

remain to be determined, it is clear that  $C_8H_8^{2-}$  is generated from 1,5- $C_8H_{12}$  in this reaction.

Several control reactions were conducted to define the role of praseodymium in this remarkable conversion. The reaction of 1,5- $C_8H_{12}$  with K alone at room temperature does not lead to formation of  $K_2C_8H_8$ . Such a reaction is not necessarily a valid control, however, since it is possible that the  $PrCl_3$  is incompletely reduced by potassium, forming, instead, a potassium-praseodymium-chloride matrix which contains active potassium with a large effective surface area. Reduced metal matrices of this type are postulated in the K-KI-metal halide preparations of activated metals by the Rieke method.<sup>15</sup> To examine the effects of larger potassium surface area and more severe conditions,<sup>16</sup> we reacted potassium with 1,5- $C_8H_{12}$  at 97 °C over a 5-day period. The volatile products of this reaction are *cis*-bicyclo[3.3.0]oct-2-ene and a trace of 1,3-cyclooctadiene, as previously reported.<sup>17</sup> The solid residue which remains following the removal in vacuo of volatiles can be extracted with THF to give an intense purple solution.<sup>18</sup> Removal of the THF gives a gray-purple solid which by IR, NMR, and elemental analysis contains  $C_8H_8^{2-}$ .<sup>19</sup> Air oxidation gives 1,3,5,7- $C_8H_8$ , identified by NMR and GC-mass spectroscopy. In a higher temperature, large-scale reaction, 1,5- $C_8H_{12}$  (108 g, 1 mol) at reflux reacted with K (4.5 g, 0.12 mol) in 10 h to form, following THF extraction and solvent removal, 14.2 g of gray-green solids which either could be used directly in syntheses requiring  $C_8H_8^{2-}$  or could be converted to 1,3,5,7- $C_8H_8$  in 30% yield.<sup>21</sup> Although the yield based on 1,5- $C_8H_{12}$  is not large, the reaction does provide a method of obtaining quantities of  $C_8H_8^{2-}$  and 1,3,5,7- $C_8H_8$  for laboratory synthesis directly from potassium and 1,5- $C_8H_{12}$ , and is more efficient than the praseodymium-based synthesis.

To determine if  $PrCl_3$  acts only as a partially reducible matrix which generates a large surface area for the remaining potassium in the room temperature conversion of 1,5- $C_8H_{12}$  to  $C_8H_8^{2-}$ , a reaction analogous to the  $PrCl_3$ -K reaction was investigated using  $MgCl_2$  as the reducible halide. The reaction itself is similar to the praseodymium reaction and a red-brown product is also obtained. This product, however, does not react with  $UCl_4$  to form  $U(C_8H_8)_2$ , does not give IR or NMR spectra consistent with  $K_2C_8H_8$ , and cannot be air oxidized to 1,3,5,7- $C_8H_8$ .

Although the above result does not exclude the possibility that  $PrCl_3$  acts as a dispersing agent for K, it does suggest that there are specific metal requirements for the room temperature reaction. Initial studies with other lanthanide trichlorides show that not all lanthanides are as effective as praseodymium; i.e., there appears to be a differentiation in the chemistry of the lanthanides in these reduction reactions. These above results and the possibility that lower valent lanthanide complexes of 1,5- $C_8H_{12}$  or  $C_8H_8$  are involved in the 1,5- $C_8H_{12}$  to  $C_8H_8^{2-}$  conversion are under further investigation.

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- Part 1: W. J. Evans, S. C. Engerer, and A. C. Neville, *J. Am. Chem. Soc.*, preceding paper in this issue.
- Prepared from the hydrated chloride by dehydration with  $NH_4Cl$ : M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962).
- All reactions were conducted in an inert atmosphere using standard techniques: D. F. Shriver, "Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
- Brown-colored filtrates were sometimes observed but did not appear to affect subsequent reactions. This brown product is under investigation.
- Purified by passing through a column of neutral alumina, Brockmann activity grade I, followed by degassing.
- Yields vary depending on reaction times. For a 2-day reaction, 0.2 to 0.3 g are usually obtained. For reaction times of 5 days, 0.8 to 1.0 g are commonly isolated.
- Identified by NMR and GC-mass spectrum. The oxidative decomposition was accomplished by bubbling air through an NMR sample of I. Yields are variable depending on the age of the sample.
- IR (Nujol,  $cm^{-1}$ ): 680 (s), 800 (s), 880 (m), 975 (s), 1020 (s), 1260 (s).  $^1H$  NMR (THF):  $\delta$  5.77 (s).
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- For example in one synthesis the following analytical data were obtained. Found: C, 49.67; H, 4.57; K, 26.12; Pr, 17.80. Mixtures of  $K_2C_8H_8$  and  $KPr(C_8H_8)_2$ <sup>11</sup> formed by decomposition of I are possible. E.g., calcd for  $K_2PrC_8H_8$  (i.e. a  $2K_2C_8H_8$ - $KPr(C_8H_8)_2$  mixture): C, 51.09; H, 4.29; K, 25.98; Pr, 18.62.
- K. O. Hodgson, F. Mares, D. F. Starks, and A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **95**, 8650 (1973).
- After I is extracted with diethyl ether, a brown THF-soluble product, II, remains as well as a considerable amount of a THF-insoluble material, III, both of which contain praseodymium by elemental analysis. Found for II: C, 48.81; H, 4.40; K, 9.76; Pr, 35.20; Cl, 0.29. Cf. calcd for  $KPrC_{16}H_{18}$ : C, 49.33; H, 4.73; K, 10.04; Pr, 35.97. Found for III: C, 20.18; H, 1.95; K, 7.98; Pr, 57.90; Cl, 0.34.
- $K_2C_8H_8$  generated in situ and  $K[Pr(C_8H_8)_2]$  are reported to react instantly with  $UCl_4$  to form  $U(C_8H_8)_2$ .<sup>11,14</sup>
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- The reaction of 1,5- $C_8H_{12}$  with sodium-potassium alloy at room temperature does not produce significant amounts of  $C_8H_8^{2-}$ .
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- The colors of the THF extract are variable. Blue, green, and brown have been observed, but purple is the most common. In previous reactions,<sup>17</sup> the residual solids were destroyed hydrolytically.
- IR (Nujol,  $cm^{-1}$ ): 660 (w, sh), 680 (s), 720 (w), 800 (m), 880 (s), 1020 (m), 1060 (w), 1425 (w, sh), 1530 (s), 1670 (w), 1795 (w). NMR (THF):  $\delta$  5.76. Anal. Calcd for  $K_2C_8H_8$ : C, 52.69; H, 4.42; K, 42.88. Found: C, 52.00; H, 5.27; K, 41.83. A previous elemental analysis was similarly low in K.<sup>9</sup>  $K_2C_8H_8 \cdot THF$  is variably described as white or yellow.<sup>20</sup>
- H. P. Fritz and H. Keller, *Z. Naturforsch.*, **B**, **16**, 231 (1961).
- 0.2 to 0.3 mL  $C_8H_8$  can be obtained per gram of crude solid by dry air oxidation in tetrahydrofuran at 0 °C. CAUTION: This solid is pyrophoric.
- Undergraduate participants in the University of Chicago, Department of Chemistry Laboratory Option Program for sophomores.

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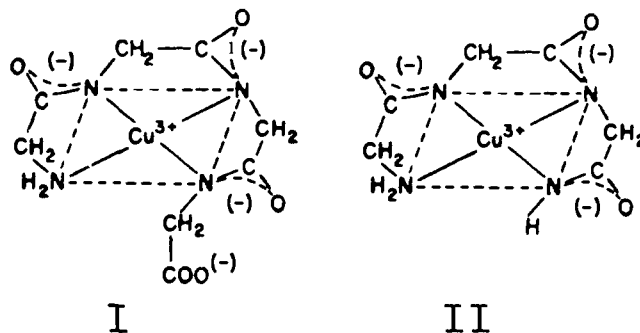
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## Resonance Raman Spectra of Copper(III) Peptide Complexes

Sir:

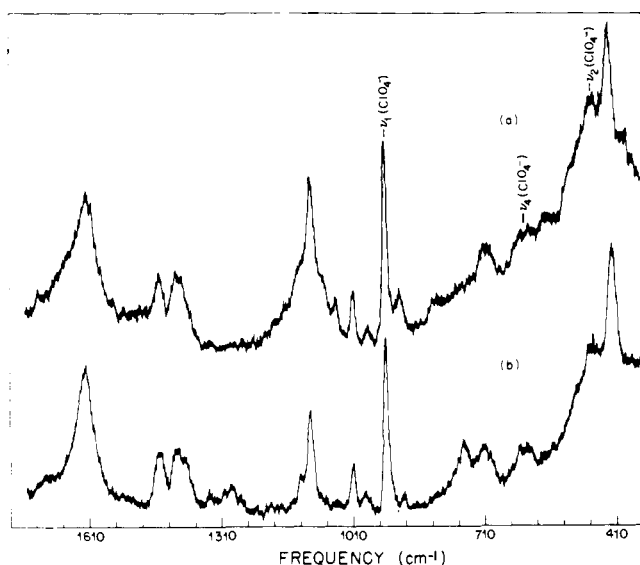
Interest in the possible role of copper(III) in biochemistry has been heightened by the evidence presented by Hamilton and coworkers<sup>1,2</sup> for its involvement in galactose oxidase, and by the demonstration by Margerum and coworkers<sup>3,4</sup> that deprotonated oligopeptide complexes of copper(III) are reasonably stable in neutral aqueous solution. Such complexes display intense absorption at 365 nm ( $\epsilon \sim 7100 M^{-1} cm^{-1}$ )<sup>3</sup> attributable to N (amide)  $\rightarrow Cu^{III}$  charge transfer, shifted to lower energy from the position (230-280 nm) of the corresponding copper(II) peptide bands<sup>5</sup> and are therefore good



**Table I.** Raman Frequencies of Copper Peptide Complexes ( $\text{cm}^{-1}$ )

$\text{Cu}^{\text{II}}\text{TG}^a$	$\text{Cu}^{\text{III}}\text{TG}^b$	$\text{Cu}^{\text{II}}\text{TGA}^a$	$\text{Cu}^{\text{III}}\text{TGA}^b$	$\text{Cu}^{\text{III}}\text{TGA}/\text{D}_2\text{O}^b$	Tentative assignment
388	420	387	417	411	$\nu(\text{Cu}-\text{N})$
	703	532	711	702	$\delta(\text{C}=\text{O})$
	903	697	759	678	$\pi(\text{N}-\text{H})$
	977	885	897	897	
	1009		983	982	
	1048		1010	1007	
	1077 (sh)		1047 (w)	1037	
	1104		1053 (w)		
	1130 (sh)		1107	1109	
			1130 (sh)	1129 (sh)	
			1286	1082	$\delta(\text{N}-\text{H})$
1414	1406	1416	1392	1385	$\nu(\text{C}-\text{N})$
			1410	1406	
	1449	1441	1449	1448	$\delta(\text{CH}_2)$
	1614		1616	1616	$\nu(\text{C}=\text{O})$

<sup>a</sup> Fully deprotonated (pH 12.5<sup>20</sup>); measured from  $\nu_1(\text{SO}_4^{2-})$  at  $982\text{ cm}^{-1}$ . <sup>b</sup> Measured from  $\nu_1(\text{ClO}_4^-)$  at  $934\text{ cm}^{-1}$ .



**Figure 1.** Raman spectra of 3 mM  $\text{Cu}^{\text{II}}\text{TG}$  (a) and 2 mM  $\text{Cu}^{\text{III}}\text{TGA}$  (b) in 0.2 M  $\text{NaClO}_4$  recorded with 363.8-nm excitation (100 mW, Spectra Physics 170  $\text{Ar}^+$  laser with UV optics and grating filter; Spex 1401 double monochromator, spectral slit width  $8\text{ cm}^{-1}$ ; RCA C31034A photomultiplier with photon counting detection, sensitivity (counts/s) 250 (a) and 330 (b); rise time 10 s; scanning speed  $12\text{ cm}^{-1}/\text{min}$ ). The broad feature between 360 and  $540\text{ cm}^{-1}$  is due to glass scattering.

candidates for near-UV resonance Raman (RR) studies. We have obtained RR spectra of tetraglycine (TG) and triglycine amide (TGA) complexes of copper(III) (structures I and II, respectively<sup>3</sup>) which indicate that the technique provides a sensitive probe for the copper(III)-peptide linkage.

The RR spectra shown in Figure 1 were obtained with 363.8-nm  $\text{Ar}^+$  excitation. Solutions of the copper(III) complexes were generated by mixing equimolar quantities of  $\text{Cu}(\text{SO}_4)\cdot 5\text{H}_2\text{O}$  and tetraglycine (Sigma Chemical Co.) or triglycine amide hydrochloride (Vega-Fox Biochemicals) in 0.2 M  $\text{NaClO}_4$ , adjusting to pH 7.2, and flowing the solutions through a  $0.5\text{ cm} \times 8\text{ cm}$  glassy carbon bed electrolysis cell<sup>6</sup> at 30 mL/h. A slight pH decrease ( $\sim 0.5$  pH unit) was noted after oxidation. Although some photodecomposition may occur,<sup>7</sup> only bands associated with the copper(III) chromophore are observed. Table I lists the frequencies observed for the copper(III) complexes, as well as those of the copper(II) complexes (nonresonance spectra) and for  $\text{Cu}^{\text{III}}\text{TGA}$  in  $\text{D}_2\text{O}$ . All of the bands in the copper(III) complex spectra are resonance enhanced, the intensities being comparable with that

of the  $\nu_1$  band of  $\text{ClO}_4^-$ , present at  $\sim 100$ -fold higher concentration. (With 457.9-nm excitation, their relative intensities are much lower.)

The strong, isolated band at  $417\text{ cm}^{-1}$  in  $\text{Cu}^{\text{III}}\text{TGA}$  and  $420\text{ cm}^{-1}$  in  $\text{Cu}^{\text{III}}\text{TG}$  is readily assignable to  $\text{Cu}^{\text{III}}-\text{N}$  (amide) stretching. In  $\text{D}_2\text{O}$  this band shifts to  $411\text{ cm}^{-1}$  for  $\text{Cu}^{\text{III}}\text{TGA}$ , but the  $420\text{-cm}^{-1}$  band of  $\text{Cu}^{\text{III}}\text{TG}$  is unshifted. From this we infer that the primary amide group of TGA is involved in the vibrational mode but the amine group, present in both TGA and TG, is not involved. (In copper(II) glycine the copper-amine stretch decreases by  $18\text{ cm}^{-1}$  in  $\text{D}_2\text{O}$ .<sup>8</sup>) The two secondary amide nitrogen atoms are deprotonated and are uninfluenced by  $\text{D}_2\text{O}$ . They are part of the chromophoric unit, however, and are expected to contribute to the RR spectrum. Since only a single  $\text{Cu}-\text{N}$  stretch is observed, and since for  $\text{Cu}^{\text{III}}\text{TGA}$  in  $\text{D}_2\text{O}$  it shifts without broadening, we surmise that it corresponds to the in-phase stretching mode of the copper(III)-peptide bonds. The out-of-phase modes are apparently not resonance enhanced.

Siiman et al.<sup>9</sup> have suggested that a band at  $\sim 388\text{ cm}^{-1}$  in various copper(II) peptide complexes should be assigned to  $\text{Cu}^{\text{II}}-\text{N}$  (amide) stretching. In conformity with this we observe strong bands at 388 and  $387\text{ cm}^{-1}$  in the nonresonance Raman spectra of  $\text{Cu}^{\text{II}}\text{TG}$  and  $\text{Cu}^{\text{II}}\text{TGA}$ . The increase of  $30\text{ cm}^{-1}$  for the copper(III) complexes is consistent with the higher oxidation state and with the removal of an electron from the antibonding  $d_{x^2-y^2}$  orbital in the square-planar complexes.<sup>10,11</sup>

The remaining RR peaks in Figure 1 can be attributed to internal vibrations of the bound peptide groups. Charge transfer from peptide to copper(III) removes an electron from a bonding peptide orbital. In the excited state the  $\text{C}-\text{N}$ ,  $\text{C}-\text{C}$ , and  $\text{C}=\text{O}$  bonds should be stretched, and the planar trigonal peptide unit may be somewhat deformed. The vibrational modes which resemble the excited-state distortion are expected to have large Franck-Condon overlaps and therefore display resonance enhancement.<sup>12,13</sup> Some assignments are given in Table I. The strong band at  $1616\text{ cm}^{-1}$  is clearly  $\nu_{\text{C}=\text{O}}$  (amide I)<sup>14,15</sup> while the weaker band at  $\sim 1445\text{ cm}^{-1}$  is assigned to  $\delta_{\text{CH}_2}$ .<sup>16,17</sup> The  $1406\text{-cm}^{-1}$   $\text{Cu}^{\text{III}}\text{TG}$  band is thought to be mainly  $\nu_{\text{C}-\text{N}}$ ;<sup>9,16</sup> its frequency decreased slightly from that observed ( $1414\text{ cm}^{-1}$ ) in the  $\text{Cu}^{\text{II}}\text{TG}$  complex. In  $\text{Cu}^{\text{III}}\text{TGA}$  this band shows a doublet structure, and shifts slightly in  $\text{D}_2\text{O}$ , apparently reflecting the involvement of the primary amide. The broad  $1286\text{-cm}^{-1}$  band of  $\text{Cu}^{\text{III}}\text{TGA}$ , shifting to  $1082\text{ cm}^{-1}$  in  $\text{D}_2\text{O}$ , is clearly the primary amide  $\delta_{\text{NH}}$ , which is absent in  $\text{Cu}^{\text{II}}\text{TG}$ . Likewise the  $759\text{-cm}^{-1}$  band, shifting to  $678\text{ cm}^{-1}$  in  $\text{D}_2\text{O}$ , is the out-of-plane primary amide deformation,  $\pi_{\text{NH}}$ .

The adjacent 711-cm<sup>-1</sup> band, which is slightly D<sub>2</sub>O sensitive, is also present in Cu<sup>II</sup>TG, and is assigned to  $\delta_{C=O}$ .<sup>18,19</sup> The group of bands between 890 and 1130 cm<sup>-1</sup> are thought to be skeletal modes of uncertain composition.<sup>17</sup>

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## Trimethylsulfonium Ion as a Ligand: Synthesis and Characterization of [(NH<sub>3</sub>)<sub>5</sub>RuS(CH<sub>3</sub>)<sub>3</sub>](PF<sub>6</sub>)<sub>3</sub>

Sir:

The instances in which a ligand carrying positive charge on the donor atom displaces a donor atom bearing negative charge from a metal ion are rare. We wish to report what we believe to be the first example of the formation of a complex of

**Table I.** Absorption Spectra for Pentaammineruthenium(II) Complexes of Sulfur Ligands

(CH <sub>3</sub> ) <sub>2</sub> S	$\lambda_{\max}$ ( $\epsilon$ )	
	(CH <sub>3</sub> ) <sub>2</sub> SO	(CH <sub>3</sub> ) <sub>3</sub> S <sup>+</sup>
358 (64)	313 (240)	320 (235)
258 (2100) <sup>a</sup>	210 (2600)	210 (7500)
235 (2050) <sup>a</sup>		

<sup>a</sup> Reference 1.

**Table II.** <sup>1</sup>H NMR Chemical Shifts for Protons in Ru(NH<sub>3</sub>)<sub>5</sub><sup>2+</sup> Complexes and in the Free Hetero Ligands

	S(CH <sub>3</sub> ) <sub>2</sub>		(CH <sub>3</sub> ) <sub>2</sub> SO		S(CH <sub>3</sub> ) <sub>3</sub> <sup>+</sup>		CO
	Free <sup>a</sup>	Bound <sup>a</sup>	Free	Bound	Free	Bound	
CH <sub>3</sub>	2.06	2.06	2.7 <sup>b</sup>	3.28 <sup>b</sup> (3.4) <sup>c</sup>	2.84 <sup>a</sup>	3.4 <sup>c</sup>	
<i>cis</i> -NH <sub>3</sub>		2.2		2.4 <sup>c</sup>		2.5 <sup>c</sup>	2.6 <sup>d</sup>
<i>trans</i> -NH <sub>3</sub>		3.0		3.6 <sup>c</sup>		3.9 <sup>c</sup>	3.7 <sup>d</sup>

<sup>a</sup> Reference 1. <sup>b</sup> C. V. Senoff, E. Maslowsky, and R. G. Goel, *Can. J. Chem.*, **49**, 3585 (1971). <sup>c</sup> This work. <sup>d</sup> Reference 9.

S(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> with a metal ion by a net substitution reaction and, in fact, the first example of a sulfonium ion complex. The species (NH<sub>3</sub>)<sub>5</sub>RuS(CH<sub>3</sub>)<sub>3</sub><sup>3+</sup> (I) was synthesized as follows. Acetone (500 mL) was deaerated with argon for a minimum of 5 h in a gas scrubbing tower. To the outlet of the tower was attached a 10-mL reaction vessel which was simultaneously deaerated and then charged with 7 mL of acetone and, typically, 100 mg (4.30 × 10<sup>-4</sup> mol) of [(CH<sub>3</sub>)<sub>3</sub>S]PF<sub>6</sub>. After 0.5 h of continuous argon bubbling, 234 mg (4.73 × 10<sup>-4</sup> mol) of freshly prepared [(NH<sub>3</sub>)<sub>5</sub>RuH<sub>2</sub>O](PF<sub>6</sub>)<sub>2</sub> was added. The reaction mixture was shielded from light and the argon flow was continued for 16 h. A very slow color change from deep orange to pale yellow was observed. The solution was poured into ether and filtered and the residue was dissolved in a minimum (1-2 mL) of 0.1 M HCl and filtered. Solid NH<sub>4</sub>PF<sub>6</sub> was then added until precipitation of the very pale yellow salt commenced. Anal: Calcd for C<sub>3</sub>H<sub>24</sub>N<sub>5</sub>SRuP<sub>3</sub>F<sub>18</sub>: C, 5.16; H, 3.46; N, 10.03; Ru, 14.50; S, 4.59; F, 48.97. Found: C, 5.44; H, 3.39; N, 9.53; Ru, 14.5; S, 4.9; F, 47.1. The yield was 25%.

The salient features of UV-vis spectrum of I are summarized in Table I. The similarity to the spectrum of the (NH<sub>3</sub>)<sub>5</sub>RuSO(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup> ion<sup>1</sup> is apparent. In both cases, the lowest energy bands are d-d transitions, while those at 210 nm are ligand centered.

A 60-MHz NMR spectrum taken in 0.24 M DCl or Me<sub>2</sub>SO-*d*<sub>6</sub> revealed three peaks with areas in the ratio of 4:3:1 corresponding to the protons located on the *cis*-ammine, methyl, and *trans*-ammine groups, respectively (see Table II). The ammine protons appear as broad peaks, while the methyl protons appear as a sharp singlet. It should be noted that each of the ligands (CH<sub>3</sub>)<sub>2</sub>S, (CH<sub>3</sub>)<sub>3</sub>S<sup>+</sup>, and CO produce downfield shifts in the *trans* relative to the *cis* ammonia ligands.

The NH<sub>3</sub> symmetric deformation frequencies occur in the infrared at 1292 (s), 1305 (w), and 1318 and 1328 cm<sup>-1</sup> (s). In compounds containing the (NH<sub>3</sub>)<sub>5</sub>Ru<sup>II</sup> or (NH<sub>3</sub>)<sub>5</sub>Ru<sup>III</sup> ion, this vibrational mode would characteristically occur either in the range 1260-1290 or 1330-1360 cm<sup>-1</sup>.<sup>2</sup> A similar effect is manifested in some compounds such as [(NH<sub>3</sub>)<sub>5</sub>RuNO]Br<sub>3</sub> which contain NO<sup>+</sup> bound to Ru<sup>II</sup> ( $\delta_{\text{NH}_3}$  1310 cm<sup>-1</sup>).<sup>3</sup>

Cyclic voltammograms were recorded in dry acetonitrile containing 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte or in 0.1 M HCl. In acetonitrile, a wave was observed at +1460 mV vs. SCE in the oxidation mode, but no corresponding reduction wave. On repeated cycling this wave disappeared with concomitant development of a reversible wave at +415 mV vs. SCE which corresponds to the [(NH<sub>3</sub>)<sub>5</sub>RuNCCH<sub>3</sub>]<sup>3+/2+</sup> redox couple.<sup>4</sup> In 0.1 M HCl, an irreversible (in the sense described above) wave was seen at 1250 mV vs. NHE which disappeared on repeated cycling producing the [(NH<sub>3</sub>)<sub>5</sub>RuCl]<sup>2+</sup> ion. The large positive redox potential is characteristic of complexes of Ru<sup>II</sup> containing ligands, which are strong  $\pi$  acids and indifferent  $\sigma$  donors, and is evidence for metal to ligand back bonding. In any case, it is impossible to understand the affinity of Ru<sup>II</sup> for S(CH<sub>3</sub>)<sub>3</sub><sup>+</sup> on the basis of a simple  $\sigma$ -bond interaction.

It seems worth-while to point out explicitly that, although within a carefully defined series, there may be a relation between the position of the  $\pi$ -d- $\pi^*$  absorption and the affinity of the  $\pi$ -acid ligand for the metal ion, there is certainly no mo-