

Comparisons of the Physical and Chemical Properties of Isomeric Pairs.¹ 2. Photochemical, Thermal, and Electrochemical Cis-Trans Isomerizations of M(Ph₂PCH₂PPh₂)₂Cl₂ (M = Ru^{II}, Os^{II})

B. PATRICK SULLIVAN* and THOMAS J. MEYER

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The complexes *cis*- and *trans*-Ru^{II}(dppm)₂Cl₂ (dppm = Ph₂PCH₂PPh₂) have been found to undergo isomerization reactions induced by light, heat, or oxidation to Ru(III). The conversion *trans* → *cis* occurs thermally while *cis* → *trans* occurs photochemically apparently by irradiation of the lowest lying d-d transition. Upon chemical or electrochemical oxidation of the *cis* isomer, the *trans* isomer of Ru(III) forms quantitatively. The *cis* isomer was found to be substitution labile in solvents that can act as ligands while the *trans* isomer is inert. Comparisons of the three-pathway isomerization of Ru(dppm)₂Cl₂ are also made with its osmium analogue and with the carbonyl complex (N,N'-Me₂Im)₂W(CO)₄, studied earlier by Rieke et al.^{7a}

Thermal isomerizations of transition-metal complexes are frequently observed to occur for octahedral d⁶ or square-planar d⁸ systems.² Physical, chemical, and theoretical studies of a few of these reactions have led to an embryonic understanding of rearrangement mechanisms,³ of electronic structural differences between isomers,⁴ and of the contrasting chemical reactivity of *cis*-*trans* isomeric pairs.^{1,5} In a more practical sense, information concerning isomerization barriers and relative reactivities of isomeric pairs is essential for rational synthetic design.

Although interconversions between isomers are commonly achieved thermally, cases are known of photochemical interconversions⁶ and of isomerization induced by oxidation or reduction.⁷ In the latter case the thermodynamically favored isomeric distribution is dependent upon the oxidation state of the metal.

In this paper we describe an interesting and relatively rare case where the *cis*-*trans* isomers of the complex Ru^{II}-(dppm)₂Cl₂ (dppm is bis(diphenylphosphino)methane, Ph₂PCH₂PPh₂) are interconverted by all three types of processes: photochemical, thermal, and redox reactions. We also compare the properties of the ruthenium system with those of the more inert osmium analogue, Os^{II}(dppm)₂Cl₂.

Experimental Section

Ultraviolet and visible spectral data were recorded with use of either Cary Model 14 or Bausch and Lomb Model 210 spectrophotometers. Photochemical conversions were performed with either a GE 500-W sunlamp or a 1000-W Hanovia mercury lamp with a focused output to a Bausch and Lomb monochromator. 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 with the assumption that 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 the total area under current vs. time curves for the complete reaction were measured. 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 with MCB Spectrograde acetonitrile as the solvent and 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) or 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. Elemental analyses were performed by Integral Microlabs, Raleigh, NC.

Materials. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium hexafluorophosphate (TBAH) were prepared by published procedures⁸ and then recrystallized from EtOH/H₂O and dried under vacuum for 10 h at 80 °C. "RuCl₃·3H₂O" and (N-H₄)₂OsCl₆ were purchased from Matthey Bishop, Inc., and used as received. Acetonitrile (MCB Spectrograde) was dried over Davison 4-Å molecular sieves for electrochemical experiments and used without drying for spectral measurements. 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 *trans*-Ru(dppm)₂Cl₂. This complex was prepared according to the method of Chatt and Hayter.⁹ Recrystallization from an ethanol-dichloromethane solution using the solvent gradient afforded yellow to yellow-orange crystals.

Preparation of *cis*-Ru(dppm)₂Cl₂. Isomerization of *trans*-Ru(dppm)₂Cl₂. Initial samples of *cis*-Ru(dppm)₂Cl₂ were prepared by the method of Chatt and Hayter. The thermal isomerization reaction of *trans*-Ru(dppm)₂Cl₂, however, was the method used in all subsequent preparations. A deaerated solution (30 mL) of 0.50 g of *trans*-Ru(dppm)₂Cl₂ in 1,2-dichloroethane was heated at reflux for 10 h under a N₂ blanket. After cooling to room temperature, the solution was poured into 150 mL of pentane. The solid so obtained was collected by suction filtration; yield 461 mg (92%). Precipitation from CH₂Cl₂ into pentane was used for further purification.

Preparation of *trans*-Os(dppm)₂Cl₂. A more convenient method of preparation of this complex than the method of Chatt and Hayter is the following: 0.25 g of tetra-*n*-butylammonium hexachlorosmate(IV) (prepared by metathesis of (NH₄)₂OsCl₆ and TBACl in aqueous solution) was heated at reflux with 0.25 g of dppm in

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- (2) See, for example: (a) Krause, R. A.; Krause, K. *Inorg. Chem.* **1980**, *19*, 2600. (b) Ofele, K.; Heberhold, M. Z. *Naturforsch., B: Anorg. Chem., Org. Chem.* **1973**, *28*, 306. (c) Barnard, C. F.; Daniels, J. A.; Jeffery, J.; Mawby, R. J. J. *Chem. Soc., Dalton Trans.* **1976**, 753. (d) Bottomley, F.; Lin, I. J. B.; Mukaida, M.; Patterson, J. L. *Ibid.* **1980**, 487.
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- (8) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.
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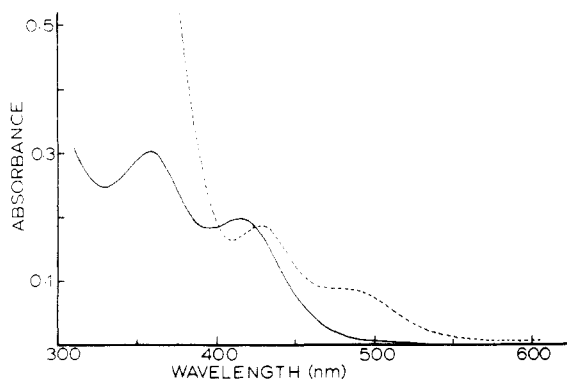


Figure 1. Absorption spectra of *cis*-Ru(dppm)₂Cl₂ (—) and *trans*-Ru(dppm)₂Cl₂ (---) in the near UV-visible region measured in CH₂Cl₂ solution in a cell of 1-cm path length.

deaerated MeOCH₂CH₂OH (10 mL) for 1.5 h. The reaction was seen to go through a dark blue stage (which is (dppm)₂Os^{III}Cl₂⁺). After the solution cooled to room temperature, the light yellow crystalline product was washed with pentane and air-dried; yield 0.17 g (57%).

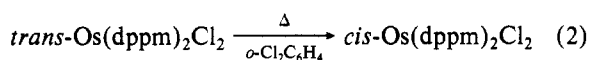
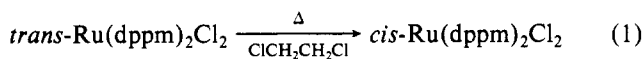
Preparation of *cis*-Os(dppm)₂Cl₂. Isomerization of *trans*-Os(dppm)₂Cl₂. To 10 mL of deaerated *o*-dichlorobenzene was added 50 mg of *trans*-Os(dppm)₂Cl₂. This solution was heated at reflux under a blanket of N₂ for 1.5 h. After this time the solution was cooled to room temperature and 70 mL of pentane was added; the pale yellow solid that formed was filtered and then washed with pentane; yield 41 mg (92%).

Preparation of *cis*-Ru(dppm)₂(CH₃CN)Cl(PF₆). To a 1:1 (20 mL) mixture of CH₃CN-H₂O was added 50 mg of *cis*-Ru(dppm)₂Cl₂. The mixture was stirred at room temperature for 30 min and then filtered by gravity with use of a fluted filter. To the filtrate was added 5 mL of saturated NH₄PF₆ solution followed by 25 mL of H₂O. The mixture was spun to ca. half-volume on a rotary evaporator. The pale yellow solid was filtered, washed with H₂O followed by Et₂O, and air-dried; yield 43 mg (75%). Anal. Calcd: C, 57.12; N, 1.28; H, 4.31. Found: C, 56.35; N, 1.37; H, 4.50.

Preparation of *cis*-[Os(dppm)₂(CH₃CN)Cl](PF₆). The procedure was essentially that for the Ru analogue except that the reaction mixture was stirred at room temperature for 1.5 h; yield 50 mg (88%). Anal. Calcd: C, 52.89; N, 1.19; H, 3.89. Found: C, 51.97; N, 1.13; H, 3.96.

Results and Discussion

Thermal and Photochemical Interconversions. The complexes *cis*- and *trans*-M(dppm)₂Cl₂ (M = Os^{II}, Ru^{II}) have been prepared previously by Chatt and Hayter⁹ using separate synthetic routes. We find that the *trans* isomers can be easily and quantitatively converted into the *cis* isomers by thermolysis in halocarbon solvents (eq 1 and 2). As shown in eq 2, the



osmium complex requires more drastic thermal conditions than its ruthenium analogue, i.e., heating at reflux in 1,2-dichlorobenzene (bp 180.5 °C) as compared to heating in 1,2-dichloroethane (bp 83.3 °C). The reactions are notable because they constitute single, quantitative synthetic procedures for preparation of the *cis* isomers that are considerably easier than the original syntheses.

Photolysis of *cis*-Ru(dppm)₂Cl₂ in CH₂Cl₂ solution with white light or with the 436-nm line of a high-pressure Xe arc lamp with a monochromator resulted in a quantitative conversion to *trans*-Ru(dppm)₂Cl₂ as judged by cyclic voltammetry or electronic spectral changes. Figure 1 shows the visible electronic spectra of *cis*- and *trans*-Ru(dppm)₂Cl₂. The two rather low-intensity transitions that are observed have been assigned by Klassen and Crosby to d-d transitions (t₂ → e_g).¹⁰

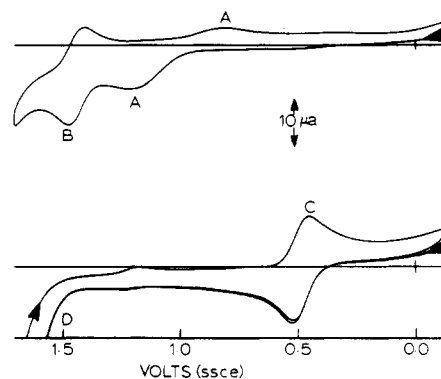


Figure 2. First-scan cyclic voltammogram of *cis*-Ru(dppm)₂Cl₂ (top) and *trans*-Ru(dppm)₂Cl₂ (bottom) recorded in 2:1 CH₂Cl₂-CH₃CN at a Pt-bead working electrode with 0.1 M TBAH as supporting electrolyte (vs. SSCE). Lettered electrochemical processes are referred to in the text.

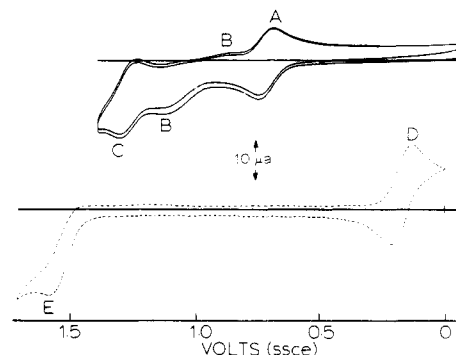
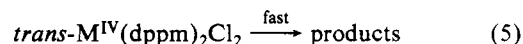
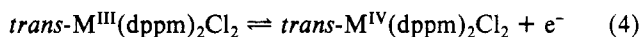
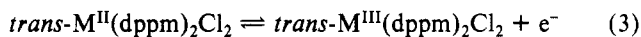


Figure 3. First-scan cyclic voltammogram of *cis*-Os(dppm)₂Cl₂ (top) and *trans*-Os(dppm)₂Cl₂ (bottom) taken in 2:1 CH₂Cl₂-CH₃CN at a Pt-bead electrode with 0.1 M TBAH as supporting electrolyte (vs. SSCE). Scan rate is 200 mv/s. Lettered electrochemical processes are referred to in the text.

It is important to note that if the spectral assignments are correct, photoisomerization is induced by direct photolysis into a d-d excited state.¹⁰ Under the same conditions no photochemical isomerization is observed for *cis*-Os(dppm)₂Cl₂.

Oxidative Isomerization of *cis*-Ru(dppm)₂Cl₂. Both *trans*-Ru(dppm)₂Cl₂ and its osmium analogue exhibit two one-electron oxidation waves in CH₂Cl₂ solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as supporting electrolyte. As shown in Figures 2 (see features C and D) and 3 (see features D and E), for Ru and Os, respectively, the first oxidation wave is reversible but the second is chemically irreversible (eq 3-5). Controlled-potential coulometry



demonstrates the first oxidation to be a reversible one-electron process for both ruthenium and osmium. Chemical oxidation with O₂ in the presence of H⁺PF₆⁻ in CH₂Cl₂ can be used to generate the green Ru(III) and the blue Os(III) cations. That the second oxidation is a one-electron process is inferred from the near-identity of the anodic currents for this oxidation wave and the Ru^{III}/Ru^{II} wave. Compare, for example, features D and E in Figure 3.

(10) Klassen, D. M.; Crosby, G. A. *J. Mol. Spectrosc.* **1968**, *25*, 398. In this paper it is demonstrated that the lowest emitting state of Ru(dppm)₂Cl₂ is d-d in nature and it is reasonable to assume that the isomerization reaction is a radiationless path that competes with emission.

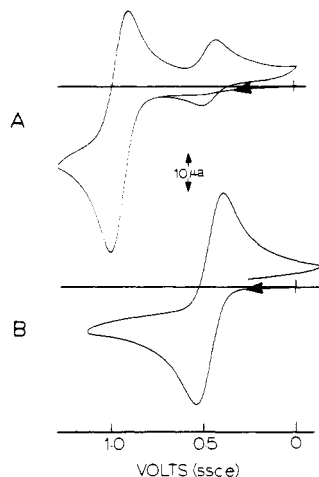


Figure 4. (A) First-scan cyclic voltammogram of *cis*-Ru(dppm)₂Cl₂. (B) First-scan cyclic voltammogram of *trans*-Ru(dppm)₂Cl₂. Both were taken in CH₂Cl₂ solution with a Pt-bead electrode and 0.1 M TBAH as supporting electrolyte (vs. SSCE).

Table I. Electrochemical Properties of $M^{\text{II}}(\text{dppm})_2\text{Cl}_2$ and Related Complexes

complex	$E_{1/2}^{\text{III/II}}$ ($M^{\text{III}}/M^{\text{II}}$), V	$i_{p,a}/i_{p,c}$ ^a	$E_{1/2}^{\text{IV/III}}$ or $E_p^{\text{IV/III}}$ (M ^{IV} /M ^{III})
<i>trans</i> -Ru(dppm) ₂ Cl ₂ ^b	0.42	0.97	1.68 ^d
<i>cis</i> -Ru(dppm) ₂ Cl ₂ ^b	0.79	0.81	>1.9 ^d
<i>cis</i> -Ru(bpy) ₂ Cl ₂ ^b	0.32	0.99	1.95
[<i>cis</i> -Ru(dppm) ₂ (CH ₃ CN)Cl]PF ₆ ^c	1.35	0.95	
<i>trans</i> -Os(dppm) ₂ Cl ₂ ^b	0.18	1.02	1.58 ^d
<i>cis</i> -Os(dppm) ₂ Cl ₂ ^b	0.64	1.01	>1.9 ^d
<i>cis</i> -Os(bpy) ₂ Cl ₂ ^b	-0.04	0.97	1.35
[<i>cis</i> -Os(dppm) ₂ (CH ₃ CN)Cl]PF ₆ ^c	+0.93	0.98	

^a Ratio of oxidizing to reducing peak currents from cyclic voltammetry for the $M^{\text{III}}/M^{\text{II}}$ couple. ^b Measured in CH₂Cl₂ solution at a Pt-bead working electrode with 0.1 M TBAH as supporting electrolyte vs. the saturated sodium chloride calomel electrode (SSCE). ^c Measured in CH₃CN solution at a Pt-bead electrode with 0.1 M TEAP as supporting electrolyte vs. SSCE. ^d Chemically irreversible oxidation. The potential cited is the peak potential for the irreversible oxidation.

The cyclic voltammogram of *cis*-Ru(dppm)₂Cl₂ in CH₂Cl₂-0.1 M TBAH is dramatically different from the *trans* isomer. The one-electron oxidation is seen (Figure 4A) to be followed by formation of a new, stable product, which is *trans*-Ru^{III}(dppm)₂Cl₂ as shown by comparison of $E_{1/2}$ values (Figure 4B). The results of a coulometry experiment demonstrated that one electron is consumed during the oxidative isomerization reaction, and the electronic spectrum of the oxidized solution showed a broad absorption band with $\lambda_{\text{max}} = 704 \text{ nm}$ (CH₂Cl₂) that is characteristic of *trans*-Ru^{III}(dppm)₂Cl₂⁺. The behavior of *cis*-Os(dppm)₂Cl₂ is different from the Ru analogue in that no isomerization occurs following oxidation by exhaustive electrolysis.

Comparisons between $E_{1/2}(M^{\text{III}}/M^{\text{II}})$ values for the *cis* isomers and for *cis*-M(bpy)₂Cl₂ (note Table I) show that the ligand dppm is considerably better at stabilizing the 2+ oxidation state of both metals than 2,2'-bipyridine (bpy). Exchange of a bpy group for a dppm chelate produces an anodic shift of 0.24 V in $E_{1/2}(M^{\text{III}}/M^{\text{II}})$ for Ru and 0.34 V for osmium. The enhanced anodic shift for Os(II) suggests greater metal to dppm back-bonding for Os(II) compared to that for Ru(II).

The differences in potentials between *cis* and *trans* isomeric pairs, $E_{1/2}(M^{\text{III}}/M^{\text{II}})^{\text{cis}} - E_{1/2}(M^{\text{III}}/M^{\text{II}})^{\text{trans}} = \Delta E'_{\text{iso}}$, is larger for Os (0.46 V) than for Ru (0.37 V). As will be discussed later this observation also supports increased back-bonding to

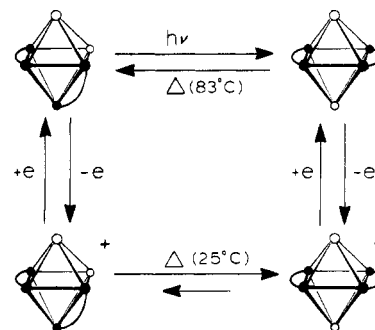
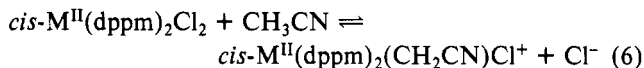


Figure 5. Scheme showing thermal, photochemical, and electrochemical interconversions in the *cis*-*trans* Ru^{II}(dppm)₂Cl₂/Ru^{III}(dppm)₂Cl₂⁺ system.

phosphorus for Os^{II} compared to that for Ru^{II}.

Relative Substitution Labilities of the *Cis* and *Trans* Isomers.

A cyclic voltammogram of *cis*-Ru(dppm)₂Cl₂ in 2:1 CH₂Cl₂-CH₃CN with 0.1 M TBAH as supporting electrolyte is shown at the top of Figure 2. In the cyclic voltammogram there is no wave attributable to the original complex; rather two electrochemical features appear, one characteristic of Cl⁻ ion in nonaqueous solvents (feature A in Figure 2) and the other a reversible one-electron oxidation (feature B), which corresponds to $E_{1/2}(\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}})$ for the complex Ru^{II}(dppm)₂(CH₃CN)Cl⁺. Thus on the time scale of dissolution of *cis*-Ru(dppm)₂Cl₂ in the solvent the substitution reaction shown in eq 6 has gone to completion.

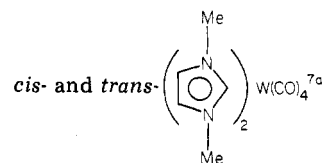


For the case of *cis*-Os^{II}(dppm)₂Cl₂ the same substitutional chemistry occurs; however, the rate is much slower. Thus, Figure 3 (top) shows the *cis* osmium complex in 2:1 CH₂Cl₂-CH₃CN with 0.1 M TBAH as supporting electrolyte, where after 30 min the original complex (feature A) can still be seen along with Cl⁻ (feature B) and the monoacetonitrile complex (feature C).

Preparation and isolation of either of the acetonitrile complexes can be achieved by allowing *cis*-M(dppm)₂Cl₂ to react in CH₃CN-H₂O solution, followed by metathesis of the released anion for PF₆⁻. Satisfactory elemental analyses were obtained for both new complexes (see Experimental Section).

The facile labilization of chloride ion in the *cis* Ru isomer provides another example of a dramatic kinetic trans effect in Ru^{II}-phosphine complexes.¹ Furthermore, the contrast in substitutional labilities between *cis*-Ru(dppm)₂Cl₂ and *cis*-Os(dppm)₂Cl₂ demonstrates the diminution in the trans effect going from the second- to the third-transition series, which is in accord with the general increase in substitution inertia for heavier transition metals down a congeneric series.

Comparison between Isomerization Reactions. The overall isomerization scheme for *cis*- and *trans*-Ru(dppm)₂Cl₂ involving photochemical, thermal, and electrochemical pathways is shown in Figure 5. The only other characterized example of a similar three-pathway isomerization scheme is that of



which differs from our example by exhibiting a thermodynamically stable, oxidized *cis* isomer.

The factors responsible for determining the thermodynamically preferred forms of the isomers are not entirely clear. However, a simple argument based on metal-ligand back-

bonding leads to the prediction of an electronic preference for *cis*-M(dppm)₂Cl₂. In idealized *D*_{4h} symmetry for the *trans* isomer the *t*₂ orbitals split into *e*_g(*xz*, *xy*) and *b*_{2g}(*xy*) and in the *C*₂ symmetry of the *cis* isomer, the *t*₂ orbitals become *a*₁(*yz*) and *a*₂(*xy*), *b*₂(*xz*). For the two isomers it is easily shown that the number of stabilizing *dπ* → *d*(P) interactions and destabilizing *dπ* ← *p*(Cl) interactions are the same. However, for the *cis* isomer there is an additional stabilization. For the *cis* isomer there are two axial Cl-M-P groupings in place of the Cl-M-Cl and P-M-P groupings of the *trans* isomer. The net effect leads to enhanced back-bonding with phosphorus through the common metal *d* orbital via a *pπ*(Cl) → *dπ*(Ru) → *dπ*(P) interaction as has been recognized for *d*⁸ square-planar complexes.¹¹

Upon oxidation to Ru^{III}(dppm)₂Cl₂⁺ the *trans* isomer becomes thermodynamically favored. This could arise if steric repulsion between ligands is important as has been suggested^{7c} for other isomerization reactions or if the *trans* cation, which has a formally doubly degenerate symmetrical ground state, undergoes a Jahn-Teller distortion. The latter effect, if it exists, would be small since no such static distortion has been observed for Ru(NH₃)₆³⁺.¹² It is interesting to note that

irradiation of the *d-d* manifold in *cis*-Ru^{II}(dppm)₂Cl₂, which labilizes metal-ligand bonds, has the effect of removing an electron from a *dπ* level, decreasing *π*-bonding stabilization. In a sense the excited state from which *cis* → *trans* photoisomerization occurs resembles the oxidized *cis* isomer and similar factors may govern the isomeric distributions in both the oxidative and the photoisomerization reaction.

Finally, isomerization reactions that exhibit all three pathways, thermal, photochemical, and electrochemical, may be a common feature of transition-metal chemistry, but this will only be known by systematic electrochemical investigations of *cis-trans* and *fac-mer* isomeric pairs, which exhibit thermal and photochemical isomerizations.

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Registry No. *trans*-Ru(dppm)₂Cl₂, 38800-82-7; *cis*-Ru(dppm)₂Cl₂, 79982-54-0; *cis*-Ru(bpy)₂Cl₂, 19542-80-4; *cis*-[Ru(dppm)₂(CH₃CN)Cl](PF₆), 79953-54-1; *trans*-Os(dppm)₂Cl₂, 79953-55-2; *cis*-Os(dppm)₂Cl₂, 79982-55-1; *cis*-Os(bpy)₂Cl₂, 79982-56-2; *cis*-[Os(dppm)₂(CH₃CN)Cl](PF₆), 79953-57-4; tetra-*n*-butylammonium hexachloroosmate(IV), 58590-70-8.

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Contribution from the Laboratoire de Spectroscopie Infrarouge, associé au CNRS (L.A. 124), University of Bordeaux I, 33405 Talence Cedex, France, and the University of Rouen, 76130 Mont Saint-Aignan, France

Spectroscopic Investigations of Complexes between Acetonitrile and Aluminum Trichloride. 1. Aluminum Chloride-Acetonitrile Solutions

M. DALIBART,*^{1a} J. DEROUAULT,^{1a} P. GRANGER,^{1b} and S. CHAPELLE^{1b}

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The AlCl₃-CH₃CN system has been investigated by infrared and Raman spectroscopy and by ³⁵Cl and ²⁷Al NMR spectrometry over the [CH₃CN]/[AlCl₃] molar ratio range 5.6-80. The system consists mainly of ionic complexes that share the same anion, AlCl₄⁻. Three octahedral cations have been characterized: Al(CH₃CN)₆³⁺, AlCl(CH₃CN)₅²⁺, and AlCl₂(CH₃CN)₄⁺. A new species, the Al(CH₃CN)₅³⁺ cation, was found in concentrated solutions. The identification of the cations was made on the basis of their individual ionic charge and their solvation number.

Introduction

Among the binary systems of aluminum halides in organic bases, AlCl₃-CH₃CN solutions have been extensively studied, but the chemical structure of the dissolved species is still unresolved. Previous studies suggest that different species are in equilibrium, which may be explained by the competition between Cl⁻ and CH₃CN ligands which leads to exchange processes.

Up to now, various techniques have been used to study these complexes: conductivity,^{2,3} polarography,⁴ ion exchange,⁵ infrared and Raman spectroscopy,⁶⁻⁸ and aluminum-27 NMR

spectrometry;⁷⁻¹³ ref 13, which appeared at the time of the writing of this paper, will be particularly commented on below. All the results of the above papers show that these solutions are mainly ionic, but if the AlCl₄⁻ anion is generally identified unambiguously, this is not the case for the cationic part. Furthermore, ref 13 suggests that a small amount of the neutral species AlCl₃·CH₃CN₂ is present.

Recent results obtained in our laboratories on solutions of AlBr₃ in CH₃CN¹⁴ encouraged us to reinvestigate AlCl₃ in

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