remarkable. No low molecular weight complexes of the type $[Fe_xO_y(OH)_z]^{3x-2y-z}$ have been isolated from aqueous media. In strongly alkaline aqueous solutions, Fe(III) exists either as solid FeO(OH) or as mononuclear $[Fe(OH)_4]^-$.[10] Also, in aqueous ethanediol, glycerol, or sorbitol solutions, the formation of mononuclear complexes has been observed at concentrations of $OH^- \geq 1$ M and polynuclear species have only been found at much lower base concentration.[11]

Acknowledgment. We thank Prof. Walter Schneider for support and discussions.

Registry No. $Na_2Fe_6O(OCH_3)_{18}\cdot 6CH_3OH$, 139494-73-8.

Supplementary Material Available: Tables SI–SV, listing crystallographic data, anisotropic displacement parameters, positional parameters of the hydrogen atoms, and interatomic distances and bond angles (8 pages); a table of calculated and observed structure factors (9 pages). Ordering information is given on any current masthead page.

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A Novel and Generalized Approach to the Synthesis of ML_3^{n+} [M = Ru(II), Rh(III); L = 2,2′-Bipyridine, 1,10-Phenanthroline, 2-(Arylazo)pyridine; *n* = 2, 3]

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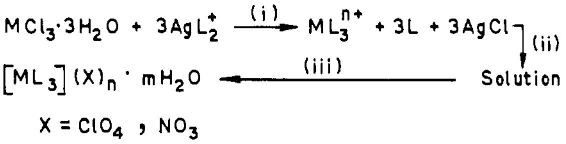
Received April 24, 1991

Introduction

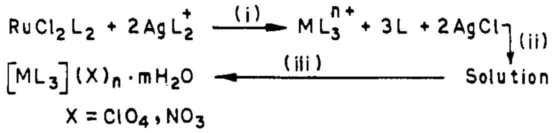
The chemistry of tris(2,2′-bipyridine)ruthenium(II) and -rhodium(III) complexes and complexes of related ligands has had an extensive literature[1-5] in recent years. The reason for this is primarily the relevance of this chemistry to photophysical, photochemical, and redox phenomena. But until now, no simple and general synthetic route has been available for the synthesis of such compounds. For example, the tris complex of 2,2′-bipyridine (L^1) is commonly synthesized[6] by fusion of MCl_3 with the ligand at a very high temperature, whereas the syntheses of the tris complexes of 1,10-phenanthroline[7] (L^2) and 2-(*m*-tolylazo)pyridine[8] (L^3) involve several steps which need extra purification at every stage to eliminate contaminated products. The standard reported synthetic routes are not only lengthy but also cumbersome, and in most of the cases the routes are inefficient. Therefore, there is an obvious need to develop new and direct procedures, of general application, for the synthesis of the important title compounds. In the present report, we describe high-yield, single-pot, and general synthetic routes to ML_3^{n+} from either hydrated MCl_3 or MCl_2L_2 [M = Ru(II), Rh(III); L = L^1–L^3] and the silver bis complex of the corresponding ligand.

Scheme I[a]



[a] Key: (i) MeOH, heat; (ii) filtration; (iii) aqueous solution of $NaClO_4$ or $NaNO_3$.

Scheme II[a]



[a] Key: (i) MeOH, heat; (ii) filtration; (iii) aqueous solution of $NaClO_4$ or $NaNO_3$.

Results and Discussion

The synthetic reactions are shown in Schemes I and II. In Scheme I, we describe the one-pot facile synthetic route to ML_3^{n+} from hydrated MCl_3 using AgL_2^+[9-11] as a synthon. The primary reaction involving hydrated MCl_3 and AgL_2^+ is carried out in boiling methanol in a 1:3 proportion to yield directly ML_3^{n+}, excess L, and insoluble AgCl. The cationic complex, ML_3^{n+}, has been isolated as either its perchlorate hydrate or its nitrate hydrate salt from solution.[12] Recrystallization, either from water or from a methanol–water mixture, yields a highly crystalline product. In the case of ruthenium, the yield lies in the range 65–70% whereas the yield of $[Rh(L^1)_3](ClO_4)_3\cdot H_2O$ is 55%. The direct synthesis of ML_3^{n+} from $MCl_3\cdot 3H_2O$, as evidenced by Scheme I, requires complete substitution of 3 mol of Cl^- by 3 mol of L. Thus, it was logically anticipated that the interaction of hydrated MCl_3 with $[AgL_2]^+$ in a 1:3 proportion might lead directly to the desired product. Accordingly, in line with the synthetic strategy, the reactions stated in the scheme were undertaken; they proceeded smoothly to yield $[ML_3](X)_n\cdot mH_2O$ [M = Ru(II), Rh(III); L = L^1–L^3; X = ClO_4, NO_3; *n* = 1, 3; *m* = 1, 2, 6] in a high yield.[13] In the case of ruthenium, it is believed that the reduction of ruthenium(III) to ruthenium(II) is accomplished[14] by the reducing

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(12) Excess L can be recovered from the reaction mixture (see Experimental Section).

(13) In the case of L^2, the reaction is relatively slow and the yields are also low. This is probably due to lesser solubility of $[Ag(L^2)_2]^+$ complexes in methanol. The reaction of hydrated $RhCl_3$ and $[Ag(L^3)_2]^+$, instead of yielding a tris complex, yields a mixture of compounds. Indications are strong that the reaction directly produces a Rh(I) bis-chelated compound as the major product. Isolation and characterization of the product are underway.

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solvent. In the reactions stated above, the silver complex, $[AgL_2]^+$, not only acts as a source of Ag^+—required for a facile halide displacement—but also supplies the required amount of the ligand for the formation of the tris complex. It is to be noted here that this class of metal-exchange reaction is most extensively used for the synthesis[15] of organo–element compounds. To the best of our knowledge, this route has not been explored for the synthesis of coordination compounds containing polypyridyl ligands. The success of this method lies in the facts that $[AgL_2]^+$ complexes are not very stable in solution and Ag^+ has a very high affinity for Cl^- to form insoluble AgCl, which can easily be removed from the reaction mixture.

The ruthenium(II) tris complexes are orange whereas $[Rh(L^1)_3]^{3+}$ is white. All of them are obtained in a highly crystalline state. The compounds are formulated by elemental analyses. The presence of water of crystallization has been assessed on the basis of IR data. The molar conductances of the ruthenium compounds lie in the range 170–200 Ω^{-1} cm^2 M^{-1} in methanol, suggesting a 1:2 type electrolytic nature,[16] but for the rhodium complex, $[Rh(L^1)_3](ClO_4)_3\cdot H_2O$, the value of Λ_M was 300 Ω^{-1} cm^2 M^{-1}, suggesting[16] a 1:3 electrolytic nature. Selected spectral data for the compounds, summarized in Experimental Section, agree well with the reported data.[2b,8,17,18] Thus, the results suggest that the compounds are the same as those described earlier.

We now consider the reactions described in Scheme II. The reaction of $RuCl_2L_2$ and $[AgL_2]^+$ in boiling methanol occurs[19] even at a much faster rate compared to the reaction described in Scheme I. The yields are almost quantitative (ca. 90%). It may be noted here that the optimum ratio of the reagents required for the above reaction (MCl_2L_2:$[AgL_2]^+$) is 1:2, as expected. We find that this route (Scheme II) has been particularly useful in synthesizing the mixed-ligand[8,14,20] tris complexes. For example, $RuCl_2(L^1)_2$ reacts smoothly with $[Ag(L^3)_2]^+$ in a 1:2 proportion to yield cationic $[Ru(L^3)(L^1)_2]^{2+}$, whereas the standard procedure for the mixed-ligand tris complex involves boiling the reaction mixture for a much longer period.[14,20]

Conclusion

In conclusion, it may be stated that the synthetic routes developed by us for the synthesis of tris-chelated complexes of ruthenium(II) and rhodium(III) seem to be a general ones for polypyridine and related ligand systems and the strategy used can be regarded as a paradigm for the synthesis of similar types of compounds. The reactions are quite fast and experimentally more facile than any other reported procedure. Moreover, in all cases, recrystallization alone produces compounds of high purity, which is very important for their use as photocatalysts. The application of our method to the synthesis of other M–L complexes is underway.

Experimental Section

Materials. The salts $RuCl_3\cdot 3H_2O$ and $RhCl_3\cdot 3H_2O$ were obtained from Arora Matthey, Calcutta, and used without further purification. The silver complexes $[AgL_2]X$ (X = ClO_4, NO_3) were synthesized as before.[9-11] Dichloro bis-chelated complexes, $RuCl_2L_2$, were prepared[14,21,22] by published procedures.

Physical Measurements. Elemental analyses were carried out on a Heraeus elemental analyzer, CHN-O-RAPID. Infrared spectra were obtained on KBr disks (4000–600 cm^{-1}) with a Perkin-Elmer IR-297 spectrophotometer. Solution electronic spectra were recorded on a Hitachi 330 spectrophotometer. Solution electrical conductivity measurements were performed on an Elico CM 82T conductivity bridge with a solute concentration of ca. 10^{-3} M.

Preparations. Caution! Perchlorate salts of metal complexes are potentially explosive. Adequate care should be taken in the handling of such complexes.

(i) Synthesis of $[ML_3]X_n\cdot mH_2O$ [M = Ru(II), L = L^1–L^3; X = ClO_4, NO_3; n = 2; m = 1, 2, 6] from $MCl_3\cdot 3H_2O$. The compounds were synthesized using the general procedure described below.

To a sample of $MCl_3\cdot 3H_2O$ (1 mmol) dissolved in 15 mL of methanol was added a solution of $[AgL_2]X$ (3 mmol) in 15 mL of methanol. The mixture was heated to reflux for 30 min. It was cooled and filtered through a G-4 sintered-glass funnel to remove insoluble products. The filtrate was concentrated to 10 mL, and to it was added 1 mL of an aqueous saturated solution of $NaClO_4$ or $NaNO_3$. The orange precipitate thus formed was filtered out and washed thoroughly with diethyl ether. The filtrate and the washings were collected to recover excess L obtained from the reaction mixture. Recrystallization of the precipitate from either water or a 9:1 water–methanol mixture yielded the crystalline compound.

The light brown filtrate and the washings obtained above were concentrated and extracted with benzene. The benzene layer on evaporation yielded free L. The yields and analytical, spectral, and solution molar conductance data of the complexes are given below.

$[Ru(L^1)_3](ClO_4)_2\cdot H_2O$: yield = 70%. Anal. Calcd for $C_{30}H_{26}N_6O_9Cl_2Ru$: C, 45.80; H, 3.30; N, 10.68. Found: C, 46.01; H, 3.20; N, 10.74. λ_{max}(MLCT, CH_3CN) = 454 nm (ϵ 14 400 M^{-1} cm^{-1}); Λ_M(MeOH) = 175 Ω^{-1} cm^2 M^{-1}.

$[Ru(L^1)_3](NO_3)_2\cdot 6H_2O$: yield = 65%. Anal. Calcd for $C_{30}H_{36}N_8O_{12}Ru$: C, 44.94; H, 4.49; N, 13.98. Found: C, 44.78; H, 4.40; N, 14.09. λ_{max}(MLCT, CH_3CN) = 454 nm (ϵ 14 350 M^{-1} cm^{-1}); Λ_M(MeOH) = 180 Ω^{-1} cm^2 M^{-1}.

$[Ru(L^2)_3](ClO_4)_2\cdot H_2O$: yield = 55%. Anal. Calcd for $C_{36}H_{26}N_6O_9Cl_2Ru$: C, 50.35; H, 3.03; N, 9.79. Found: C, 50.05; H, 2.90; N, 10.05. λ_{max}(MLCT, CH_3CN) = 445 nm (ϵ 18 300 M^{-1} cm^{-1}); Λ_M(MeOH) = 180 Ω^{-1} cm^2 M^{-1}.

$[Ru(L^2)_3](NO_3)_2\cdot 2H_2O$: yield = 55%. Anal. Calcd for $C_{36}H_{28}N_8O_8Ru$: C, 53.93; H, 3.49; N, 13.98. Found: C, 53.54; H, 3.40; N, 14.20. λ_{max}(MLCT, CH_3CN) = 445 nm (ϵ 19 050 M^{-1} cm^{-1}); Λ_M(MeOH) = 178 Ω^{-1} cm^2 M^{-1}.

$[Ru(L^3)_3](ClO_4)_2\cdot H_2O$: yield = 70%. Anal. Calcd for $C_{36}H_{35}N_9O_9Cl_2Ru$: C, 47.52; H, 3.85; N, 13.86. Found: C, 47.43; H, 3.50; N, 13.75. λ_{max}(MLCT, CH_3CN) = 492 nm (ϵ 9740 M^{-1} cm^{-1}); Λ_M(MeOH) = 175 Ω^{-1} cm^2 M^{-1}.

$[Rh(L^1)_3](ClO_4)_3\cdot H_2O$ was prepared similarly from $RhCl_3\cdot 3H_2O$ with the following modification. The methanolic solution of $[Rh(L^1)_3]^{3+}$, obtained above after removal of insoluble AgCl, was concentrated to 10 mL. On cooling, white crystals were deposited. These were filtered out, washed with diethyl ether, and finally dried in vacuo over P_4O_{10}; yield = 55%. Anal. Calcd for $C_{30}H_{26}N_6O_{13}Cl_3Rh$: C, 40.56; H, 2.93; N, 9.46. Found: C, 40.72; H, 2.80; N, 9.71. λ_{max}(CH_3OH) = 320, 307 nm (ϵ 30 250, 27 900 M^{-1} cm^{-1}); Λ_M(MeOH) = 300 Ω^{-1} cm^2 M^{-1}.

(ii) Synthesis of $[Ru(L)_3](X)_2\cdot mH_2O$ [L = L^1–L^3; X = ClO_4, NO_3; m = 1, 2, 6] from $RuCl_2L_2$. The reactions were performed by using the general procedure described below.

To a suspension of $RuCl_2L_2$ (1 mmol) in 15 mL of methanol was added a solution of $[AgL_2]X$ (2 mmol) in 15 mL of methanol. The mixture was heated to reflux for 15 min. The rest of the procedure was the same as that described in section i. The yields of the complexes were as follows: $[Ru(L^1)_3](ClO_4)_2\cdot H_2O$, 95%; $[Ru(L^1)_3](NO_3)_2\cdot 6H_2O$, 90%; $[Ru(L^2)_3](ClO_4)_2\cdot H_2O$, 75%; $[Ru(L^2)_3](NO_3)_2\cdot 2H_2O$, 75%; $[Ru(L^3)_3](ClO_4)_2\cdot H_2O$, 95%. Analytical, spectral, and solution molar conductance data of the complexes, thus obtained, exactly correspond to those of authentic samples.

(iii) Synthesis of Mixed-Ligand Tris Complexes from $RuCl_2L_2$ (L = L^1, L^3). The syntheses of this class of complexes were performed by using a general procedure. A representative example is described below.

$[Ru(L^1)_2(L^3)](ClO_4)_2\cdot H_2O$. To a suspension of $RuCl_2(L^1)_2$ (1 mmol) in 15 mL of methanol was added a solution of $[Ag(L^3)_2](ClO_4)$ (2 mmol) in 15 mL of methanol, and the mixture was heated to reflux for 15 min. The rest of the procedure is the same as that described in section ii.

Yields and analytical, spectral, and solution molar conductance data are given below.

$[Ru(L^1)_2(L^3)](ClO_4)_2\cdot H_2O$: yield = 85%. Anal. Calcd for $C_{32}H_{29}N_7O_9Cl_2Ru$: C, 46.42; H, 3.50; N, 11.85. Found: C, 46.65; H, 3.55; N, 12.02. λ_{max}(MLCT, CH_3CN) = 494 nm (ϵ 8500 M^{-1} cm^{-1}); Λ_M(MeOH) = 180 Ω^{-1} cm^2 M^{-1}.

$[Ru(L^1)(L^3)_2](ClO_4)_2\cdot H_2O$: yield = 85%. Anal. Calcd for $C_{34}H_{32}N_8O_9Cl_2Ru$: C, 47.00; H, 3.68; N, 12.90. Found: C, 47.29; H,

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3.72; N, 13.06. λ_{max}(MLCT, CH_3CN) = 512 nm (ϵ 10 250 M^{-1} cm^{-1}); Λ_M(MeOH) = 180 Ω^{-1} cm^2 M^{-1}.

Acknowledgment. Financial assistance received from the CSIR, New Delhi, is gratefully acknowledged.

Registry No. $[Ru(L^1)_3](ClO_4)_2$, 15635-95-7; $[Ru(L^1)_3](NO_3)_2$, 67062-86-6; $[Ru(L^2)_3](ClO_4)_2$, 14767-24-9; $[Ru(L^2)_3](NO_3)_2$, 14126-11-5; $[Ru(L^3)_3](ClO_4)_2$, 139242-61-8; $[Rh(L^1)_3](ClO_4)_3$, 28018-83-9; $[Ru(L^1)_2(L^3)](ClO_4)_2$, 77321-15-4; $[Ru(L^1)(L^3)_2](ClO_4)_2$, 139342-07-7; $[Ag(L^1)_2](ClO_4)$, 86783-78-0; $[Ag(L^2)_2](ClO_4)$, 58034-59-6; $[Ag(L^3)_2](ClO_4)$, 131972-14-0; $RuCl_2(L^1)_2$, 15746-57-3; $RuCl_2(L^2)_2$, 85718-09-8; $RuCl_2(L^3)_2$, 81600-80-8; $[Ag(L^1)_2](NO_3)$, 33971-93-6; $[Ag(L^2)_2](NO_3)$, 60939-16-4.

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High-Pressure Thermodynamic and Kinetic NMR Study of Nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium: The "Merry-Go-Round" Process

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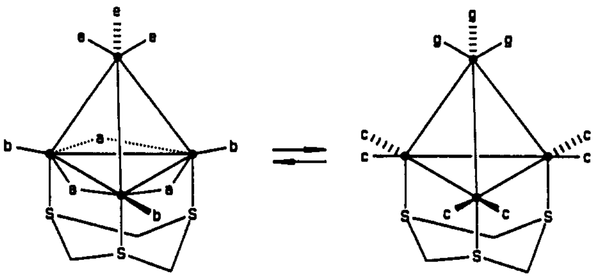
Received October 17, 1991

Introduction

Numerous studies have demonstrated the importance of including pressure as a kinetic parameter in the elucidation of inorganic reaction mechanisms.[1-4] These studies have led to a better understanding and a systematic classification of solvent exchange and ligand substitution reactions of octahedral complexes of transition metals. Data on the activation volumes of reactions involving organometallic compounds are, on the other hand, less numerous and generally deal with the intermolecular exchange of ligands. The only data on intramolecular processes involving carbonyl complexes are those concerning the isomerization of *ttt*-$RuCl_2(CO)_2(PR_3)_2$ and *trans*-$RuCl_2(CO)(PR_3)_3$.[5] In both cases a positive activation volume indicates a mechanism primarily dissociative in nature.

This paper deals with the quantitative characterization of a "merry-go-round" site exchange of CO's, commonly observed in carbonyl clusters but whose intermediate has never been observed.[6] In a previous paper,[7] we reported on the dynamic behavior of the cluster $[Ir_4(CO)_9(\mu_3\text{-}1,3,5\text{-trithiane})]$ (**1**) studied by IR and variable-temperature ^{13}C-NMR spectroscopy. Depending on the solvent used for crystallization, the title compound can be obtained in either the bridged **1b** (C_{3v} symmetry) or unbridged **1u** (T_d symmetry) forms whose crystal structures have been determined. An endothermic isomerization equilibrium **1b** ⇄ **1u** (eq 1) takes place in solution and involves an exchange mechanism on the NMR time scale which corresponds to a merry-go-round of the bridging and terminal CO's of the basal face.



1b **1u** (1)

This system is therefore the first example where the unbridged intermediate of a merry-go-round process is sufficiently stable to be observed. We have thus studied this system by variable-pressure ^{13}C-NMR spectroscopy to quantitatively characterize the CO site exchange process by the determination of the activation and reaction volumes. This system is particularly suitable for a variable-pressure study as there is no charge creation or annihilation on forming the transition state or the product. Therefore, in this case the electrostriction can be neglected. The resulting activation and reaction volumes reflect molecular volume changes and can be directly used for mechanistic studies. The reaction volume will subsequently be compared to the value obtained from crystallographic data.

Experimental Section

Chemicals and Solutions. Nonacarbonyl(μ_3-1,3,5-trithiane)tetrairidium, $[Ir_4(CO)_9(SCH_2)_3]$ (**1**), was synthesized as previously described.[7] The ^{13}C-enrichment of CO was ca. 50%. ^{13}C-NMR (THF, 168 K): **1b**, δ 233.3 (a), 183.5 (b), 160.2 (e); **1u**, δ 169.8 (c), 160.8 (g). The concentration of the solution used for the variable-pressure ^{13}C-NMR study was 0.04 m, where m are moles per kilogram of solvent, in tetrahydrofuran, THF.

NMR Measurements. Spectra at variable pressure were recorded using a Bruker AC-200 spectrometer working at 50.323 MHz for carbon-13. Measurements were made up to 200 MPa using a home-built high-pressure probe, designed for a Bruker wide-bore cryomagnet, which has been previously described.[8] The resonance frequency was tuned to 50.3 MHz using the same capacitive network as used for ^{17}O NMR at 9.4 T (54.2 MHz) adjusting the matching/tuning capacitors. The 90° pulse length was found to be 35 μs. A built-in platinum resistor allowed temperature measurements with an accuracy ±1 K after all corrections.[9] By the pumping of thermostated synthetic oil through the bomb, the temperature was stabilized to ±0.2 K. Spectra were obtained by using 4K data points resulting from 35 000–45 000 scans accumulated over a total spectral width of 11 kHz. To improve the signal to noise ratio, a zero-filling to 16K data points and an exponential filter (line-broadening) of 5 Hz were used. ^{13}C-NMR chemical shifts are referred to TMS and measured with respect to the solvent THF signal at 68.8 ppm.

Computation Method. The analysis of the equilibrium and rate constant data, using the required equations, was performed using ITERAT,[10] a nonlinear least-squares program fitting the values of the desired parameters. Reported errors are one standard deviation.

Results and Discussion

Equilibrium Constant. The equilibrium between the bridged **1b** and unbridged **1u** isomers was followed as a function of pressure at 274 K. At this temperature the two species are in fast exchange on the NMR time scale, and therefore, only an average chemical shift δ can be measured. The equilibrium constants, defined as $K = [\mathbf{1u}]/[\mathbf{1b}]$, were obtained from the population dependence of the ^{13}C chemical shift (see Figure 1). The shift variation is given by eq 2, where P_i is the population of site i and δ_i is the

$$\delta = P_a\delta_a + P_b\delta_b + P_c\delta_c \qquad (2)$$

$$P_a + P_b + P_c = 1 \qquad P_a = P_b$$

chemical shift of the corresponding site (see eq 1) obtained at low temperature in the slow exchange region. It is assumed that CO chemical shifts within both species (δ_a, δ_b, δ_c) do not vary significantly with pressure. This is substantiated by the observation that no pressure dependence was detected for the shifts of car-

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