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Synthesis of N-Heterocyclic Complexes of Osmium, Ruthenium, Cobalt, and Rhodium Pentaammines

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Examples are given of the improved syntheses of a variety of N-heterocyclic complexes, which are prepared by the reaction of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ either with the neat ligand or with an excess of the ligand, in a poorly coordinating solvent. However, due to base-catalyzed disproportionation reactions, such methods are unsuitable for the syntheses of the Os and Ru complexes, especially with the more basic of the N-heterocyclic ligands. For Ru, the best method of synthesis involves the reduction of $[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$ to the Ru(II) complex, prior to the reaction with the appropriate ligand. Such methods are not suitable for Os, but the in situ reduction of the $[Os(NH_3)_5(\text{N-heterocycle})]^{3+}$ complexes, as they form, proves to be a high-yielding method. The $[M(NH_3)_5(pzH)]^{4+}$ ions are isolated conveniently by the dissolution of $[M(NH_3)_5(pz)]^{3+}$ in neat CF_3SO_3H, followed by the precipitation of $[M(NH_3)_5(pzH)](CF_3SO_3)_4$ with diethyl ether. The best method for the preparation of the Ru(II) and Os(II) complexes with N-heterocyclic ligands is by the reduction of the M(III) complexes, in nonaqueous solvents. The shift in the redox potential of the M(III/II) couples of the N-heterocyclic complexes (in comparison to that of $[M(NH_3)_6]^{3+/2+}$) is approximately twice as large for Os in comparison to Ru, which shows that the degree of π-back-bonding is much larger for Os(II) than for Ru(II). The stabilization of Os(II) by π-back-bonding is even more pronounced than is indicated from the electrochemistry, because Os(III) (but not Ru(III)) is also stabilized significantly by π-back-bonding.

Introduction

The effect of π-back-bonding on the properties of pentaammineruthenium(III/II) complexes with π-acid ligands has been a matter of some interest.[1-3] In the study of these effects, the N-heterocyclic ligands, in both binuclear and mononuclear complexes, have played a central role.[2-10] More recently, the syntheses of some analogous osmium complexes have been achieved,[11,12] which makes feasible a comparison of the effects of π-back-bonding on the properties of complexes of the congeners. The $[Os(NH_3)_5(py)]^{3+/2+}$ system has also come to notice as the first example of a simple redox couple for which the redox properties in an adsorbed state have been examined by surface-enhanced Raman spectroscopy (SERS),[13] and since then, the SERS spectra of several other Os(III)/Os(II) couples and analogous Ru(II) complexes have been reported.[14,15] Because of the interest in these complexes, we report here improved syntheses of osmium and ruthenium ammine complexes of N-heterocyclic ligands and also of the cobalt and rhodium analogues.

Experimental Section

Absorption spectra (UV, visible, and near-IR) were recorded on a Beckman Model 5270 spectrophotometer. The spectra in the near-IR region were recorded for samples pelletized in KBr or CsI and/or dissolved in 0.1 M DCl/D_2O solutions. Spectra of air-sensitive complexes were obtained by reducing them with Zn(Hg) in a Zwickel flask under an argon atmosphere and then transferring the solutions (Ar atmosphere) to a Beckman spectrophotometer cell.[16,17] IR spectra were recorded as KBr or CsI discs on a Perkin-Elmer Model 621 IR spectrophotometer and/or a Nicolet 7199 FTIR spectrophotometer. The latter instrument was also used to measure some of the near-IR spectra. Electrochemical measurements were made with a PAR 173 potentiostat/galvanostat in conjunction with a PAR 175 universal programmer, using the conventional three-electrode system and a SCE reference electrode. Controlled-potential electrolysis and coulometry experiments were performed with the PAR 173 potentiostat/galvanostat and 179 digital coulometer.

Argon (high purity) was deoxygenated (Cr^{2+}) and dried (H_2SO_4) prior to use. $(NH_4)_2OsCl_6$ was prepared from OsO_4[18] (Alfa) and converted to $[Os(NH_3)_5(N_2)]Cl_2$ by a modification[19,20] of the literature methods.[21-23] Oxidation of this complex by Br_2 in neat CF_3SO_3H afforded a quantitative yield of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$.[12,19,24] $[Ru(NH_3)_5Cl]Cl_2$ was prepared from $[Ru(NH_3)_6]Cl_3$.[25,26] $[Co(NH_3)_5Cl]Cl_2$,[27] $[Ru(NH_3)_5Cl]Cl_2$, and $[Rh(NH_3)_5Cl]Cl_2$ (obtained from Alfa or prepared as in ref 28) were converted to their triflato complexes by standard procedures.[26,29-32]

$[Rh(NH_3)_5(pz)](CF_3SO_3)_3$. $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.10 g, 0.16 mmol) is ground with neat dry excess pyrazine (0.5 g, 6.2 mmol). The mixture is heated until the pyrazine melts (~55 °C) and is maintained at this temperature for 10 min. After it has cooled to room temperature, the solid is broken up and the excess pyrazine is extracted with diethyl ether (3 × 10 mL). The solid is collected on a sintered-glass filter, washed three times with diethyl ether, and air-dried. The yield is quantitative. Anal. ($C_7H_{19}N_7O_9S_3F_9Rh$) C, H, N. If $[Rh(NH_3)_5(OSO_2CF_3)](OSO_2CF_3)_2$ is contaminated with the aqua complex or the py-

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(1) Ligand abbreviations used here: pz = pyrazine; py = pyridine; pm = pyrimidine; pd = pyridazine; bpy = 4,4′-bipyridine; isna = isonicotinamide; 4-Phpy = 4-phenylpyridine; pzH = pyrazinium; pzMe = 1-methylpyrazinium; pzEt = 1-ethylpyrazinium; DMF = *N*,*N*-dimethylformamide; DMSO = dimethyl sulfoxide.
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razine is wet, a considerable amount of $[Rh(NH_3)_5(OH_2)]^{3+}$ results as an impurity. This is removed conveniently by recrystallization of the pz complex as the perchlorate salt.[8] If the sample is strongly contaminated, it is best purified by chromatography, in the following manner. The residue is heated in 5 M HCl for 1 h at 90 °C to convert the aqua complex to the chloro complex. The solvent is removed by rotary evaporation, the residue is dissolved in 0.01 M HCl, and the solution is passed through a column of SP-Sephadex C-25. The yellow $[Rh(NH_3)_5Cl]Cl_2$ is removed by 0.2 M HCl (and recovered for subsequent use), and the desired complex is eluted with 0.3 M HCl. The eluate is evaporated to dryness to yield the chloride salt, which is dissolved in the minimum of neat CF_3SO_3H. The mixture is then cooled in an ice bath, and diethyl ether is added dropwise, with stirring, to precipitate the triflate salt. This is collected, as before.

Caution! The precipitation of the Ru and Os complexes as the perchlorate salts should be avoided as they are unpredictably explosive and present an extreme hazard.

$[Os(NH_3)_5(pz)]Cl_3·2H_2O$ (Method 1a). $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (93 mg) and excess pyrazine (200 mg, 20-fold excess) are dissolved in dry, distilled triethyl phosphate (~0.5 mL) contained in a stoppered test tube. The solution is heated to ~40 °C for 2 h, with constant stirring, during which time it turns a deep yellow. The solution is diluted with 1 M HCl (100 mL) and the mixture is passed through a small column of Dowex 50W-X2 (9 × 1.5 cm). A pale yellow solution is eluted with 3 M HCl (containing a mixture of $[Os(NH_3)_5(OH_2)]^{3+}$, $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$, and $[Os(NH_3)_5Cl]^{2+}$, which slowly converts to $[Os(NH_3)_5Cl]Cl_2$ on standing). The dark brown protonated pyrazine complex is removed with 4 M HCl, and the eluate is evaporated to dryness. The yield of $[Os(NH_3)_5(pzH)]Cl_4$ is 56%. The complex $[Os(NH_3)_5(pz)]Cl_3·2H_2O$ may also be obtained from the crude product, in the manner described previously.[11]

$[Os(NH_3)_5(pzH)](CF_3SO_3)_4$ and $[Os(NH_3)_5(pz)](CF_3SO_3)_3$. A sample of the chloride salt is dissolved in the minimum of neat CF_3SO_3H.[33] The dark brown solution is cooled in an ice bath, and an equal volume of diethyl ether is added dropwise, with stirring, to precipitate the triflate complex. The precipitate is collected and washed with diethyl ether containing a few drops of triflic acid (2 × 5 mL) and air-dried. Anal. ($C_8H_{20}F_{12}N_7O_{12}S_4Os$) C, H, N. This solid is converted to the anhydrous triflate complex of the unprotonated pyrazine ligand by stirring repeatedly a suspension of the solid diethyl ether. After many such washings, the complex changes color from the dark brown of $[Os(NH_3)_5(pzH)]^{4+}$ to the yellow of $[Os(NH_3)_5(pz)]^{3+}$. Anal. ($C_7H_{19}F_9N_7O_9S_3Os$) C, H, N.

$[Os(NH_3)_5(pz)]Cl_3·2H_2O$ (Method 1b) and $[Os(NH_3)_5(pz)](CF_3SO_3)_3·H_2O$. Dry distilled sulfolane or dry AR acetone is preferable to triethyl phosphate as a solvent because, with the latter, the high temperatures and long reaction times required to give good yields of $[Os(NH_3)_5(pz)]^{3+}$ also result in the formation of $[Os(NH_3)_5(pzEt)]^{4+}$.[34] A sulfolane solution of $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (ca. 0.2 M) and pyrazine (8-fold excess) is kept at 60–70 °C for 2 h. A brown solution results. This is cooled and diluted by a factor of 25 with 0.2 M HCl, and the mixture is passed through a SP-Sephadex C-25 column. The fraction eluted with 0.4–0.5 M HCl is collected and rotary-evaporated to dryness, whereupon $[Os(NH_3)_5(pzH)]Cl_4$ is left as a nearly black solid. This is taken up in the minimum volume of 0.01 M CF_3SO_3H, and solid $NaCF_3SO_3$ is added. The mixture is warmed to 50–60 °C in order to take the solid into solution and subsequently is cooled slowly. The orange crystals are collected by filtration and washed with dry glyme and then diethyl ether. Yield: 35%. Anal. ($C_7H_{21}F_9N_7O_{10}S_3Os$) C, H, N. The yield of the crude complex is much higher, but considerable amounts of the complex are lost on crystallization due to the high solubility of the triflate salt.

By use of acetone of sulfolane at higher temperatures and extended reaction times in the initial reaction medium, 70–80% yields of $[Os(NH_3)_5(pzH)]Cl_4$ are realized under optimal conditions of dry solvent and reactants. It should be noted that molecular sieves in the reaction mixture should be avoided because they favor the formation of polynuclear nitrido-bridged complexes. The products from these reactions are chromatographed successfully on SP-Sephadex C-25, whereupon $[Os(NH_3)_5Cl]^{2+}$ and $[Os(NH_3)_5(OH_2)]^{3+}$ are removed with 0.25 M HCl and $[Os(NH_3)_5(pz)]^{3+}$ (yellow band) is eluted with 0.35–0.4 M HCl. The binuclear nitrides and pyrazine-bridged complexes are removed only by stronger acid (~0.7 M).

$[Os(NH_3)_5(pz)]Cl_3$ (Method 2). The synthesis is performed in essentially the same manner as that reported for the rhodium analogue. The solution often becomes intensely colored due to the formation of binuclear species. Furthermore, chromatography on SP-Sephadex C-25 reveals a band trailing $[Os(NH_3)_5(pz)]^{3+}$, which comprises a bis(pyrazine) species. The yields vary greatly, and this is not a method of choice.

$[Os(NH_3)_5(pz)]Cl_3$ (Method 3). Pyrazine (0.30 g) is dissolved in a degassed (Ar) solution of 0.1 M $NaCF_3SO_3$ or 0.1 M $(Me_4N)[CF_3SO_3]$ in acetone contained in an electrolysis cell. (**Note**: Perchlorate salts should be avoided as background electrolytes not only because they are an explosion hazard but also because the perchlorate ion undergoes irreversible redox reactions with both Ru(II) and Os(II).) $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.100 g) is added, and the electrolysis is performed at −0.50 V vs the SCE, with either a mercury pool or a platinum mesh working electrode. Electrolysis is allowed to proceed for 3 h at room temperature, and the osmium(III) complex is isolated, as before, after allowing for aerial oxidation. The yield varies: ~60–85%.

If the goal is to prepare an Os(II) species, $[Os(NH_3)_5(pz)]Cl_2$ is precipitated directly after electrolysis by using Et_4NCl, but it is often contaminated by $[(NH_3)_5OspzOs(NH_3)_5]^{4+}$ and unidentified binuclear species. It is best to isolate the pure Os(III) complex and then reduce it, in order to obtain the Os(II) complex.

$[Os(NH_3)_5(pz)]Cl_2$ and $[Os(NH_3)_5(pz)]I_2$. $[Os(NH_3)_5(pz)](CF_3SO_3)_3$ is reduced by Zn(Hg) in acetone, and the complex is precipitated by adding a deaerated acetone solution of $(Et_4N)Cl$ or $(Bu_4N)I$. ($ZnCl_2$ and ZnI_2 are very soluble in these solvents and are not coprecipitated.) The mixture is filtered under an Ar atmosphere, and the solid is washed with diethyl ether and dried over P_4O_{10} in an Ar atmosphere.

$[Os(NH_3)_5(pz)](BF_4)_2$. $[Os(NH_3)_5(pz)]Cl_3$ in 0.001 M CF_3CO_2H is reduced by Zn(Hg) under argon. The pH is adjusted rapidly to ~9 with solid Na_2CO_3, and the osmium(II) complex is precipitated by adding an aqueous deaerated solution of $NaBF_4$.

$[Os(NH_3)_5(pzH)]Cl_3$ is obtained by passing gaseous HCl through a nonaqueous solution of $[Os(NH_3)_5(pz)]^{2+}$ (in the absence of Zn(Hg)).

$[Ru(NH_3)_5(pz)]Cl_2$ and $[Ru(NH_3)_5(pz)](BF_4)_2$. $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (0.10 g, 0.16 mmol) is dissolved in degassed (30 min, Ar) acetone (AR, 10 mL) contained in a Zwickel flask. The outlet is connected to a second bubble flask containing pyrazine (0.5 g, 6.2 mmol, AR grade) in degassed acetone (AR, 10 mL). After the oxygen is removed (~30 min), a piece of Zn(Hg) is added to reduce the Ru(III) complex. The reduction is allowed to proceed for 30 min, and then the Ru(II) solution is transferred into the flask containing the ligand. (It is essential that O_2 is rigorously excluded, as the green $[(NH_3)_5RuORu(NH_3)_5]^{5+}$ ion results from the reaction of Zn(Hg) with Ru(II) in acetone.[35]) The transfer is made over ~15 min, in order to minimize the formation of binuclear species. Almost immediately, the solution turns a deep purple, but the reaction is allowed to proceed for a further 30 min (over Zn(Hg)) to complete the reaction. After removal of the Zn(Hg), Et_4NCl (0.5 g in 10 mL of acetonitrile) is added to the resulting solution. The red-purple precipitate is collected on a sintered-glass filter (under Ar), washed with degassed CH_3CN (5 mL) and then degassed acetone (5 mL), and dried in vacuo. The yield is quantitative. Anal. ($C_4H_{19}N_7Cl_2Ru$) C, H, N, Cl. The crude product is recrystallized as the tetrafluoroborate salt, in the manner reported previously.[36] Anal. ($C_4H_{19}N_7B_2F_8Ru$) C, H, N.

$[Ru(NH_3)_5(pz)]Cl_3$, $[Ru(NH_3)_5(pz)](CF_3SO_3)_3$, and $[Ru(NH_3)_5(pzH)](CF_3SO_3)_4$. The Ru(III) complexes are prepared by oxidation of the appropriate Ru(II) complex by the standard technique.[36] The protonated and unprotonated triflate salts are prepared as for osmium analogues.

$[Co(NH_3)_5(pz)](CF_3SO_3)_3$ is prepared in quantitative yield from $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$, in the same manner as that described for the rhodium analogue.

$[M(NH_3)_5(py)](CF_3SO_3)_3$ and $[M(NH_3)_5(bpy)](CF_3SO_3)_3$ (M = Rh(III), Co(III)). Pyridine is distilled over KOH prior to use, and method 2 is employed. The dihydrate of the bpy ligand is dehydrated by heating it at 150 °C for ~5 min, and the reaction of the ligand with the triflate salt is carried out according to method 1. The yield is quantitative, in all instances, so long as the reagents are sufficiently dry.

$[M(NH_3)_5(py)]^{n+}$ (M = Ru, Os; n = 2, 3). Pyridine proved to be too basic to give reliable yields to the desired products by use of either method 1 or 2; in the case of osmium, the solution turns red rapidly and deepens in color. Even after relatively short reaction times, considerable quantities of $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$, $[Os(NH_3)_5(OH_2)]^{3+}$, and *cis*-$[Os(NH_3)_4(py)_2]^{3+}$ (HPLC) are present.[37] Multiple substitution pathways are not prevented by the addition of neat CF_3SO_3H (≤1 M in CF_3SO_3H). Method 3 results in high yields (≥90%) of the desired products. The M(II) species are isolated, as before.

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$[M(NH_3)_5(pd)]^{n+}$, $[M(NH_3)_5(pm)]^{n+}$, and $[M(NH_3)_5(isna)]^{n+}$ are best prepared by method 3. Multiple substitution pathways are not as serious as for pyridine, due to the decreased basicities of the nitrogen donors, and all three methods are successful.

$[Os(NH_3)_5(bpy)]Cl_3\cdot HCl$. This is prepared by method 1 from $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ (188 mg), anhydrous bpy (250 mg) in dry sulfolane (0.5 mL), at a reaction temperature of 40 °C for 1.5 h. The solution is quenched with 0.2 M HCl (150 mL) and is passed through a column of Dowex 50W-X2. After the column is washed with 3 M HCl, the bright orange band is eluted with 4 M HCl. A minor brown band of the binuclear species is eluted with 6 M HCl, while higher polymeric species remained at the top of the column.

$[Os(NH_3)_5(4\text{-}Phpy)]Cl_3\cdot 2H_2O$ and *cis*-$[Os(NH_3)_4(4\text{-}Phpy)_2]Cl_3\cdot 1^1/_2H_2O\cdot {}^1/_2HCl$. These complexes are prepared by method 1b from 4-phenylpyridine (3 fold excess) and $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$. The monosubstituted complex is eluted in 40% yield by 0.4 M HCl from a Sephadex C-25 column. Anal. ($C_{11}H_{28}N_6O_2Cl_3Os$) C, H, N. The disubstituted complex is eluted with 0.6 M HCl in ~18% yield. Anal. ($C_{22}H_{33.5}N_6O_{1.5}Cl_{3.5}Os$) C, H, N.

$[Os(NH_3)_5(pzMe)]Cl_4$ and $[Os(NH_3)_5(pzMe)](BF_4)_4$. These are prepared by method 1b in sulfolane as the solvent from $(Mepz)BF_4$ (obtained by metathesis from the iodide salt[38]) and $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$ as the reagents. The desired complex is purified by cation-exchange chromatography from SP-Sephadex C-25, as for the pz complex. The yield of the chloride salt is ~30%. The crude chloride salt is recrystallized from aqueous $NaBF_4$, to yield the BF_4^- salt. Anal. ($C_5H_{22}B_4F_{16}N_7Os$) C, H, N.

Results

Syntheses. $[M(NH_3)_5L]^{3+}$ (where L = N-heterocycle)[1] complexes are prepared in moderate to high yields by the reaction of $[M(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, either with L as a neat liquid or in acetone or sulfolane solution. If care is taken to ensure that all of the solvents and reactants are dry, this procedure results in essentially quantitative yields of the rhodium and cobalt complexes, but it is not the best method for the osmium and ruthenium complexes. Reactions involving the latter metal ions result in multiple substitution and/or the formation of nitrido-bridged oligomers, in addition to the required product. For the osmium complexes, the most high-yielding method for synthesizing the N-heterocyclic complexes is based on the reduction of the $[Os(NH_3)_5(N\text{-heterocycle})]^{3+}$ products, as they form. In the case of ruthenium, the use of both aqueous and nonaqueous solvents as the media for the reactions of $[Ru(NH_3)_5(solvent)]^{2+}$ (generated in situ) result in high yields. As the basicity of the N-heterocycle increases, it becomes more critical to use Ru(II) intermediates for the synthesis of the Ru complexes or to use method 3 for the Os complexes. In the case of pyridine, the in situ reduction procedure is far superior to those methods that do not involve reduction of the M(III) reactants and/or products.

The diazine heterocycles (pyrazine and pyrimidine) of the M(III) complexes are protonated in neat CF_3SO_3H and their properties are similar to those of the 1-methyldiazinium (e.g. 1-methylpyrazinium) complexes. Such complexes are isolated by the addition of diethyl ether to the neat CF_3SO_3H solutions but are deprotonated when the solid is washed with copious quantities of diethyl ether.

The Ru(II) and Os(II) complexes are isolated by reducing pure samples of the M(III) ions in neutral or basic aqueous media or in nonaqueous solvents. Reduction of the osmium complexes in acidic aqueous media using Zn(Hg) results in varying degrees of hydrogenation of the heterocycles when the reaction mixture is allowed to stand for prolonged times.[11] Therefore, reductions in nonaqueous solvents are preferable.

Electrochemistry. The electrochemical results are summarized in Table I for Ru and Os. The Rh and Co complexes are reduced irreversibly, while the Ru and Os complexes show well-behaved reversible redox couples. The effect of π-back-bonding ligands in stabilizing the M(II) state, with respect to the M(III) state, is greater for Os than for Ru. The diazinium ions particularly stabilize the M(II) oxidation state with respect to the M(III) oxidation state, and both protonation or alkylation of the uncoordinated N-donor groups affect the redox potentials in a similar manner.

Table I. Redox Potentials of Pentaammine Complexes of Ru and Os[a]

complex	Ru	Os
$[M(NH_3)_6]^{3+/2+}$	+0.05 (0.00)[b]	−0.78 (0.00)[49]
$[M(NH_3)_5(pz)]^{3+/2+}$	+0.49 (+0.44)[b]	−0.09 (+0.69)[11]
$[M(NH_3)_5(pm)]^{3+/2+}$	+0.44 (+0.39)[c]	−0.26 (+0.52)[11]
$[M(NH_3)_5(pd)]^{3+/2+}$		−0.21 (+0.57)[11]
$[M(NH_3)_5(py)]^{3+/2+}$	+0.30 (+0.25)[b]	−0.395 (+0.38)[11]
$[M(NH_3)_5(pzMe)]^{4+/3+}$	+0.87 (+0.82)[8]	+0.546 (+1.33)[12]
$[M(NH_3)_5(bpy)]^{3+/2+}$	+0.33 (+0.28)[d]	−0.22 (+0.56)[e]
$[M(NH_3)_4(4\text{-}Phpy)]^{3+/2+}$		−0.372 (+0.41)[e]
$[M(NH_3)_5(isna)]^{3+/2+}$	+0.35 (+0.30)[b]	−0.240 (+0.54)[11]
cis-$[M(NH_3)_4(4\text{-}Phpy)_2]^{3+/2+}$		−0.090 (+0.69)[e]

[a] Potentials in volts vs the NHE. The values in parentheses are relative to the appropriate $[M(NH_3)_6]^{3+/2+}$ couple. [b] Matsubara, T.; Ford, P. C. *Inorg. Chem.* **1976**, *15*, 1107–1110. [c] Richardson, D. E. Ph.D. Thesis, Stanford University, 1981. [d] Matsubara, T., unpublished results, quoted in ref 9. [e] This work; 0.1 M HCl.

Table II. Visible/UV Spectra of Osmium(III/II) Complexes

complex	λ_{max} (ϵ_{max})[a]
	Osmium(III)
$[Os(NH_3)_5(pzH)]^{4+}$	264 (5.03 × 10^3), 324 (1.86 × 10^3), 391 (4.48 × 10^3), ~530 (650)[b]
$[Os(NH_3)_5(pzMe)]^{4+}$	268 (4.9 × 10^3), 360 (2.15 × 10^3), 420 (5.00 × 10^3), ~600 sh (494)
$[Os(NH_3)_5(4\text{-}Phpy)]^{3+}$	261, 272, 309, ~345
cis-$[Os(NH_3)_4(4\text{-}Phpy)_2]^{3+}$	268 (broad), 312, ~385 sh
	Osmium(II)[c]
$[Os(NH_3)_5(pzMe)]^{3+}$	435, 1150
$[Os(NH_3)_5(4\text{-}Phpy)]^{2+}$	483, 662
cis-$[Os(NH_3)_4(4\text{-}Phpy)_2]^{2+}$	406, 476, 623
cis-$[Os(NH_3)_4(pz)_2]^{2+}$	255, 389, 482, 650[d]
cis-$[Os(NH_3)_4(pzH)(pz)]^{3+}$	256, 265 sh, 360, 520 (broad)[e]

[a] λ_{max} in nm; ϵ_{max} in M^{-1} cm^{-1}. [b] Neat CF_3SO_3H. [c] It is difficult to obtain accurate ϵ_{max} values for the Os(II) complexes in water because of their tendency to undergo irreversible ligand reductions. However, the most intense bands (those in the visible region ~450–500 nm) had intensities of the order of 10^4 M^{-1} cm^{-1}. [d] pH 7.0. [e] 0.1 M CF_3SO_3H.

Absorption Spectra. UV/visible absorption spectra of the previously unreported Os(III) complexes are collected in Table II. These spectra are dominated by the π → π* internal ligand transitions and by the intense MLCT transitions in the UV/visible region, which give the complexes their color. Protonations of the coordinated diazene ligands result in considerable shifts of the MLCT transitions to lower energies, giving more intensely colored solutions. The spectral properties resemble those observed for the $[M(NH_3)_5(pzMe)]^{4+}$ complexes. All of these Os(III) complexes also exhibit a previously unreported series of ill-defined lower energy shoulders on the MLCT bands.

The internal electronic transitions within the t_2^5 electronic configuration are bought about by the effects of spin–orbit coupling on the Os(III) ground state and appear in the near-IR region.[11,12,39] The relevant data for these transitions are summarized in Table III. These transitions are more intense for the diazinium complexes as compared to complexes with N-heterocyclic ligands.

Spectral data for the Os(II) complexes are collected in Table II. The MLCT transitions for the M(II) ions occur at lower energies in comparison to those for the M(III) ions, and the solutions are much more intensely colored. The MLCT features move to still lower energies for the complexes containing diazinium ions, and the lowest energy MLCT bands are in the near-IR region for these complexes.

Some figures of the Os(III) UV/vis and near-IR electronic and MCD spectra[39] and details of the vibrational spectroscopy[13-15] of these complexes have been published elsewhere.

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Table III. Near-IR Transitions of Osmium(III) Complexes in DCl/D_2O or KBr Disks

complex	λ_{max} (ϵ_{max})[a]
$[Os(NH_3)_5(pz)]^{3+}$	1748 (~12), 1802 (~8), 1905 (~4), 2075 (~40)[b]
$[Os(NH_3)_5(py)]^{3+}$	1750 (<10), 1840 (<10), 1930 (<10), 2065 (50)[b]
$[Os(NH_3)_5(pm)]^{3+}$	1750 (<10), 1840 (<10), 2073 (42)[b]
$[Os(NH_3)_5(pd)]^{3+}$	1744 (10), 1837 (14), 1898 (11), 2082 (51), 2151 (11)[b]
$[Os(NH_3)_5(4\text{-Phpy})]^{3+}$	1568 (6), 1765 (6), 1852 (23), 1910 (11), 2008 sh (5), 2097 (100), 2914 (60),[d] ~3130 (120)[c,e]
$[Os(NH_3)_5(isna)]^{3+}$	1730 (~4), 1831 (~7), 1886 (~5), 2064 (62)[b]
cis-$[Os(NH_3)_4(4\text{-Phpy})_2]^{3+}$	1613 (3), 1804 (19), 1883 (23), 1960 (6), 2176 (100), 2912 (66),[d] 3180 (94)[c,e]

[a] λ_{max} in nm; ϵ_{max} in $M^{-1}\,cm^{-1}$; 0.1 M DCl/D_2O solutions. [b] 0.12 M DCl/D_2O; ref 11. [c] KBr disks. Relative intensities are given in parentheses, taking the intensity of the band at ~2100 nm as having an arbitrary value of 100. [d] O–H stretch in the IR region. [e] N–H stretch in the IR region.

Discussion

Syntheses. With the exception of $[Os(NH_3)_5(bpy)]^{3+/2+}$, $[Os(NH_3)_5(pzMe)]^{4+/3+}$, $[Os(NH_3)_5(4\text{-Phpy})]^{3+/2+}$ and *cis*-$[Os(NH_3)_4(4\text{-Phpy})_2]^{3+/2+}$, the complexes reported here have been prepared previously by other methods.[4,6,8,11,12,40–48] The ruthenium complexes have been synthesized mainly by the methods of Taube and co-workers, in which labile $[Ru(NH_3)_5(solvent)]^{2+}$ intermediates are generated by the in situ reduction of $[Ru(NH_3)_5Cl]^{2+}$ by zinc amalgam.[2–9] Yields obtained by using these procedures are typically 60–80% starting from $[Ru(NH_3)_5Cl]Cl_2$. A modification of this method, which was employed by Meyer and co-workers, is to isolate $[Ru(NH_3)_5(OH_2)](PF_6)_2$ as an intermediate and to use deaerated acetone as the medium for the reaction of the aqua complex with the desired ligand.[45] These two methods have led to the syntheses of a large variety of $[Ru^{III/II}(NH_3)_5L]^{n+}$ complexes but have not been applicable to the analogous osmium chemistry, due to the rapid reduction of water[49] by $[Os(NH_3)_5(OH_2)]^{2+}$ and even by some of the desired product complexes. Despite early success in the syntheses of *cis*-$[Os(NH_3)_4(N_2)L]^{2+}$ (L = N-heterocycle) and related complexes,[50] it was not until 1979 that a general method for the syntheses of the $[Os(NH_3)_5L]^{3+}$ complexes was achieved.[11] This method involves the generation of $[Os(NH_3)_5(OP(OEt)_3)]^{3+}$ as a reactive intermediate in the Ag^+ oxidation of $[Os(NH_3)_5(N_2)]Cl_2$ in triethyl phosphate,[11] but the yields were moderate at best (≤40%). By contrast, the syntheses of $[M(NH_3)_5L]^{3+}$ complexes (M = Co, Rh; L = N-heterocycle) are well-known and depend on the replacement of the DMSO or DMF ligands, at elevated temperatures, to give moderate to high yields of the appropriate complexes.[8,41–48]

Because the usefulness of the labile triflato group for the syntheses of a large range of pentaammine complexes has been amply demonstrated,[12,19,24,26,29–34,40] it was obvious that they would be well suited for the synthesis of pentaammine complexes containing N-heterocycles. The use of triflato complexes, in the case of Co(III) and Rh(III), has the advantage of shorter and milder reaction conditions than those published previously. However, while the reaction of the M(III) triflato complexes with excess ligand works well for the Co(III) and Rh(III) ions, it is of variable utility for synthesizing Os(III) complexes and presents great problems in synthesizing Ru(III) complexes. These reactions are found to become increasingly troublesome as the basicity of the heterocycle increases, and it is evident that the side reactions, and indeed substitution to form the desired products, are both base-catalyzed. The susceptibility of the Ru(III) and Os(III) complexes toward base-catalyzed disproportionation to M(II) and M(IV) species[7,24,51] is believed to be the source of the problems. The binuclear and polynuclear nitrido-bridged complexes are a well-known class of molecules, which have been studied in detail by Griffith and co-workers[52,53] and which are isolated during the syntheses of binuclear pyrazine-bridged complexes.[34] The base-catalyzed disproportionation of $[Ru^{(III)}(NH_3)_5(py)]^{3+}$ to $[Ru^{II}(NH_3)_5(py)]^{2+}$ and *trans*-$[Ru^{IV}(NH_3)_4(NH_x)(py)]^{n+}$ has been known for some time.[7] Similar reactions occur for the osmium analogues, and the Os(IV) complex produced is no doubt a precursor to the formation of nitrido-bridged complexes and to multiple substitution. Substitution reactions of the $[M(NH_3)_5(\text{N-heterocycle})]^{2+}$ ions are too slow to be implicated in the formation of *cis*-$[M(NH_3)_4(\text{N-heterocycle})_2]^{3+}$. The cis geometry of these complexes was established by comparing the properties of the products with those of the known cis and trans ruthenium complexes and with the properties of complexes obtained from the substitution reactions of *cis*-$[Os(NH_3)_4(OSO_2CF_3)_2](CF_3SO_3)$ with the appropriate N-heterocycle.[54] It is to be noted that multiple substitution is more favored with respect to nitrido-bridged complex formation for ruthenium. This is probably a reflection of the greater lability of the amines coordinated to Ru(IV) in comparison to that of the amines coordinated to Os(IV). Low-spin d^4 systems tend to be much more labile than low-spin d^5 or d^6 systems.

The possibility of a strong π-bonding interaction involving the N^{3-} ligand and the N-heterocycle is believed to result in a geometry in which these ligands are mutually trans. π-electron density can be transferred from the N^{3-} ligand to the N-heterocycle via a metal t_2 orbital. This would strengthen the N^{3-}–M(IV)–(N-heterocycle) interaction and favor substitution in the equatorial plane by weakening the cis M(IV)–NH_3 bonds.

When the Ru(II) triflato or solvent complexes are used in these synthetic reactions, the above problems are eliminated. The reactions are also faster because of the enhanced lability of complexes of the Ru(II) oxidation state in comparison to the lability of those of the Ru(III) oxidation state. While the conventional preparative methods depended on labile $[Ru(NH_3)_5(solvent)]^{2+}$ species,[2–6,45] the use of $[Ru(NH_3)_5(OSO_2CF_3)]^{2+}$ is more convenient and generally results in higher yields of the desired products.

Pentaammineaquaosmium(II) is too readily oxidized by water[49] to be synthetically useful, so $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ was reduced in nonaqueous solvents in order to test the synthetic utility of $[Os(NH_3)_5(solvent)]^{2+}$ complexes as intermediates. Initially, the reductions were performed in acetone in the presence of excess ligand and resulted in high to moderate yields of the desired products. However, it was shown subsequently[55] that the 2+ acetone complex has the ligand bound in an η^2-(*C,O*) configuration, producing a seven-coordinate complex that is nonlabile. Ap-

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parently, the reactive intermediate in these reactions is still the $[Os(NH_3)_5(acetone)]^{3+}$ complex, which was present in small amounts due to oxygen contamination.[55] It is uncertain, as yet, whether similar reactions are occurring in the preparations carried out by using bulk electrolysis in sulfolane. Similar types of reactions occur with the $[Ru(NH_3)_5(acetone)]^{2+}$ complex,[56] but the labile η^1 complex is in equilibrium with the inert η^2 complex, which enables the Ru(II) acetone complex to be a useful synthetic intermediate.

The in situ reduction of the $[Os(NH_3)_5(\text{N-heterocycle})]^{3+}$ complexes, as they form, minimizes the disproportionation and multiple substitution pathways that have been outlined previously. This results in substantially higher yields of products than the methods in which the $[Os(NH_3)_5(\text{solvent})]^{3+}$ or $[Os(NH_3)_5(OSO_2CF_3)]^{2+}$ complexes are used.[11,12] The use of $[Os(NH_3)_5(\text{solvent})]^{2+}$ complexes that are not as inert as the acetone complex are being investigated further.[55]

Electrochemistry and Spectroscopy. The M(II) oxidation state is stabilized with respect to the M(III) oxidation state by π-accepting ligands. This effect is larger for osmium than for ruthenium, as is illustrated in Table I, where the shift in the redox potential against the appropriate $[M(NH_3)_6]^{3+/2+}$ couple is observed to be approximately twice as great for osmium as for ruthenium, throughout the series of ligands. However, this is not solely a reflection of the π-back-bonding in the M(II) oxidation states; π-back-bonding is important also for Os(III), but not Ru(III). This has been well demonstrated by the crystal structures of the $[(NH_3)_5MpzM(NH_3)_5]^{6+}$ ions,[10,57,58] where the M–N(pz) bond is the shortest M–N bond for osmium and the longest (within experimental error) for ruthenium. Similarly, the greatly enhanced stability of $[(NH_3)_5OsN_2Os(NH_3)_5]^{6+}$ in comparison to that of its ruthenium analogue[59] and the stability of $[Os(NH_3)_5(NCCH_3)]^{3+}$ toward hydrolysis of the nitrile[24] are strong evidence of the importance of π-back-bonding for Os(III) in comparison to the case of Ru(III). Back-bonding for Os(III) will oppose the positive shift in the Os(III)/Os(II) redox potentials brought about by the stabilization of Os(II) by π-back-bonding, and thus, the Os(II) oxidation state is stabilized by the N-heterocycles to a greater degree than is indicated by the shifts in the redox potentials.

The greater π-back-bonding indicated for both Os(II) and Os(III), in comparison to that for their ruthenium counterparts, is due, to a large measure, to the t_2 orbitals being closer in energy to the π^*-ligand orbitals for ions of the third transition row as compared to those of the second row, leading to more efficient orbital overlap. The greater extension of the d orbitals of the metal ions of the 3rd transition element row additionally favors π-back-bonding, for Os in comparison to Ru. This arises because the lanthanide contraction is more important for the s and p orbitals than it is for the d orbitals.[60]

A consequence of the stronger π-back-bonding in Os(II) is that increased electron density is placed in the π^* orbitals of the N-heterocycles. The expected weakening of the bonds within the heterocycle manifests itself in the enhanced susceptibilities of the N-heterocycles to reductive hydrogenation in the presence of Zn(Hg) and protons.[11] The greatly enhanced basicities of the uncoordinated nitrogens of coordinated diazenes of Os(II) in comparison to the case of Ru(II) is another clear indication of enhanced π-back-bonding.[11] Such effects are also evident in the pK_a values of protonated M(III) diazene complexes. While the pK_a values of protonated diazene complexes have not been measured as yet, preliminary experiments using visible absorption spectra show that the Os(III) complexes are more readily protonated than their Ru(III) analogues.

As discussed previously,[11] the position of the charge-transfer bands (for the different ligands) in the visible region of the Os(III) complexes is consistent with their assignment to MLCT bands. These transitions are at lower energies than those for their Ru(III) analogues, which is consistent with Os(III) t_2 orbitals being closer in energy to the ligand π^* orbitals than to the Ru(III) t_2 orbitals.

The Os(III) complexes also exhibit electronic transitions in the near-IR region[11,39,50] (Table III). These arise due to the effects of spin–orbit coupling on the ground state and are observed to be much more intense when a π-acid ligand replaces a saturated one.[24] The splitting of the electronic states may be arrived at by adding spin–orbit coupling to the splitting of the states by π-back-bonding and by the C_{2v} symmetry, or by the effects of C_{2v} symmetry on the spin–orbit states.[39] It is evident that charge transfer is mixed into the transitions arising from spin–orbit coupling, thus accounting for the increased intensities of these transitions in comparison to those where π-bonding is absent. Observed are a comparatively strong band ($\epsilon \sim 50$–$100\ M^{-1}\ cm^{-1}$) at ~2100 nm and a second band in the vicinity of 1700–1800 nm, both of which are strongly vibronically coupled to M–L and intraligand vibrational modes.[39] The detailed analysis of these transitions is currently the topic of a separate study in which MCD and single-crystal polarized spectroscopy are applied to isotopically normal and deuteriated samples.[39,61] The weaker features observed in the region of 1100–1200 nm have been shown to be N–H vibronic bands of the spin–orbit transitions.[61] They are present in all Os(III) ammine complexes and, therefore, might also be expected to occur to Ru(III). Since the spin–orbit coupling constant of Ru^{3+} is $\sim 1000\ cm^{-1}$, the electronic transitions due to spin–orbit coupling are expected to occur at $\sim 1500\ cm^{-1}$, and hence, these N–H vibronic false origins would be expected at $\sim 4500\ cm^{-1}$. Indeed, such transitions have recently been observed in this region for Ru(III) and have been distinguished from N–H vibrational combination bands by the use of MCD spectroscopy. The results of this study will be reported in detail elsewhere.[62]

Although the splitting of the MLCT transitions by $\sim 5000\ cm^{-1}$ has also been attributed[11] to spin–orbit coupling in Os(III), this assignment is faulty. The MLCT spectrum $((5d)^5(\pi^*)^0 \rightarrow (5d)^4(\pi^*)^1)$ would reveal the splitting in Os(IV) rather than in Os(III), and it is therefore necessary to consider the effects of spin–orbit coupling on Os(IV) for a meaningful analysis. Also, the delocalization of an electron onto the ligand will affect the spin–orbit coupling constant. It is, therefore, likely to be accidental that the splitting of the MLCT states is similar to the splitting due to the spin–orbit coupling of Os(III).

For the M(II) complexes, the splitting of the energies of the t_2 orbitals by π-back-bonding is considerably greater than that for the M(III) complexes. The net result is well-separated MLCT transitions that dominate the visible region of the spectra, giving rise to intensely colored solutions. No spin–orbit splitting of the ground state occurs for the d^6 electronic configuration. Therefore, the transitions due to spin–orbit coupling that are present for M(III) complexes are absent for M(II) ions. However, spin–orbit

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(60) The lanthanide contraction arises from poor shielding of the nuclear charge by the electrons in the 4f subshell, because of the diffuse distribution of these electrons. Since the 6s and 5p subshells are not well shielded by the 4f electrons, the higher nuclear charge that they feel causes them to contract toward the nucleus so that their spatial distributions are similar to those of the 5s and 4p electrons, respectively, of their congeners. On the other hand, the 5d orbitals are more diffuse than either the 6s or 5p orbitals, and hence they are better shielded by the 4f orbitals than is the case for the 6s and 5p orbitals. The net result is that the lanthanide contraction is much less important for the 5d orbitals only. Thus, the lanthanide contraction manifests itself to a greater degree in σ-bonding involving sp^3d^2-hybridized orbitals than it odes in π-bonding involving the 5d orbitals. This point does not appear to have been considered in arguments that discuss the relative effects of π-bonding down a group.

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coupling does affect the $t_2^5(\pi^*)^1$ charge-transfer states, and hence, the MLCT transitions are also split by spin–orbit coupling contributions, although such splitting has not been distinguished in the present studies. The *cis*-$[Os(NH_3)_4(N\text{-heterocycle})_2]^{2+}$ complexes exhibit splittings of the MLCT transitions similar to those observed for ruthenium analogues due to the C_{2v} symmetry of the complexes.[63]

Conclusions

The preparative methods described make possible high-yielding syntheses of a large variety of N-heterocyclic complexes. The pentaammine(N-heterocycle)metal(III) and -metal(II) ions are of interest for a variety of reasons, including the syntheses of binuclear ions,[2,3,8-10,24,39,64] the study of π-back-bonding effects, intramolecular electron transfer,[65-67] SERS spectra for complexes absorbed onto Ag electrodes,[13-15] electron-transfer reactions, and various spectroscopic studies.[39,61,62] The results of further studies in these areas will be reported subsequently.

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Registry No. $[Rh(NH_3)_5(pz)](CF_3SO_3)_3$, 115244-78-5; $[Os(NH_3)_5(pzH)]Cl_4$, 115244-79-6; $[Os(NH_3)_5(pzH)](CF_3SO_3)_4$, 115244-80-9; $[Os(NH_3)_5(pz)](CF_3SO_3)_3$, 83781-35-5; $[Os(NH_3)_5(pz)]Cl_2$, 115244-81-0; $[Os(NH_3)_5(pz)]I_2$, 115244-82-1; $[Os(NH_3)_5(pz)](BF_4)_2$, 115244-83-2; $[Os(NH_3)_5(pzH)]Cl_3$, 115244-84-3; $[Ru(NH_3)_5(pz)]Cl_2$, 104626-96-2; $[Ru(NH_3)_5(pz)](BF_4)_2$, 41481-91-8; $[Co(NH_3)_5(pz)](CF_3SO_3)_3$, 73090-59-2; $[Rh(NH_3)_5(py)](CF_3SO_3)_3$, 115244-85-4; $[Rh(NH_3)_5(bpy)](CF_3SO_3)_3$, 115244-87-6; $[Co(NH_3)_5(bpy)](CF_3SO_3)_3$, 115244-88-7; $[Ru(NH_3)_5(py)]^{2+}$, 21360-09-8; $[Ru(NH_3)_5(py)]^{3+}$, 33291-25-7; $[Os(NH_3)_5(py)]^{2+}$, 70252-47-0; $[Os(NH_3)_5(py)]^{3+}$, 83781-38-8; $[Os(NH_3)_5(bpy)]Cl_3$, 115244-89-8; $[Os(NH_3)_5(4\text{-Phpy})]Cl_3$, 115244-90-1; *cis*-$[Os(NH_3)_4(4\text{-Phpy})_2]Cl_3$, 115244-91-2; $[Os(NH_3)_5(pzMe)]Cl_4$, 115244-92-3; $[Os(NH_3)_5(pzMe)](BF_4)_4$, 83781-37-7; $[Rh(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84254-57-9; $[Os(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 83781-30-0; $[Os(NH_3)_5(pz)]Cl_3$, 70252-37-8; $[Ru(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_2$, 84278-98-8; $[Ru(NH_3)_5(pz)](CF_3SO_3)_3$, 76584-38-8; $[Ru(NH_3)_5(pzH)](CF_3SO_3)_4$, 115244-93-4; $[Co(NH_3)_5(OSO_2CF_3)](CF_3SO_3)_3$, 115245-01-7; $[Os(NH_3)_5(bpy)]^{2+}$, 94352-56-4; $[Os(NH_3)_5(4\text{-Phpy})]^{2+}$, 115244-94-5; *cis*-$[Os(NH_3)_4(4\text{-Phpy})_2]^{2+}$, 115244-95-6; $[Os(NH_3)_5(pzMe)]^{3+}$, 115244-96-7; *cis*-$[Os(NH_3)_4(pz)_2]^{2+}$, 115244-97-8; *cis*-$[Os(NH_3)_4(pzH)(pz)]^{3+}$, 115244-98-9; $[Os(NH_3)_5(pm)]^{3+}$, 83781-39-9; $[Os(NH_3)_5(pd)]^{3+}$, 70252-41-4; $[Os(NH_3)_5(isna)]^{3+}$, 115244-99-0.

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Preparation, Structures, and Electrochemistry of Tetranuclear Sulfido Clusters $Cp_2M_2M'_2S_{2-4}$ (M = Mo, W; M′ = Fe, Co, Ni)

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The reaction of $R_2M_2(CO)_4$ (R = C_5H_5 (Cp), C_5H_4Me (Cp′); M = Mo, W) with $Fe_2(\mu\text{-}S_2)(CO)_6$ gives high yields of the cluster $R_2Mo_2Fe_2(CO)_8(\mu_3\text{-}S)_2$, which was isolated in two isomeric forms, planar (**3**) and butterfly (**4**), where M = Mo. For M = W, the analogous W butterfly was also isolated. The reactions of $[CpMo(\mu\text{-}S)(\mu\text{-}SH)]_2$ with $Fe_2(CO)_9$, $Co_2(CO)_8$, and $Ni(CO)_4$ gave the clusters $Cp_2Mo_2Fe_2(CO)_6(\mu_3\text{-}S)_4$ (**7**), $Cp_2Mo_2Co_2(CO)_4(\mu_3\text{-}S)_2(\mu_4\text{-}S)$ (**6**), and $Cp_2Mo_2Ni_2(CO)_2(\mu_3\text{-}S)_4$ (**9**). Crystallographic data are as follows. For **3b** (R = Cp′): $a = 9.219$ (2), $b = 6.899$ (2), $c = 10.441$ (2) Å; $\alpha = 73.34$ (2), $\beta = 113.68$ (2), $\gamma = 95.98$ (2)°; $V = 582.5$ (3) Å^3; $Z = 1$; space group $P\bar{1}$; $\rho_{calcd} = 2.14$ g/cm^3. For **6**: $a = 10.404$ (3), $b = 11.015$ (3), $c = 9.962$ (2) Å; $\alpha = 99.78$ (2), $\beta = 96.99$ (2), $\gamma = 66.11$ (2)°; $V = 1002.0$ (4) Å^3; $Z = 2$; space group $P\bar{1}$; $\rho_{calcd} = 2.24$ g/cm^3. For **9**: $a = 9.712$ (2), $b = 20.303$ (4), $c = 9.787$ (1) Å; $\beta = 98.30$ (1)°; $V = 1909.5$ (6) Å^3; $Z = 4$; space group $P2_1/n$; $\rho_{calcd} = 2.27$ g/cm^3. The Mo–Mo distance in these clusters (and in related compounds) shows a marked dependence on the number of S atoms that bridge the Mo–Mo bond. Mo–Mo distance (Å)/number of μ-S atoms: 3.0–3.1/1, 2.8–2.9/2, 2.65–2.8/3, 2.6/4. These sulfido clusters show complex electrochemical behavior that has been ascribed to structural reorganizations of the clusters upon reduction.

Introduction

Synthetic approaches to metal cluster formation and/or alteration are varied and difficult to systematize.[1] However, several major themes may be identified for clusters with sulfido ligands. Condensation reactions that increase cluster nuclearity are well documented[2-4] and may involve initial coordination of unsaturated metal fragments to filled lone-pair orbitals on the sulfido ligand.[5-7] In the course of these reactions, the S ligand expands its connectivity ($\mu_2 \rightarrow \mu_3 \rightarrow \mu_4$).

A second approach, exploited effectively by Vahrenkamp,[8] is the transmetalation reaction. This reaction leaves the cluster nuclearity unchanged while exchanging one metal for another. The sulfide ligands in these reactions may act as the cluster "glue"

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