that further, possibly interesting, redox chemistry is taking place in these systems, but we have not explored this chemistry further.

The relevance of these studies for catalysis lies in the observation that even nonoxidizing acids having conjugate bases which coordinate weakly with platinum (II) are capable of oxidizing platinum(0) to platinum (II), provided that the hydrogen ion activity of the medium is sufficiently high. At pH $\simeq 7$, **2** is unprotonated; between pH $\simeq 2$ and $H_0 \simeq -10$, **2** exists as $(Ph_3P)_3PtH^+$; at $H_0 < -10$, **2** reacts and generates dihydrogen. Although these estimates of ranges are very approximate, they provide evidence that redox chemistry involving metals and hydrogen ions in very strongly acidic media may be qualitatively different from that in weaker acids.

Experimental Section

General Methods. Reactions involving organometallic compounds were carried out by using standard inert atmosphere techniques.[9] THF was distilled from disodium benzophenone anion, and benzene from P_2O_5. Preparations of trifluoromethanesulfonic anhydride,[10] trifluoromethanesulfonic acid-*d*,[10] 100% sulfuric acid,[11] **1**,[12] and **2**[13] followed literature procedures. Silver triflate (99%, Ventron), triflic acid (3M Co.), and D_2SO_4 (Columbia Chemicals Co.) were used as purchased.

Hydrogen analyses were carried out by measuring evolved gas volumes on a vacuum line. Reaction was carried out on the line, and the volume of gas which was not condensed at −196 °C was taken to be that of dihydrogen. The working volume of the line was calibrated by using known quantities of dihydrogen generated by reaction of magnesium metal with an excess of 50% aqueous sulfuric acid. In certain instances these analyses were confirmed by measuring evolved gas volumes over water and identifying dihydrogen by mass spectroscopy.

Reactions of 1 with Acids: General Procedures. An argon-filled flask equipped with a side arm was charged with **1** (~ 0.3 mmol). Acid (~1 mL) was placed in the side arm, and the flask capped with a No-Air stopper. The apparatus was connected to a water-filled gas buret by a cannula, the acid added to the **1**, and the volume of evolved gas measured. The gas was identified as ethane by GLC. To identify the platinum-containing product from **1** and triflic acid, the excess triflic acid was removed under vacuum (0.005 torr). The residue was treated with 0.1 g of lithium chloride and 30 mL of acetone. The resulting mixture was allowed to stir for 0.5 h and then worked up by washing with water (2 × 15 mL) and recrystallization from ethylene chloride–heptane. The $(Ph_3P)_2PtCl_2$ had mp 310–312 °C dec (lit.[14] mp 310 °C dec) and IR and ^{31}P NMR spectra indistinguishable from authentic material.

Reactions of 2 with Acids: General Procedures. A flask containing the platinum compound (either as a solid or a solution, 0.6 mmol) and having the acid (1 mL) in a side arm was attached to the vacuum line and evacuated to 0.005 torr. The acid was added to 0 °C, and the volume of the evolved gas measured.

The reaction of **1** with acids was also carried out in benzene solution, and the ethane produced analyzed by GLC using cyclopentane as internal standard. Parallel analysis by expansion in a calibrated vacuum line yielded similar results. The IR spectrum of the gas (10-cm gas cell) was indistinguishable from authentic ethane. The isotopic composition of the mixture of deuterated ethanes produced on reaction of **1** with deuterated acids was analyzed by using fragmentation patterns from the literature.[15]

Reactions of 1 with THF–H_2SO_4 Mixtures. Colorless solutions of H_2SO_4 in THF were made by successive dilutions of 100% H_2SO_4 with THF at 0 °C. Aliquots (0.1 mL) of each solution were immediately mixed with benzene solutions of **1**. The quantity of ethane produced was measured relative to a propane internal GLC standard. The yield of ethane had reached its maximum value in 2 min and did not change in the following 4 h.

Preparation and Reaction of 5. In a dry, argon-filled 200-mL one-necked flask was placed *trans*-$(Ph_3P)_2PtHCl$ (0.427 g, 0.567 mmol) and 50 mL of methylene chloride. The solution was stirred vigorously by using a magnetic stirring bar, and silver triflate (0.15 g, 0.56 mmol, partially soluble) was added. After 2 h, the solution was separated from silver chloride (0.078 g, 0.55 mmol) by centrifugation. The solution was concentrated under vacuum, leaving an off-white solid. An attempt to obtain an NMR spectrum of this material in C_6D_6 was unsuccessful: **5** appeared to react with the benzene. A sample of **5** (0.319 g, 0.37 mmol) was treated with 1 mL of triflic acid: a quantity of gas (uncondensable at −196 °C and 0.005 torr) corresponding to a 37% yield of dihydrogen was released.

Registry No. **1**, 12120-15-9; **2**, 14221-02-4; **3**, 10199-34-5; **4**, 16841-99-9; **5**, 72926-39-7.

---

[9] Brown, H.C.; Cramer, G. W.; Levy, A. B.; Midland, M. M. "Organic Synthesis via Boranes"; Wiley: New York, 1975.

[10] Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 4069–79.

[11] Garst, J.; Walmsky, D.; Hewitt, C.; Richards, W.; Zabolotny, E. *J. Am. Chem. Soc.* **1964**, *86*, 409–12.

[12] Malatesta, L.; Cariello, C. *J. Chem. Soc.* **1958**, 2323–8.

[13] Cook, C. D.; Janhal, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 1464–7.

[14] Hartley, F. R. *J. Organomet. Chem.* **1970**, 119–37.

[15] Amenomiya, Y.; Pottie, R. F. *Can. J. Chem.* **1968**, *46*, 1735–9, 1741–6. Quinn, E. I.; Maohler, F. L. *J. Res. Natl. Bur. Stand., Sect. A* **1961**, *65*, 93–5.

Contribution from the Department of Chemistry,
The University of North Carolina,
Chapel Hill, North Carolina 27514

Cis–Trans Isomerism in (trpy)$(PPh_3)RuCl_2$. Comparisons between the Chemical and Physical Properties of a Cis–Trans Isomeric Pair

B. Patrick Sullivan,* Jeffrey M. Calvert, and Thomas J. Meyer

Received August 30, 1979

Although cis–trans isomerism in octahedral metal complexes is a common occurrence, there are relatively few studies defining the contrasting chemical and physical properties of a cis–trans pair, especially of the second- and third-row transition metals. We report here the synthesis of complexes derived from the planar, tridendate ligand 2,2′,2″-terpyridine (trpy) of the type $(trpy)Ru^{II}(L)Cl_2$ (L = PPh_3, $P(p\text{-}C_6H_4Me)_3$, pyridine). The syntheses are based on the synthetically useful precursor complex $(trpy)RuCl_3$. Also reported are some rather striking differences in the properties of the cis and trans isomers of the phosphine derivatives.

Experimental Section

Measurements. Ultraviolet, visible, and near-infrared spectra were recorded by using either a Cary Model 14 or Bausch and Lomb Model 210 spectrophotometer. Molar extinction coefficients were obtained from absorbance measurements on at least two different concentrations of complex. Proton and ^{31}P NMR spectra were recorded on a Varian 10-MHz Fourier transform spectrometer with Me_4Si as an internal standard for protons and 15% H_3PO_4 in D_2O as an external standard for phosphorus. Electrochemical measurements were made vs. the saturated sodium chloride calomel electrode (SSCE) at 23 ± 2 °C and are uncorrected for junction potential effects. The $E_{1/2}$ values for the reversible couples were calculated from half the difference between E_p values for the anodic and cathodic waves from cyclic voltammetry. $E_{1/2}$ values are used as formal reduction potentials, assuming differences in diffusion coefficients for oxidized and reduced species are negligible. The measurements were made by using a PAR Model 173 potentiostat for potential control with a PAR Model 175 universal programmer as a sweep generator for voltammetry measurements. Values for *n*, where *n* is the total number of electrons transferred per complex in an exhaustive oxidative electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. The reactions were considered complete after the current had fallen to 1% of the initial value. Values of *n* for the rereduction of the oxidized product were determined by the same criterion. All coulometry measurements were performed at platinum screen electrodes using MCB Spectrograde acetonitrile as the solvent and 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the electrolyte. Elemental analyses were

0020-1669/80/1319-1404$01.00/0

performed by Integral Microlabs, Raleigh, NC.

Materials. TBAH was prepared in accordance with previously published techniques, recrystallized from hot ethanol–water three times and vacuum dried at 70 °C for 10 h. "$RuCl_3 \cdot 3H_2O$" was purchased from Matthey Bishop. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical experiments and used without drying for spectral measurements. Deuterated solvents were purchased from Stohler Isotope Chemicals. Water was deionized and then distilled from alkaline permanganate. All solvents used for preparations were reagent grade and used without further purification. All other reagents were purchased from either Aldrich or Strem Chemical Co. and were used as received.

Preparation of Ru^{III}(trpy)Cl_3. To 125 mL of absolute ethanol in a 200-mL round-bottom flask was added 262 mg of "$RuCl_3 \cdot 3H_2O$" and 233 mg of 2,2′,2″-terpyridine. The mixture was heated at reflux for 3 h while vigorous magnetic stirring was maintained. After this time the reaction was cooled to room temperature, and the fine brown powder which had appeared was filtered from the reddish yellow solution. The product was washed with 3 × 30-mL portions of absolute ethanol followed by 3 × 30-mL portions of Et_2O and air-dried; yield 440 mg (88%).

Reactions of Ru^{III}(trpy)Cl_3 with Ligands (L). Preparation of *trans*-Ru^{II}(trpy)(L)Cl_2. To 30 mL of $CHCl_3$ was added 110 mg (0.25 mmol) of Ru^{III}(trpy)Cl_3 followed by a two- to tenfold excess of the desired ligand. One milliliter of Et_3N was then added and the mixture was heated at reflux for 1.5 h. Upon cooling of the mixture, a small crop of violet crystals could generally be directly filtered from the dark blue to violet solution. To the filtrate was added 30 mL of absolute ethanol, and the solution was reduced to a small volume (~20 mL) on a rotary evaporator. The dark violet crystalline solid which had appeared was filtered from a light, yellow-brown solution. Both crops of crystalline products were dissolved in a minimum volume of warm 1:1 $CHCl_3$/EtOH, filtered by gravity, and then crystallized by slow evaporation using a rotary evaporator. A typical yield of crystalline product for *trans*-Ru(trpy)(PPh_3)Cl_2 was 121 mg (72%). The products were vacuum dried at room temperature for 3 days since they appeared to retain considerable amounts of solvent in the solid state.

Conversion of *trans*- to *cis*-Ru(trpy)(L)Cl_2 (L = PPh_3, P(*p*-tolyl)$_3$). A solution containing 50 mL of deoxygenated 1,2-dichloroethane and 45 mg of *trans*-Ru(trpy)(PPh_3)Cl_2 was heated at reflux for 10 h under a blanket of N_2. The solvent was removed on a rotary evaporator, and the solid which remained was recrystallized as described above from 1:1 $CHCl_3$/EtOH. A near quantitative yield of the pink to red cis isomer was obtained. The cis P(*p*-tolyl)$_3$ derivative was prepared in the same manner except that the period of reflux was ca. 7 h.

Preparation of *cis*-Ru(trpy)(PPh_3)Cl_2 from Ru(PPh_3)$_3$$Cl_2$. The direct reaction between trpy (120 mg) and Ru(PPh_3)$_3$$Cl_2$ (480 mg) in 50 mL of N_2-deaerated benzene heated at reflux for 1 h gave the crystalline cis isomer in virtually quantitative yields (330 mg, 96%). The complex was filtered directly, washed with benzene and hexane, and dried under vacuum at room temperature for 3 days.

Reactions of *cis*- and *trans*-Ru(trpy)(PPh_3)Cl_2 with CO. An 80-mg sample of either *cis*- or *trans*-Ru(trpy)(PPh_3)Cl_2 was added to ca. 70 mL of 1,2-dichloroethane in a two-necked, 100-mL round-bottom flask. One neck of the flask was fitted with a serum cap through which a needle that was connected to a CO gas line was inserted; the other neck was fitted with a reflux condenser. The CO gas pressure was adjusted so that a steady stream of gas bubbles broke the quiescent solvent surface. [Note: This step should be carried out in a well-ventilated hood!] The mixture was heated at reflux for 13 h in the case of *cis*-Ru(trpy)(PPh_3)Cl_2 and for 6 h in the case of *trans*-Ru(trpy)(PPh_3)Cl_2. After this period the solvent was removed on a rotary evaporator in a hood and the red to red-brown solid was recrystallized as indicated above from 1:1 $CHCl_3$/EtOH.

Reactions of *cis*- and *trans*-Ru(trpy)(PPh_3)Cl_2 with PPh_3. In a small Erlenmeyer flask were placed 50 mg of the phosphine complex and 105 mg of free PPh_3. To this was added 20 mL of acetone and 10 mL of EtOH, and the mixture was stirred at room temperature in the dark for 3 h. After this period no reaction had occurred for the trans isomer as judged by visible spectroscopy, but in the solution containing the cis complex, a yellow-brown, soluble product had appeared. The solvent from the latter reaction was removed, and the residue was dissolved in ca. 100 mL of H_2O, the solution was filtered, and solid NH_4PF_6 (~1 g) was added. The yellow-brown precipitate that formed was collected by suction filtration and air-dried. The dry solid was dissolved in a minimum of acetone and slowly dropped into ether. The flocculent precipitate thus produced was filtered and dried at the pump for 3 days. Yields obtained were in the range 85–90% on the basis of the initial amount of complex used.

Results and Discussion

The complex (trpy)$Ru^{III}Cl_3$ had been prepared previously[1] from the thioether mixed-ligand Ru(III), [(*i*-C_3H_7)-SC_6H_5]$_2$(CH_3OH)$Ru^{III}Cl_3$,[2] by a simple displacement reaction. As shown here the direct stoichiometric reaction between "$RuCl_3 \cdot 3H_2O$" and trpy at gentle reflux in ethanol provides a route to the complex by a more convenient, high yield (88%) reaction.

In the presence of the reductant Et_3N and added neutral ligands, Ru(trpy)Cl_3 is converted into the violet crystalline complexes (trpy)(L)$RuCl_2$,[3] as shown, for example, in eq 1

$$\text{(trpy)Ru}^{\text{III}}\text{Cl}_3 + \text{PPh}_3 \xrightarrow[\text{MeOH/Et}_3\text{N}]{\Delta} \underset{\mathbf{1}}{\text{(trpy)(PPh}_3\text{)Ru}^{\text{II}}\text{Cl}_2} \quad (1)$$

using PPh_3 as the example. The products arising from the oxidation of triethylamine were not established. The violet compound, **1**, is converted slowly but virtually quantitatively (96%) in 1,2-dichloroethane at reflux (or with white light) under argon to a pink isomer, **2**, which is thermally stable under these conditions for at least 24 h. The pink isomer could also be prepared in high yield by the direct reaction between 2,2′,2″-terpyridine and Ru(PPh_3)$_3$$Cl_2$ as shown in eq 2. The latter reaction is a convenient, high-yield (96%) route to large amounts of **2**.

$$\text{trpy} + \text{Ru(PPh}_3\text{)}_3\text{Cl}_2 \xrightarrow[\text{benzene}]{\Delta} \underset{\mathbf{2}}{\text{(trpy)(PPh}_3\text{)RuCl}_2} + 2\text{PPh}_3 \quad (2)$$

The lability of chloride ion in the pink isomer is strikingly greater than in the violet isomer. The latter in acetone–ethanol at room temperature is inert in the presence of a tenfold excess of PPh_3 while the pink isomer undergoes a rapid, quantitative reaction under the same conditions to give the yellow-brown ion [(trpy)(PPh_3)$_2$RuCl]$^+$.

The ^{31}P NMR spectrum of the bis(phosphine) complex in CH_3CN solution[4] has one resonance characteristic of coordinated PPh_3 at +20.1 (vs. PO_4^{3-}) ppm which is consistent with a trans stereochemistry. On consideration of the mild conditions under which *trans*-[(trpy)(PPh_3)$_2$RuCl]$^+$ was prepared, its precursor, the pink isomer of (trpy)(PPh_3)$RuCl_2$ (**2**), is almost surely *cis*-(trpy)(PPh_3)$RuCl_2$. If this assignment is correct, the violet isomer (**1**) is then *trans*-(trpy)(PPh_3)$RuCl_2$. Both isomers and some of their substitutional chemistry are illustrated in Figure 1 where it should be remembered that the 2,2′,2″-terpyridine ligand is constrained to be a planar ligand.

The implied difference in substitutional reactivity between *cis*- and *trans*-(trpy)(PPh_3)$RuCl_2$ is a graphic example of the

---

(1) B. P. Sullivan, T. J. Meyer, and T. R. Weaver, Abstracts, 174th National Meeting of the Americal Chemical Society, Aug 28–Sept 3, 1977, Chicago, IL; B. P. Sullivan, T. R. Weaver, J. M. Calvert, and T. J. Meyer, manuscript in preparation.

(2) J. Chatt, G. J. Leigh, and A. P. Storace, *J. Chem. Soc. A*, 1380 (1971).

(3) All compounds reported here yielded satisfactory elemental analyses, e.g.: Calcd for (trpy)(PPh_3)$RuCl_2$: C, 59.36; N, 6.32; H, 4.08; Cl, 10.64. Found for the trans complex: C, 59.12; N, 6.07, H, 3.90; Cl, 10.55. Found for the cis complex: C, 59.04; N, 5.93; H, 3.76; Cl, 10.46. Calcd for [(trpy)(PPh_3)$_2$RuCl](PF_6): C, 58.93; N, 4.04; H, 4.33. Found: C, 58.77; N, 4.30; H, 4.14. Calcd for (trpy)(CO)$RuCl_2$: C, 44.39; N, 9.74; H, 2.56. Found for the trans complex: C, 44.39; N, 9.48; H, 2.43. Found for the cis complex: C, 44.28; N, 9.47; H, 2.33.

(4) All ^{31}P NMR spectral shifts are referenced to 15% H_3PO_4 in D_2O; the external lock signal was D_2O; downfield shifts are positive in sign from the reference.

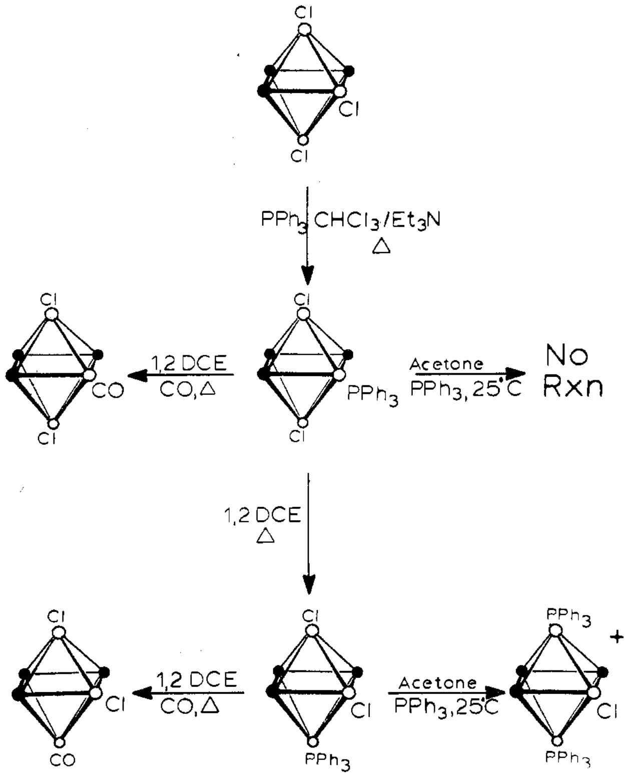

Figure 1. Synthesis of *trans*-$Ru^{II}(trpy)PPh_3Cl_2$ from $Ru^{III}(trpy)Cl_3$ and the characteristic chemistry of *cis*- and *trans*-$Ru^{II}(trpy)PPh_3Cl_2$. The filled circles represent the bound N atoms of the 2,2′,2″-terpyridyl ligand which is constrained to be planar. 1,2-DCE is 1,2-dichloroethane.

Table I. Spectral and Reduction Potential Values

complex	$E_{1/2}$ ($i_{p,a} - i_{p,c}$)[a]	λ_{max},[b] nm	ϵ_{max}, mol^{-1} L^{-1}
cis-$(trpy)(CO)RuCl_2$	1.05 (80)[c]	419[c]	3.38×10^3
trans-$(trpy)(CO)RuCl_2$	0.94 (80)[c]	461[c]	1.71×10^3
cis-$(trpy)(PPh_3)RuCl_2$	0.58 (65)[c]	530[c]	5.15×10^3
trans-$(trpy)(PPh_3)RuCl_2$	0.46 (70)[c]	552[c]	4.29×10^3
cis-(trpy)[*p*-$P(C_6H_4$-$CH_3)_3]RuCl_2$	0.44 (80)[c]	538[c]	5.18×10^3
trans-(trpy)[*p*-$P(C_6H_4$-$CH_3)_3]RuCl_2$	0.29 (70)[c]	558[c]	4.30×10^3
[*trans*-$(trpy)(PPh_3)_2$-$RuCl](PF_6)_2$	0.89 (70)[d]	473[d]	3.65×10^3
trans-$(trpy)(py)RuCl_2$	0.43 (75)[d]	561[c]	4.12×10^3
$[(NH_3)_5Ru(py)](PF_6)_2$	0.38 (65)[d]		
cis-$(bpy)_2RuCl_2$	0.32 (65)[d]		

[a] As reduction potentials for the appropriate Ru(III)/Ru(II) couples vs. the saturated sodium chloride calomel electrode with tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte at a Pt bead working electrode. $E_{1/2}$ values were calculated as the mean of anodic and cathodic peak potentials from cyclic voltammetry waves. The values in parentheses are peak potential differences, ΔE_p, at a scan rate of 200 mV/s: $\Delta E_p = E_{p,oxidation} - E_{p,reduction}$. [b] Value for the most intense peak in the $\pi^*(trpy) \leftarrow Ru(d\pi)$ manifold. [c] CH_2Cl_2 solution. [d] CH_3CN solution.

trans effect of phosphorus ligands bound to Ru(II). A similar trans-labilizing effect has been observed by Franco and Taube[5] in phosphite–ammine complexes of Ru(II).

Both *cis*- and *trans*-$(trpy)(PPh_3)RuCl_2$ are reactive toward CO in 1,2-dichloroethane at reflux to give the cis and trans carbonyl complexes, *cis*- and *trans*-$(trpy)(CO)RuCl_2$, respectively (Figure 1). The retention of stereochemistry in the two CO-containing products is supported by ν(CO) values in Nujol mulls. They occur at 1957 cm^{-1} for the isomer assigned as *cis*-$(trpy)(CO)RuCl_2$ and at 1943 cm^{-1} for the trans isomer. The assignments are reasonable since in the cis isomer there is an electron-donating Cl^- group trans to CO and in the trans isomer a pyridyl group trans to CO (Figure 1).[6] $E_{1/2}$ values as measured by cyclic voltammetry for the two Ru(III)/Ru(II) couples also support the structural assignments made here as discussed below.

As indicated by the difference in color between *cis*- and *trans*-$(trpy)(PPh_3)RuCl_2$, the electronic properties in the Ru(II) state are considerably different for the two isomers. Shown in Table I are relevant spectroscopic and electrochemical data for the two isomers of $(trpy)(L)RuCl_2$ and for related complexes of Ru(II) which are included for purposes of comparison. The lowest energy absorption band in the complexes is actually a manifold of transitions which is predominantly trpy(π*) ← Ru(dπ) in character. For the cis isomers, the λ_{max} value for the low-energy absorption band is ca. 20 nm higher in energy than for the corresponding trans isomers. The shift to higher energy and the more positive Ru(III)/Ru(II) potentials for the cis isomers are both consistent with stabilization of the dπ levels in the cis compared to the trans case. The presence of the π*(trpy) levels then allows the trpy groups to function as "spectator" ligands for the electronic interactions between the Ru(II) ion and the remaining ligands in the inner coordination sphere. The bpy ligands in complexes of the type $(bpy)_2RuL_2^{2+}$ and $(bpy)_2Ru(L)Cl^+$ have been found to serve in the same role, where L can be a wide variety of ligands such as NH_3, pyridine, phosphine, isocyanide, or olefin.[7]

$E_{1/2}$ values for the reversible Ru(III)–Ru(II) couples were determined by cyclic voltammetry in either CH_3CN or CH_2Cl_2 solution with TBAH as supporting electrolyte (Table I). The values show that Ru(III)/Ru(II) potentials for the cis isomers are ca. 130 mV more positive than for the trans isomers, an effect which also has been observed for cis–trans pairs of the type $(NH_3)_4RuL_2^{n+1/n}$ [where L = Cl ($n = 0$) and L = pyridine, pyrazine ($n = 2$)].[8] From all these examples, the $E_{1/2}$ values appear to be a convenient method for distinguishing between cis and trans isomeric pairs in octahedral d^6 metal complexes.

That the trans isomers have more total available electron density at Ru(II) is further supported by the ^{31}P NMR shifts for *cis*- and *trans*-(trpy)[P(*p*-$C_6H_4CH_3)_3]RuCl_2$ in CH_2Cl_2 solution.[4] The trans isomer has a single resonance at +41.6 ppm whereas the cis isomer has a resonance which is shifted considerably upfield (+27.3 ppm) and can simply be interpreted as greater shielding of the phosphorus atom due to enhanced donation to the πd(P) orbitals in the cis isomer relative to the trans isomer.

Finally it should be noted that *trans*-$(trpy)(py)RuCl_2$ has a reversible reduction potential that is very near to that found for $(NH_3)_5Ru(py)^{2+}$ (0.44 vs. 0.38 V) under the same conditions. The comparison is an interesting one to make in that it suggests that the *trans*-$(trpy)RuCl_2^+$ group may be a mimic for the $Ru(NH_3)_5^{2+}$ group with regard to the availability of dπ electron density for π-acceptor ligands. This fact may in turn foreshadow an even more extensive chemical similarity with the $Ru(NH_3)_5^{2+}$ group perhaps toward such ligands as nitrosyl, acetylenes,[7] or even dinitrogen.[9]

---

(5) D. W. Franco and H. Taube, *Inorg. Chem.*, **17**, 571 (1978).

(6) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", 2nd ed., Wiley, New York, 1967.

(7) B. P. Sullivan, J. A. Baumann, T. J. Meyer, D. J. Salmon, H. Lehmann, and A. Ludi, *J. Am. Chem. Soc.*, **99**, 7368 (1977); W. L. Bowden, W. F. Little, D. J. Salmon, and T. J. Meyer, *ibid.*, **97**, 6897 (1975); J. A. Connor, T. J. Meyer, and B. P. Sullivan, *Inorg. Chem.*, **18**, 1388 (1979); B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *ibid.*, **17**, 3334 (1978).

(8) H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, **11**, 1460 (1972); T. Matsubara and P. C. Ford, *ibid.*, **15**, 1107 (1976).

(9) H. Taube, *Surv. Prog. Chem.*, **6** (1973).

Acknowledgments are made to the Department of Energy under Grant No. ER-78-S-05-6034 for support of this research.

Registry No. *cis*-(trpy)(CO)$RuCl_2$, 72983-34-7; *trans*-(trpy)(CO)$RuCl_2$, 72905-33-0; *cis*-(trpy)(PPh_3)$RuCl_2$, 72905-34-1; *trans*-(trpy)(PPh_3)$RuCl_2$, 72937-76-9; *cis*-(trpy)[*p*-$P(C_6H_4CH_3)_3$]$RuCl_2$, 72905-25-0; *trans*-(trpy)[*p*-$P(C_6H_4CH_3)_3$]$RuCl_2$, 72937-75-8; [*trans*-(trpy)$(PPh_3)_2$RuCl](PF_6), 72905-27-2; *trans*-(trpy)(py)$RuCl_2$, 72905-28-3; [$(NH_3)_5$Ru(py)]$(PF_6)_2$, 72905-29-4; *cis*-$(bpy)_2RuCl_2$, 19542-80-4; Ru^{III}(trpy)Cl_3, 72905-30-7; $Ru(PPh_3)_3Cl_2$, 15529-49-4.

Contribution from the Istituto di Chimica Analitica,
Università di Torino, 10125 Torino, Italy

Micellar Effect on Electron Transfer.[1] 3. Kinetics of Substituted 1,10-Phenanthroline Complexes of Iron(III) with Iron(II) in the Presence of Sodium Dodecyl Sulfate

Ezio Pelizzetti* and Edmondo Pramauro

Received June 28, 1979

In a previous paper,[1a] the effect of the micelle-forming surfactant sodium dodecyl sulfate (SDS) on the electron-transfer rate between tris(2,2′-bipyridine)ruthenium(III), $Ru(bpy)_3^{3+}$, and negatively charged complexes like $Mo(CN)_8^{4-}$ and $Fe(CN)_6^{4-}$ was reported: a decrease of 2–3 orders of magnitude was observed.

The study of the reaction between $Ru(bpy)_3^{3+}$ and Fe^{2+}(aq) in the presence of SDS provided only an estimate of a lower limit of the reaction rate, since its half-time is much shorter than the mixing time of our stopped-flow apparatus.

In the present note, the effect of SDS on the electron-transfer reactions between substituted 1,10-phenanthroline complexes of iron(III), FeL_3^{3+}, and Fe^{2+}(aq) according to

$$FeL_3^{3+} + Fe^{2+}(aq) \rightarrow FeL_3^{2+} + Fe^{3+}(aq) \qquad (1)$$

is reported. Since these reactions exhibit a smaller driving force,[2] the catalytic effect of micelles can be followed over a large concentration range of surfactant.

Experimental Section

Reagents. The following tris(1,10-phenanthroline)iron(II) derivatives were prepared and recrystallized as perchlorate according to the procedure described in the literature:[2] 5,6-dimethyl- (5,6-Me_2phen), 4,7-dimethyl- (4,7-Me_2phen), and 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen). The corresponding FeL_3^{3+} were prepared by electrooxidation or PbO_2 oxidation.[2] $FeSO_4$ solutions were standardized by oxidimetric titration. Sodium dodecyl sulfate (Merck) was recrystallized several times. All other reagents were of the highest purity available. Doubly distilled water was used.

Procedure. The kinetic runs were followed at the wavelength of maximum absorption of the FeL_3^{2+} complexes,[2] by means of a Durrum–Gibson stopped-flow spectrophotometer. [FeL_3^{3+}] was in the range (3–5) × 10^{-6} M, while [Fe^{2+}(aq)] was from 6 × 10^{-6} M to 1 × 10^{-4} M, depending on the half-time of the reactions. SDS was added to both solutions before mixing. The rate constants were evaluated according to first- or second-order rate laws. Also the method proposed by Corbett gave satisfactory results.[3] Each value reported in Tables I–IV (supplementary material) was averaged over four to eight separate measurements. The data were analyzed by using a weighted least-squares method, and weights were assigned on the basis of the standard deviation of each point. All measurements were carried out at 25.0 °C.

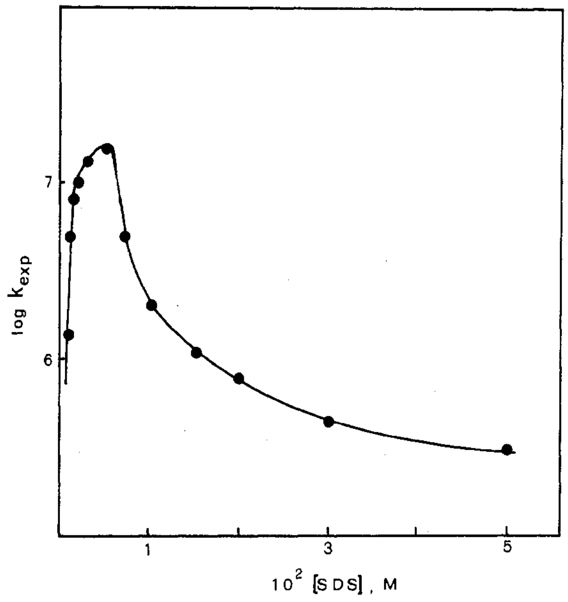

Figure 1. Plot of the observed second-order rate constants as a function of SDS concentration, for the reaction of $Fe(Me_4phen)_3^{3+}$ with Fe^{2+}(aq) ([H_2SO_4] = 0.005 M, 25.0 °C).

Results and Discussion

Kinetics. The linear dependence of the pseudo-first-order rate constants on [Fe^{2+}(aq)], as well as the linearity of the second-order plots, both in absence of surfactant and over the presently studied SDS concentration range, supports that for reaction 1 the following rate law holds:

$$-d[FeL_3^{3+}]/dt = k_{exptl}[FeL_3^{3+}][Fe^{2+}(aq)] \qquad (2)$$

In the absence of surfactant ([H_2SO_4] = 0.02 M, [$NaNO_3$] = 0.04 M) the following rate constants were obtained: Fe(5,6-$Me_2phen)_3^{3+}$, $k = (6.0 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$; Fe(4,7-$Me_2phen)_3^{3+}$, $k = (9.0 \pm 0.4) \times 10^3\ M^{-1}\ s^{-1}$; $Fe(Me_4phen)_3^{3+}$, $k = (3.3 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$. These values are comparable with the results in 0.5 M H_2SO_4, previously reported.[2] For $Fe(Me_4phen)_3^{3+}$ the rate constant measured in [H_2SO_4] = 0.005 M was $(4.1 \pm 0.2) \times 10^3\ M^{-1}\ s^{-1}$.

General Features of Micellar Catalysis. Since both reactants can interact with anionic micelles, Berezin's approach[4] can be adopted in the analysis of the present results. According to this model

$$k_{exptl} = \frac{(k_M P_A P_B + k_M' P_A + k_M'' P_B) C\bar{V} + k_w(1 - C\bar{V})}{(1 + K_A C)(1 + K_B C)} \qquad (3)$$

where P_i and K_i are the partition coefficient and the binding constant, respectively, and $\bar{V}$ is the partial volume of the surfactant monomer; these three parameters are interconnected by the equation $K_i = (P_i - 1)\bar{V}$. The subscripts M, w, A, and B refer to the micellar and aqueous phases and to the reactants (in the present report A refers to FeL_3^{3+} and B to Fe^{2+}(aq)). k_M and k_w are the rate constants for the reaction when both reactants are in micellar and aqueous phases, respectively; k_M' refers to the reaction between compound A in the micellar phase with B in aqueous phase and k_M'' to the reverse situation; C is the stoichiometric surfactant concentration minus the critical micellar concentration (cmc). A relevant extension of the Berezin approach has been recently given by Romsted,[5]

---

[1] (a) Part 1: Pelizzetti, E.; Pramauro, E. *Inorg. Chem.* **1979**, *18*, 882. (b) Part 2: *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 996.

[2] Ford-Smith, M. H.; Sutin, N. *J. Am. Chem. Soc.* **1961**, *83*, 1830.

[3] Corbett, J. F. *J. Chem. Educ.* **1972**, *49*, 663.

[4] Berezin, I. V.; Martinek, K.; Yatsimirskii, A. K. *Russ. Chem. Rev.* (*Engl. Transl.*) **1973**, *42*, 787.

0020-1669/80/1319-1407$01.00/0