$^{3+}$ at low energy (675 nm) of similar intensity (ϵ = 410) that have been assigned as L → Ru(III) charge transfer.[12]

Electrochemistry. Electrochemical measurements were made on solutions of Ru(4′-MeL)$_2$ (3) and (4′-MeL)RuL–LRu(4′-MeL) (6) in *N,N*-dimethylformamide (DMF). Cyclic voltammograms of the metal oxidation waves are presented in Figure 2. Identical electrochemistry is observed for the Ru(III) complexes. The cyclic voltammogram of the mononuclear complex exhibits a single reversible oxidation wave with anodic current equal to cathodic current. The anodic to cathodic peak potential separation of 65 mV is independent of scan rate over the range 20–500 mV/s. Coulometry at a potential anodic of the oxidation wave verifies that this is a one-electron process.

The cyclic voltammogram of the binuclear complex 6 has a broad oxidation wave at approximately the same potential as observed for the mononuclear complex. The electrochemical wave has equal anodic and cathodic currents. The anodic to cathodic peak potential separation is independent of scan rate, indicating two reversible overlapping oxidation waves rather than an irreversible process. Coulometry at a potential anodic
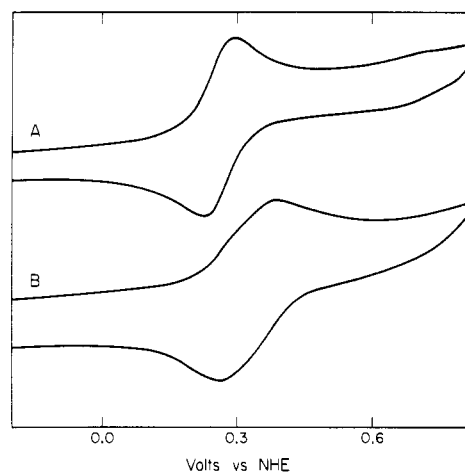
Figure 2. Cyclic voltammograms of DMF solutions: (A) Ru(4′-MeL)$_2$; (B) (4′-MeL)RuL–LRu(4′-MeL).
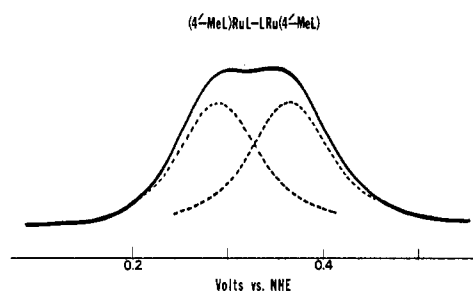
Figure 3. Observed differential pulse voltammogram of (4′-MeL)-RuL–LRu(4′-MeL) in DMF (solid line). The dotted lines represent the two one-electron oxidation waves that constitute the observed voltammogram. The positions of the two oxidation waves were determined by graphically simulating the observed voltammogram.

of the metal oxidations confirms a two-electron process.

The electrochemistry observed for the mononuclear and binuclear complexes is essentially reversible. Anodic to cathodic peak potential separations were always observed to be greater than the expected 58 mV for a reversible process;[13] however, the separation of 65 mV seen for Ru(4′-MeL)$_2$ was identical with the separation observed for the reversible couple ferrocene/ferrocenium[14] under the same conditions. The increased broadening of the wave is likely due to uncompensated solution resistance.[15] Because of the greater breadth of the electrochemical waves it was not possible to use the equations of Richardson and Taube[16] to calculate the separation between the two oxidation waves of the binuclear complex.

The separation of the two oxidation waves was estimated by a graphical approach. The electrochemistry observed for the binuclear complex 6 was simulated by the addition of two one-electron waves separated by varying amounts. The electrochemistry observed for the mononuclear complex, Ru-(4′-MeL)$_2$, was used as the one-electron model. With use of a differential pulse voltammogram obtained for Ru(4′-MeL)$_2$, a good recreation of the oxidation wave observed for the binuclear complex was found at a separation of the two waves of $E_1 - E_2 = 75 \pm 5$ mV (Figure 3).

Ligand reductions similar to those seen for complexes of Mn(II), Fe(II), Co(II), Ni(II), and Zn(II) are observed for

(11) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *J. Am. Chem. Soc.* **1980**, *102*, 4096.
(12) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275.

(13) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.
(14) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.
(15) Instrumentation to compensate for the solution resistance was not used because of difficulties with overcompensation that had been encountered previously.[14]
(16) Richardson, D. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 1278.

Table II. Electrochemical Potentials for Mononuclear and Binuclear Ruthenium Complexes As Measured in DMF (vs. NHE)

complex	E^f, V	$E_{pa} - E_{pc}$, [a] mV	n [b]	ligand waves, E^f, V
		M(II/III)		
Ru(4'-MeL)$_2$	0.278	65	0.98	−1.381
				−1.662
(4'-MeL)RuL–LRu(4'-MeL)	0.325 (0.288, 0.363)[c]	120	2.02	−1.128
				−1.401
				−1.644
				−1.805

[a] Anodic peak to cathodic peak potential separation of metal wave in cyclic voltammetry. [b] The number of electrons involved in metal oxidation was determined by constant-potential electrolysis. [c] Potentials of the two one-electron oxidation waves were determined graphically.

Table III. Electrochemical Potentials (Measured in DMF vs. NHE)

no.	complex	E^f, V	$E_{pa} - E_{pc}$,[a] mV
		Ru(II/III)	
10	(4'-MeL)RuL–LRu(5'-ClL)	0.310, 0.480	65[b]
6	(4'-MeL)RuL–LRu(4'-MeL)	0.325 (0.288, 0.363)[c]	120
8	(4'-MeL)RuL–O(CH$_2$)$_3$O– LRu(4'-MeL)	0.265	65
9	(4'-MeL)RuL–LH	0.324	70
12	(4'-MeL)RuL–LPdCl	0.323	65
11	(4'-MeL)RuL–LCu(OAc)	0.308	70
3	Ru(4'-MeL)$_2$	0.278	65

[a] Anodic peak to cathodic peak separation of metal wave in cyclic voltammetry, at a scan rate of 200 mV/s. [b] Anodic peak to cathodic peak separations of both waves are equal. [c] Potentials of the two one-electron oxidation waves were determined graphically.

these mononuclear and binuclear complexes of ruthenium.[2] The mononuclear complex, Ru(4'-MeL)$_2$, has two reduction waves (Table II). The binuclear species has two reductions at approximately the same potentials as those of the mononuclear complex. A third ligand reduction appears at a more positive potential, which is presumably due to reduction of the bridging ligand. In addition, a fourth reduction wave is observed at very negative potentials. For binuclear complexes of the first-row transition metals, only iron shows four reduction waves, and this most negative reduction has not been studied further.

The electrochemical behavior of the trinuclear ruthenium complex 14, (4'-MeL)RuL–LRuL–LRu(4'-MeL), was studied. Overlapping metal oxidation waves were observed in the same region as in the mononuclear and binuclear complexes, approximately 0.3 V vs. NHE. The detail of the differential pulse voltammogram indicated initial oxidation of the two terminal Ru(II) ions at nearly the same potential, followed by oxidation of the middle Ru(II) ion at slightly higher potential.

The electrochemistry of two other ruthenium binuclear complexes was also investigated. The binuclear complex 10, (4'-MeL)RuL–LRu(5'-ClL), contained the two metal ions in different chemical environments. The difference in the environments of the metal ions was great enough that two separate one-electron waves were observed (Table III).

The electrochemical behavior of the binuclear Ru(II) complex 8, (4'-MeL)RuL–O(CH$_2$)$_3$O–LRu(4'-MeL), was also explored. In this complex, the bridging ligand, 7, is not conjugated, and the metal ions should be totally isolated from one another. The binuclear Ru(II) complex 8 shows one reversible oxidation wave in cyclic voltammetry. This oxidation wave
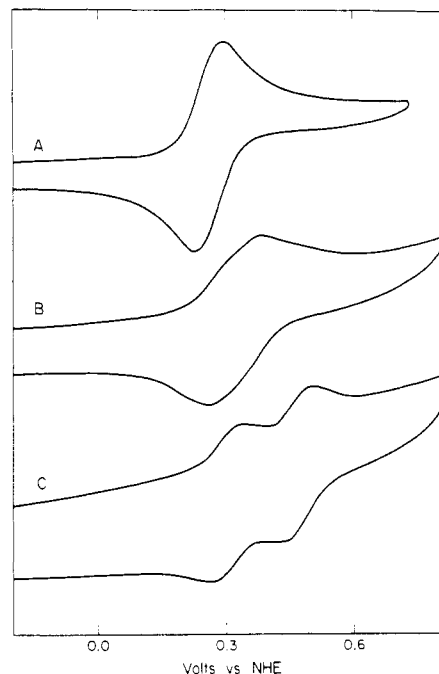
Figure 4. Cyclic voltammograms of DMF solutions: (A) (4'-MeL)RuL–O(CH$_2$)$_3$O–LRu(4'-MeL); (B) (4'-MeL)RuL–LRu-(4'-MeL); (C) (4'-MeL)RuL–LRu(5'-ClL).

has the shape of a one-electron wave with an anodic to cathodic peak separation of 65 mV (Table III). Coulometry confirmed that this is a two-electron oxidation (n = 1.96).

The electrochemistry of the three binuclear complexes (4'-MeL)RuL–LRu(5'-ClL), (4'-MeL)RuL–LRu(4'-MeL), and (4'-MeL)RuL–O(CH$_2$)$_3$O–LRu(4'-MeL) illustrates the different types of behavior that may be expected for binuclear complexes (Figure 4). For binuclear complexes in which the metals are in different environments, or where there is sufficient interaction between the two metals,[17] one observes two separate one-electron waves. As the interaction between identical metals in a binuclear complex decreases, as in (4'-MeL)RuL–LRu(4'-MeL), the two one-electron waves overlap, producing a single broadened electrochemical wave. In the extreme case where the metals are isolated from one another, a single two-electron electrochemical wave with the shape of a one-electron wave is observed.[18]

So that the extent of metal–metal interaction in the binuclear ruthenium complex 6, (4'-MeL)RuL–LRu(4'-MeL), could be quantified, the electrochemistry of mixed-metal complexes was investigated (Table III). In a previous study the delocalization energy of a mixed-valent Cu^{II}Cu^{I} macrocyclic complex was estimated by studying the electrochemistry of some mixed-metal binuclear complexes having similar charge and structure as for the homobinuclear complex.[17] Cyclic voltammograms of the mixed-metal complexes (4'-MeL)RuL–LPdCl (12) and (4'-MeL)RuL–LCu(OAc) (11) exhibit reversible ruthenium oxidation waves. (The complex 9, (4'-MeL)RuL–LH, may also be considered if charge is the primary concern.) These complexes have ruthenium oxidation waves more positive than the first oxidation of (4'-MeL)-RuL–LRu(4'-MeL). Since other effects such as charge and coordination environment are the same for ruthenium, the change in the electrochemical potential between the heterobinuclear and homobinuclear complexes may be ascribable to the delocalization energy in the mixed-valent ruthenium

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Table IV. Comparison of Data for Ruthenium
Binuclear Complexes

complex	d, Å[a]	$E_1 - E_2,$[b] mV	K_{com}[c]
(4'-MeL)RuL–LRu(4'-MeL)	11[d]	75	19
$(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5$	11.1[e]	82[f]	24[f]

[a] Distance between the metals in the binuclear complex. [b] Separation of the two one-electron oxidation waves. [c] Comproportionation equilibrium constant. [d] Reference 5. [e] Reference 6. [f] Reference 20.

species. The mixed-valent ruthenium complex can delocalize the odd electron over both metals. This delocalization is not energetically favorable when the two metals are not identical. The Ru(II/III) oxidation is at a higher electrochemical potential for the mixed-metal complexes, as expected, if the mixed-valent ion, (4'-MeL)RuL–LRu(4'-MeL)$^+$, is stabilized by electron delocalization. However, the magnitude of the shift is small (20–30 mV). Accounting for the statistical contribution to the shift of the oxidation wave, approximately 18 mV,[19] makes the stabilization energy, if any, even smaller.

Preparation of the Mixed-Valent Ion (4'-MeL)RuL–LRu-(4'-MeL)$^+$. Equilibrium solutions containing the mixed-valent ion (4'-MeL)RuL–LRu(4'-MeL)$^+$ were prepared by mixing solutions of the reduced Ru^{II}Ru^{II} complex with the oxidized Ru^{III}Ru^{III} binuclear complex. Spectroscopic measurements of the mixed-valent ion were complicated by the presence of the Ru^{II}Ru^{II} and Ru^{III}Ru^{III} binuclear species in solution, related by the equilibrium in eq 14. The constant describing

$$Ru^{II}Ru^{II} + Ru^{III}Ru^{III2+} \rightleftharpoons 2Ru^{II}Ru^{III+} \qquad (14)$$
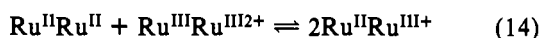
this comproportionation equilibrium can be calculated knowing the separation of the two one-electron waves as determined graphically. A value of 75 ± 5 mV for the electrochemical potential separation of the two waves yields a comproportionation equilibrium constant of 19 ± 4. A pure sample of the mixed-valent complex was not isolable in the solid state.

Comparisons may be made between the ruthenium isoindoline binuclear complex **6**, (4'-MeL)RuL–LRu(4'-MeL), and the ruthenium ammine binuclear species where the metals are bridged by 4,4'-bipyridine (Table IV). The properties of the two complexes are quite similar, indicating that the interaction between the metals may also be similar. The properties of the intervalence transfer (IT) band for ruthenium mixed-valent complexes containing 4,4'-bipyridine may give an indication of what to expect for (4'-MeL)RuL–LRu(4'-MeL)$^+$. The mixed-valent complexes $(NH_3)_5Ru(4,4'-bpy)Ru(NH_3)_5^{5+}$ and $(bpy)_2ClRu(4,4'-bpy)Ru(bpy)_2Cl^{3+}$ exhibit broad absorptions in the near-infrared between 900 and 1200 nm (depending on the solvent), with extinction coefficients ranging from 100 to 1000.[6,20,21] In these cases the position of the IT band shows the solvent dependence predicted by Hush for weakly coupled binuclear complexes.[22] From the Hush theory, a rate of thermal intramolecular electron transfer can be calculated to be in the range 10^7–10^8 s^{-1} for these complexes.

A distinct band was not observed in the near-infrared region of the spectrum of the mixed-valent ion (4'-MeL)RuL–LRu(4'-MeL)$^+$ in methylene chloride. This was due to the tailing of the very intense Ru(II) → L charge-transfer band present for the Ru^{II}Ru^{II} binuclear species (Figure 1) as well

as the mixed-valent ion. (The charge-transfer band may be slightly shifted in the mixed-valent complex, but because of the weak metal–metal interaction it is expected to be very similar to the band observed for the Ru^{II}Ru^{II} complex.[6]) The charge-transfer band in the binuclear Ru(II) complex has an extinction coefficient of 420 at 1000 nm. This makes it impossible to observe a broad relatively weak intervalence transfer band in this region of the spectrum.

Conclusions

Discrete binuclear and trinuclear ruthenium complexes containing the bridging ligand **1** were prepared by a stepwise synthesis. The binuclear ruthenium complex (4'-MeL)RuL–LRu(4'-MeL) undergoes a two-electron oxidation with the two electrons being transferred at approximately the same potential. The analogous trinuclear complex shows similar behavior, with three closely spaced one-electron oxidations. The ability of these complexes to undergo multielectron oxidation with all of the electrons transferred at approximately the same potential may be a very desirable property for their possible use as multielectron-transfer reagents. An estimate of the rate of intramolecular electron transfer in the polynuclear complexes was not obtainable from spectroscopic measurements.

Experimental Section

Synthesis of Ligands. The synthesis of the mononuclear chelating isoindoline ligands **2**[8] and the binucleating ligand **1**[2] have been reported previously.

Preparation of Ru(4'-MeL)$_2$ (3) from RuCl$_3$·xH$_2$O. A solution containing 325 mg (1.2 mmol) of hydrated ruthenium trichloride, 900 mg (2.7 mmol) of 4'-MeLH, and 160 mg (3 mmol) of sodium methoxide in 50 mL of methanol was heated at reflux for 48 h in air. After cooling, a fine blue powder was collected from the solution and dried in vacuo. The yield of the product was 15%.

The reaction time could be reduced by addition of 450 mg (12 mmol) of sodium borohydride to the refluxing solution of hydrated ruthenium trichloride and 4'-MeLH after 30 min. The solution was refluxed for 2 h and cooled. A 19% yield of the product was obtained.

The complex, Ru(4'-MeL)$_2$, gave a ^{1}H NMR spectrum in CDCl$_3$ with the following peaks in ppm (vs. Me$_4$Si at 34 °C): benzene protons 8.25 (m) and 7.66 (m); pyridine protons 7.33 (d), 7.26 (s), and 5.99 (d); methyl protons 2.02 (s).

Anal. Calcd for C$_{40}$H$_{32}$N$_8$Ru: C, 63.74; H, 4.28; N, 18.58. Found: C, 63.35; H, 4.6; N, 18.15.

Preparation of Ru(4'-MeL)$_2$ (3) from Ru(Me$_2$SO)$_4$Cl$_2$. To 50 mg (0.1 mmol) of tetrakis(dimethyl sulfoxide)dichlororuthenium(II) (Strem) and 66 mg (0.2 mmol) of 4'-MeLH in 7 mL of methanol was added 0.5 mL of triethylamine. The mixture was heated with stirring at reflux for 10 h. After cooling to the ambient temperature, the dark-blue crystalline solid was collected by filtration, washed with methanol, and dried. Yields of the analytically pure complex ranged from 60 to 80%. The product was identical with the solid prepared from hydrated ruthenium trichloride.

Preparation of (4'-MeLH)RuCl$_3$·C$_2$H$_5$OH (5). A solution containing 0.5 g (2.1 mmol) of hydrated ruthenium trichloride dissolved in 150 mL of ethanol was heated at reflux with nitrogen bubbling through the solution. After 1 h, 0.5 g (1.5 mmol) of 4'-MeLH was added. Heating was continued for an additional $1^1/_2$ h with continued nitrogen purge. After cooling, a dark microcrystalline solid was collected, washed with ethanol, and dried in vacuo. The yield of the product was 60%.

Anal. Calcd for C$_{20}$H$_{17}$N$_5$RuCl$_3$·C$_2$H$_5$OH: C, 45.49; H, 3.99; N, 12.06. Found: C, 45.3; H, 4.05; N, 12.0.

Preparation of (5'-ClLH)RuCl$_3$·C$_2$H$_5$OH. To 270 mg (1.0 mmol) of hydrated ruthenium trichloride and 370 mg (1.0 mmol) of 5'-ClLH was added 15 mL of ethanol. The mixture was heated with stirring at reflux for 39 h. After cooling to the ambient temperature, the brown suspension was filtered and the solid was washed with ethanol and dried. The product was obtained as dark brown microcrystals in 36% yield.

Anal. Calcd for C$_{18}$H$_{11}$N$_5$Cl$_5$Ru·C$_2$H$_5$OH: C, 38.63; H, 2.76; N, 11.27. Found: C, 38.2; H, 2.5; N, 11.4.

Preparation of Ru(4'-MeL)$_2$ (3) from (4'-MeLH)RuCl$_3$·C$_2$H$_5$OH. To 58 mg (0.10 mmol) of (4'-MeLH)RuCl$_3$·C$_2$H$_5$OH and 39 mg (0.12

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mmol) of 4'-MeLH was added 10 mL of dioxane and 1 mL of tri-ethylamine. The mixture was heated with stirring at reflux for 42 h. After cooling to the ambient temperature, the solvent was allowed to evaporate. The residue was washed several times with methanol, leaving behind a 37-mg (49%) yield of dark blue crystals, which were spectroscopically identical with the complex prepared by other routes.

Preparation of (4'-MeL)RuL–LRu(4'-MeL) (6). A solution containing 300 mg (0.52 mmol) of (4'-MeLH)RuCl₃·C₂H₅OH and 190 mg (0.26 mmol) of HL–LH in 80 mL of ethanol was heated at reflux for 3 h. During this time the solution became dark green. To this solution was added 70 mg (1.3 mmol) of sodium methoxide, and the solution was stirred at ambient temperature for 45 min. The solution was filtered, and a dark solid was collected. Methylene chloride (10 mL) was added to the solid, resulting in a dark green solution. The solution was filtered to remove undissolved NaCl. To the filtrate was added 5 mL of methanol. After slow evaporation of the methylene chloride, a dark green microcrystalline solid formed. The solid was washed with methanol and dried in vacuo. The calculated yield was 10–15%.

The binuclear complex gave a ¹H NMR spectrum in CDCl₃ with the following peaks in ppm (vs. Me₄Si at 34 °C): *sec*-butyl protons 0.70 (t), 0.97 (d), 1.50 (m), and 2.40 (m); methyl protons 2.07 (s). The aromatic protons showed many overlapping peaks from 6.1 to 9.2 ppm.

Anal. Calcd for $C_{86}H_{82}N_{20}Ru_2$: C, 64.65; H, 5.17; N, 17.53. Found: C, 64.15; H, 5.05; N, 17.55.

Without the addition of sodium methoxide a product of composition (4'-MeL)RuL–LRu(4'-MeL)·4HCl was isolated. This corresponds to the binuclear complex which contains all nondeprotonated isoindoline ligands.

Anal. Calcd for $C_{86}H_{82}N_{20}Ru_2$·4HCl: C, 59.24; H, 4.97; N, 16.07. Found: C, 59.2; H, 5.0; N, 16.4.

Preparation of (4'-MeL)RuL–LRu(4'-MeL)(ClO₄)₂. To a slurry containing 33 mg (0.02 mmol) of (4'-MeL)RuL–LRu(4'-MeL) in 25 mL of toluene was added a toluene solution containing 65 mg (0.3 mmol) of silver perchlorate. The blue-green solution turned red-brown, with a dark solid forming. After the solution was stirred for 1 h, the solid was collected and washed with toluene. The solid was dissolved in 10 mL of methylene chloride and filtered through a fine frit to remove silver metal. A red-brown crystalline solid was collected from the filtrate, in 90% yield, after addition of 2 mL of toluene and slow evaporation of the solution. The solid was dried in vacuo. Multiple analyses were consistent with toluene present in the product.

Anal. Calcd for $C_{80}H_{82}N_{20}Ru_2Cl_2O_8$·1.5C₇H₈: C, 59.90; H, 4.90; N, 14.48. Found: C, 60.1; H, 4.75; N, 14.4.

Preparation of Ru(4'-MeL)₂ClO₄ (4). The mononuclear Ru(III) complex was prepared by oxidation of Ru(4'-MeL)₂ with AgClO₄. The procedure used was the same as described above for the binuclear complex. Dark red-brown crystals were isolated in 70% yield. The proton NMR spectrum of the product in CDCl₃ showed the presence of toluene and methylene chloride, consistent with the analytical data.

Anal. Calcd for $C_{40}H_{32}N_{10}RuClO_4$·C₇H₈·³/₄CH₂Cl₂: C, 56.84; H, 4.15; N, 13.88. Found: C, 56.55; H, 4.45; N, 13.9.

Alternatively the Ru(III) complex, isolated as its PF₆⁻ salt, was prepared by oxidation of Ru(4'-MeL)₂ with oxygen. A solution containing 53 mg (0.07 mmol) of Ru(4'-MeL)₂ in 7 mL of methylene chloride was added to a suspension of 16 mg (0.1 mmol) of ammonium hexafluorophosphate in 2 mL of acetonitrile. The mixture was allowed to stand at ambient temperature until the solvent had evaporated. The residue was extracted with methylene chloride, and the extract was filtered. Toluene was added to the filtrate, and upon standing, dark crystals deposited. The crystals were collected, washed with toluene, and dried to afford a 52% yield of the Ru(III) salt.

Anal. Calcd for $C_{40}H_{32}N_{10}RuPF_6$·⁵/₄CH₂Cl₂: C, 49.29; H, 3.46; N, 13.94. Found: C, 49.37; H, 3.33; N, 13.52.

Preparation of (4'-MeL)RuL–O(CH₂)₃O–LRu(4'-MeL) (8). To 73 mg (0.10 mmol) of HL–O(CH₂)₃O–LH²³ and 116 mg (0.20 mmol) of (4'-MeLH)RuCl₃·C₂H₅OH was added 10 mL of dioxane. The mixture was heated at reflux with stirring, and after 20 min, 1 mL of triethylamine was added. Heating was continued for 24 h. The dark green suspension was allowed to cool, and the solvent was allowed to evaporate. The residue was extracted with toluene, and the extract was passed over a column of silica gel. With additional toluene a

green band was eluted. Evaporation of the toluene yielded 35 mg (22%) of green microcrystalline powder, which was a single compound by TLC (SiO₂, CHCl₃).

Anal. Calcd for $C_{83}H_{68}N_{20}O_2Ru_2$: C, 63.10; H, 4.34; N, 17.74. Found: C, 62.95; H, 4.4; N, 17.35.

Preparation of (4'-MeL)RuL–LH (9). To 120 mg (0.20 mmol) of (4'-MeLH)RuCl₃·C₂H₅OH and 550 mg (0.74 mmol) of bridging ligand HL–LH was added 25 mg (0.22 mmol) of 1,4-diazabicyclo-[2.2.2]octane, Dabco, and 10 mL of dioxane. The mixture was heated with stirring at reflux for 24 h, and the solvent was then allowed to evaporate at ambient temperature in the dark. The residue was extracted with cyclohexane, and the extract was passed through a column of neutral alumina. The column was eluted with toluene, and the first green band was collected. The solvent was evaporated, and the residue was recrystallized from methylene chloride–heptane to give dark green crystals. Yields ranged from 15 to 35%.

Anal. Calcd for $C_{66}H_{67}N_{15}Ru$·H₂O: C, 66.64; H, 5.85; N, 17.67. Found: C, 66.95; H, 5.7; N, 17.5.

Preparation of (4'-MeL)RuL–LRu(4'-MeL) (6) from (4'-MeL)-RuL–LH (9). A mixture of 34 mg (0.029 mmol) of (4'-MeL)RuL–LH and 50 mg (0.087 mmol) of (4'-MeLH)RuCl₃·C₂H₅OH in 7 mL of dioxane was heated with stirring at reflux. Once the mixture was refluxing, 0.5 mL of triethylamine was added; heating was continued for 44 h. The reaction mixture was allowed to cool, a few drops of methanol were added, and the solvent was allowed to evaporate in the dark. The residue was extracted with toluene, and the extract was passed over a column of neutral alumina. Elution with additional toluene removed a green band from which 27 mg (79% yield) of dark green powder was obtained. The powder was spectroscopically identical with material obtained by the alternate route.

Preparation of (4'-MeL)RuL–LRu(5'-ClL) (10). A mixture of 108 mg (0.092 mmol) of (4'-MeL)RuL–LH and 86 mg (0.14 mmol) of (5'-ClLH)RuCl₃·C₂H₅OH in 10 mL of dioxane was heated with stirring to reflux; 1 mL of triethylamine was added, and the heating was continued for 42 h. The reaction mixture was transferred to a beaker, and the solvent was allowed to evaporate at ambient temperature. The residue was washed with cyclohexane and then extracted with toluene. The toluene extract was placed on a column of neutral alumina, and the column was eluted with additional toluene. A green material was eluted first that gave a single spot by TLC (SiO₂, CHCl₃). The toluene was evaporated at ambient temperature, and the residue was recrystallized from CH₂Cl₂–heptane to afford a 61% yield of dark green crystals that exhibited an IR spectrum similar to that of (4'-MeL)RuL–LRu(4'-MeL).

Anal. Calcd for $C_{84}H_{76}Cl_2N_{20}Ru_2$·H₂O: C, 60.91; H, 4.74; N, 16.91. Found: C, 61.1; H, 4.9; N, 16.65.

Preparation of (4'-MeL)RuL–LCu(OAc) (11). To 40 mg (0.034 mmol) of (4'-MeL)RuL–LH and 14 mg (0.068 mmol) of cupric acetate hydrate was added 10 mL of methylene chloride. The suspension was stirred at ambient temperature for 3.5 h, after which time none of the starting Ru(II) complex was detectable by TLC (SiO₂, EtOAc). The mixture was filtered, and the residue was washed with methylene chloride. Heptane was added to the combined washes and filtrate, and they were allowed to stand in the dark. After partial evaporation of the solvent dark green microcrystals deposited. A yield of 36 mg (82%) was obtained.

Anal. Calcd for $C_{68}H_{70}N_{15}O_2RuCu$: C, 63.11; H, 5.45; N, 16.24. Found: C, 63.15; H, 5.4; N, 16.1.

Preparation of (4'-MeL)RuL–LPdCl (12). To 37 mg (0.032 mmol) of (4'-MeL)RuL–LH in 6 mL of methylene chloride was added an equimolar amount (12.1 mg) of dichlorobis(benzonitrile)palladium(II) in 5 mL of methylene chloride. After the solution stirred for 30 min at ambient temperature, the starting Ru(II) complex had disappeared, as found by TLC (SiO₂, CHCl₃). The reaction mixture was allowed to stand overnight at ambient temperature and was then filtered. The filtrate was placed on a column of neutral alumina. Elution with methylene chloride–ethyl acetate removed a green band from the column, from which a dark green microcrystalline powder was obtained; yield 26 mg (61%). The 1640-cm⁻¹ band characteristic of the unchelated end of the starting material was greatly diminished in the product.

Anal. Calcd for $C_{66}H_{66}N_{15}ClPdRu$·H₂O: C, 59.60; H, 5.15; N, 15.79. Found: C, 59.7; H, 5.25; N, 15.4.

Preparation of HL–LRuL–LH (13). To 49 mg (0.10 mmol) of tetrakis(dimethyl sulfoxide)dichlororuthenium(II) and 447 mg (0.60 mmol) of the bridging ligand 1, HL–LH, was added 15 mL of dioxane

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(23) The preparation of this and related ligands will be discussed in a separate publication.

and 1 mL of triethylamine. The mixture was heated, with stirring, at reflux for 31 h. After cooling, the solvent was allowed to evaporate at ambient temperature. The residue was extracted with cyclohexane, and the extract was placed on a column of neutral alumina. The column was eluted with toluene to remove a green band which contained a single component, as found by TLC (SiO_2, $CHCl_3$). Evaporation of the solvent yielded 35 mg (22%) of dark green microcrystalline powder.

Anal. Calcd for $C_{92}H_{102}N_{20}Ru$: C, 69.54; H, 6.47; N, 17.63. Found: C, 69.65; H, 6.4; N, 17.55.

Preparation of (4'-MeL)RuL–LRuL–LRu(4'-MeL) (14). To 70 mg (0.044 mmol) of HL–LRuL–LH and 52 mg (0.11 mmol) of (4'-MeLH)RuCl$_3$·C$_2$H$_5$OH was added 10 mL of dioxane and 1 mL of triethylamine; the mixture was heated at reflux with stirring for 24 h. The solvent was allowed to evaporate at ambient temperature, and the residue was extracted with cyclohexane and with toluene. The combined extracts were chromatographed over neutral alumina. A green band was eluted with toluene that produced a single spot on TLC (SiO_2, $CHCl_3$). A 70% yield of dark green microcrystals was obtained from cyclohexane–diethyl ether.

Anal. Calcd for $C_{132}H_{134}N_{30}Ru_3$: C, 64.87; H, 5.53; N, 17.20. Found: C, 64.55; H, 5.2; N, 17.2. Molecular weight: calculated, 2444; found, 2450 ± 70 (50 °C, toluene).

Physical Measurements. Procedures for making electrochemical measurements have been described previously.[2] Cyclic voltammograms and differential pulse voltammograms were obtained on millimolar solutions of the compound of interest. Potentials for the complexes were measured vs. that of ferrocene.[14] The formal potentials were then adjusted to potentials vs. NHE with assumption of a value of 0.400 V for the ferrocene/ferrocenium couple. When ferrocene overlapped with the wave under investigation, the cobaltocene/cobaltocenium couple, −0.936 V vs. NHE, was used as an internal standard. Magnetic susceptibility measurements were obtained on samples at ambient temperature with use of a Cahn Instruments Faraday balance, with HgCo(SCN)$_4$ as a calibrant. Diamagnetic corrections were made with use of Pascal's constants. Proton NMR spectra were obtained on a Varian EM-390 NMR spectrometer with CDCl$_3$ as the solvent and tetramethylsilane as a reference. Electronic spectra were recorded on a Cary 14 spectrophotometer. Solution spectra were obtained with use of 1-cm matched quartz cells. Elemental analyses were performed by the California Institute of Technology analytical facility and by Galbraith Laboratories, Knoxville, TN. Molecular weight determinations by vapor osmometry were made with a Wescan/Corona molecular weight apparatus.

Registry No. 3, 82056-43-7; 4, 82044-84-6; 5, 82044-85-7; 6, 82044-86-8; 8, 82044-87-9; 9, 82044-88-0; 10, 82044-89-1; 11, 82056-44-8; 12, 82044-90-4; 13, 82044-91-5; 14, 82056-45-9; (5'-ClLH)RuCl$_3$, 82056-46-0; (4'-MeL)RuL–LRu(4'-MeL)(ClO$_4$)$_2$, 82044-93-7; Ru(4'-MeL)$_2$PF$_6$, 82044-94-8; Ru(Me$_2$SO)$_4$Cl$_2$, 11070-19-2; dichlorobis(benzonitrile)palladium(II), 14220-64-5.

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Ethylidenesulfur Tetrafluoride[1]

BRIGITTE PÖTTER and KONRAD SEPPELT*

In a multistep preparation $CH_3CH{=}SF_4$ is prepared starting from $CH_3C{\equiv}COR$ and $SClF_5$. It is a colorless liquid and undergoes slow decomposition at room temperature. Its structure is a trigonal-bipyramidal environment of sulfur with two axial and two equatorial fluorine atoms, and the ethylidene ligand is in an equatorial position also. The methyl group lies in the same plane with the axial fluoride atoms and sulfur. This is derived mainly from its NMR spectra and by comparison with the well-known structure of $CH_2{=}SF_4$, the only other known species of this type.

Introduction

Sulfur ylides do not have the importance of phosphorus ylides, mainly because of their more limited use in organic preparations. They are well documented, however,[2] and are derivatives of either $(CH_3)_2S^{\delta+}CH_2^{\delta-}$ or $(CH_3)_2SO^{\delta+}CH_2$.[3] The preparation[4] and structural investigations[5–8] of $CH_2{=}SF_4$ opened a new area of sulfur ylide chemistry. This compound is remarkable for its high stability and having a sulfur–carbon double bond with little ylidic character. These features seemed to be so unique that we undertook a long search to determine if any other related species of $CH_2{=}SF_4$ could be made. The only successful result so far is the preparation of $CH_3CH{=}SF_4$, which is described here in detail.

Experimental Section

General Data. ^1H and ^{19}F NMR spectra were recorded on a Varian EM 360 instrument; IR spectra were taken on a Beckman IR 12 and mass spectra on a Varian MAT CH 4.

Reagents. Sulfur chloride pentafluoride was either prepared from ClF and SF$_4$[9] or purchased from PCR Inc., Gainsville, FL. 1-Methoxy-2-methylacetylene and 1-ethoxy-2-methylacetylene were prepared according to literature methods.[10,11]

1-Methyl-1-(pentafluorosulfonyl)-2-chloro-2-methoxyethene. A 1-mol sample of sulfur chloride pentafluoride and 200 mL of dry CFCl$_3$ (Freon 11) as solvent are condensed into a 500-mL glass vessel using a glass vacuum line. After addition of 1 atm of dry argon, the glass vessel was equipped with a −50 °C reflux cooler, magnetic stirrer, and a dropping funnel. A 1-mol sample of 1-methoxy-2-methylacetylene in 50 mL of CFCl$_3$ is added slowly, and the liquid mixture is irradiated by a focusable 500-W mercury high-pressure lamp. The reaction temperature is allowed to rise from −20 °C (boiling point bp of SClF$_5$) to +23 °C boiling point of solvent over a period of several

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