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

Comparisons of the Physical and Chemical Properties of Isomeric Pairs.[1] 2. Photochemical, Thermal, and Electrochemical Cis–Trans Isomerizations of $M(Ph_2PCH_2PPh_2)_2Cl_2$ ($M = Ru^{II}, Os^{II}$)

B. PATRICK SULLIVAN* and THOMAS J. MEYER

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The complexes *cis*- and *trans*-$Ru^{II}(dppm)_2Cl_2$ (dppm = $Ph_2PCH_2PPh_2$) 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 $Ru(dppm)_2Cl_2$ are also made with its osmium analogue and with the carbonyl complex $(N,N'\text{-}Me_2Im)_2W(CO)_4$, studied earlier by Rieke et al.[7a]

Thermal isomerizations of transition-metal complexes are frequently observed to occur for octahedral d^6 or square-planar d^8 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 interconversions[6] 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 $Ru^{II}(dppm)_2Cl_2$ (dppm is bis(diphenylphosphino)methane, $Ph_2PCH_2PPh_2$) 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, $Os^{II}(dppm)_2Cl_2$.

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 procedures[8] and then recrystallized from $EtOH/H_2O$ and dried under vacuum for 10 h at 80 °C. "$RuCl_3 \cdot 3H_2O$" and $(NH_4)_2OsCl_6$ 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*-$Ru(dppm)_2Cl_2$. 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*-$Ru(dppm)_2Cl_2$. Isomerization of *trans*-$Ru(dppm)_2Cl_2$. Initial samples of *cis*-$Ru(dppm)_2Cl_2$ were prepared by the method of Chatt and Hayter. The thermal isomerization reaction of *trans*-$Ru(dppm)_2Cl_2$, however, was the method used in all subsequent preparations. A deaerated solution (30 mL) of 0.50 g of *trans*-$Ru(dppm)_2Cl_2$ in 1,2-dichloroethane was heated at reflux for 10 h under a N_2 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 CH_2Cl_2 into pentane was used for further purification.

Preparation of *trans*-$Os(dppm)_2Cl_2$. 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 hexachloroosmate(IV) (prepared by metathesis of $(NH_4)_2OsCl_6$ and TBACl in aqueous solution) was heated at reflux with 0.25 g of dppm in

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(1) The first paper in the series was: Sullivan, B. P.; Calvert, J. M.; Meyer, T. J. *Inorg. Chem.* **1980**, *19*, 1404.

(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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(7) (a) Rieke, R. D.; Kojima, H. K.; Ofele, K. *J. Am. Chem. Soc.* **1976**, *98*, 6735. (b) Bond, A. M.; Colton, R.; Jackowski, J. J. *Inorg. Chem.* **1975**, *14*, 274. (c) Wimmer, F. L.; Snow, M. R.; Bond, A. M. *Ibid.* **1974**, *13*, 1617. (d) Rader, R. A.; McMillan, D. R. *Ibid.* **1979**, *18*, 545. (e) Bond, A. M.; Grabaric, B. S.; Grabaric, Z. *Ibid.* **1978**, *17*, 1003. (f) Bond, A. M.; Colton, R.; McDonald, M. E. *Ibid.* **1978**, *17*, 2842. (g) Bond, A. M.; Keene, F. R.; Rumble, N. W.; Searle, G. H.; Snow, M. R. *Ibid.* *17*, 2847.

(8) Sullivan, B. P.; Salmon, D. J.; Meyer, T. J. *Inorg. Chem.* **1978**, *17*, 3334.

(9) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.

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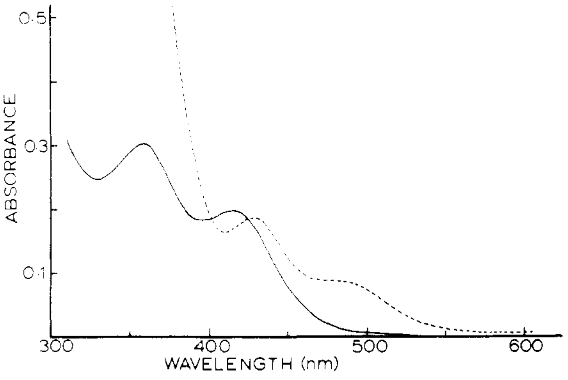

Figure 1. Absorption spectra of *cis*-Ru(dppm)$_2$Cl$_2$ (—) and *trans*-Ru(dppm)$_2$Cl$_2$ (---) in the near UV–visible region measured in CH$_2$Cl$_2$ solution in a cell of 1-cm path length.

deaerated MeOCH$_2$CH$_2$OH (10 mL) for 1.5 h. The reaction was seen to go through a dark blue stage (which is (dppm)$_2$Os^{III}Cl$_2^+$). 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)$_2$Cl$_2$. Isomerization of *trans*-Os(dppm)$_2$Cl$_2$. To 10 mL of deaerated *o*-dichlorobenzene was added 50 mg of *trans*-Os(dppm)$_2$Cl$_2$. This solution was heated at reflux under a blanket of N$_2$ 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)$_2$(CH$_3$CN)Cl(PF$_6$). To a 1:1 (20 mL) mixture of CH$_3$CN–H$_2$O was added 50 mg of *cis*-Ru(dppm)$_2$Cl$_2$. 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 NH$_4$PF$_6$ solution followed by 25 mL of H$_2$O. The mixture was spun to ca. half-volume on a rotary evaporator. The pale yellow solid was filtered, washed with H$_2$O followed by Et$_2$O, 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)$_2$(CH$_3$CN)Cl](PF$_6$). 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)$_2$Cl$_2$ (M = Os^{II}, Ru^{II}) have been prepared previously by Chatt and Hayter[9] 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

$$trans\text{-Ru(dppm)}_2\text{Cl}_2 \xrightarrow[\text{ClCH}_2\text{CH}_2\text{Cl}]{\Delta} cis\text{-Ru(dppm)}_2\text{Cl}_2 \quad (1)$$

$$trans\text{-Os(dppm)}_2\text{Cl}_2 \xrightarrow[o\text{-Cl}_2\text{C}_6\text{H}_4]{\Delta} cis\text{-Os(dppm)}_2\text{Cl}_2 \quad (2)$$

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)$_2$Cl$_2$ in CH$_2$Cl$_2$ 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)$_2$Cl$_2$ as judged by cyclic voltammetry or electronic spectral changes. Figure 1 shows the visible electronic spectra of *cis*- and *trans*-Ru(dppm)$_2$Cl$_2$. The two rather low-intensity transitions that are observed have been assigned by Klassen and Crosby to d–d transitions ($t_2 \rightarrow e$).[10]

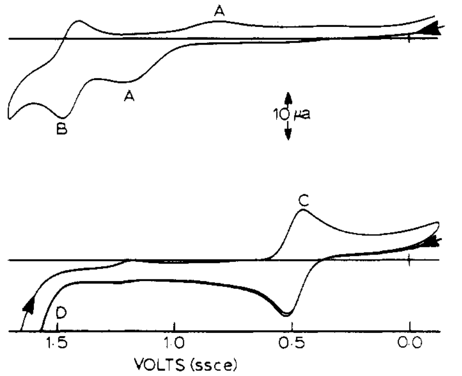

Figure 2. First-scan cyclic voltammogram of *cis*-Ru(dppm)$_2$Cl$_2$ (top) and *trans*-Ru(dppm)$_2$Cl$_2$ (bottom) recorded in 2:1 CH$_2$Cl$_2$–CH$_3$CN at a Pt-bead working electrode with 0.1 M TBAH as supporting electrolyte (vs. SSCE). Lettered electrochemical processes are referred to in the text.

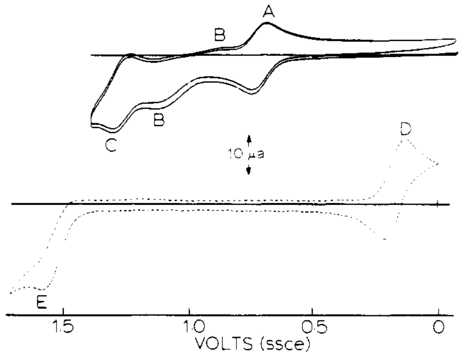

Figure 3. First-scan cyclic voltammogram of *cis*-Os(dppm)$_2$Cl$_2$ (top) and *trans*-Os(dppm)$_2$Cl$_2$ (bottom) taken in 2:1 CH$_2$Cl$_2$–CH$_3$CN at a Pt-bead electrode with 0.1 M TBAH as supporting electrolyte (vs. SSCE). Scan rate is 200 mv/s. Lettered electrochmemical processes are referred to 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)$_2$Cl$_2$.

Oxidative Isomerization of *cis*-Ru(dppm)$_2$Cl$_2$. Both *trans*-Ru(dppm)$_2$Cl$_2$ and its osmium analogue exhibit two one-electron oxidation waves in CH$_2$Cl$_2$ 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

$$trans\text{-M}^{II}\text{(dppm)}_2\text{Cl}_2 \rightleftharpoons trans\text{-M}^{III}\text{(dppm)}_2\text{Cl}_2 + e^- \quad (3)$$

$$trans\text{-M}^{III}\text{(dppm)}_2\text{Cl}_2 \rightleftharpoons trans\text{-M}^{IV}\text{(dppm)}_2\text{Cl}_2 + e^- \quad (4)$$

$$trans\text{-M}^{IV}\text{(dppm)}_2\text{Cl}_2 \xrightarrow{\text{fast}} \text{products} \quad (5)$$

demonstrates the first oxidation to be a reversible one-electron process for both ruthenium and osmium. Chemical oxidation with O$_2$ in the presence of H$^+$PF$_6^-$ in CH$_2$Cl$_2$ 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.

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(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)$_2$Cl$_2$ is d–d in nature and it is reasonable to assume that the isomerization reaction is a radiationless path that competes with emission.

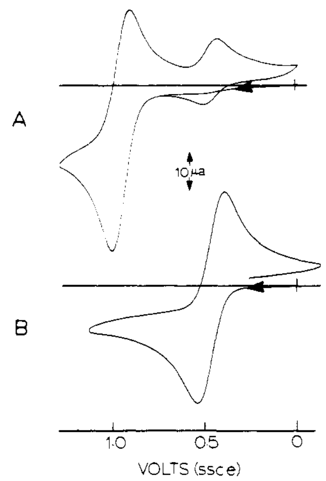


Figure 4. (A) First-scan cyclic voltammogram of *cis*-$Ru(dppm)_2Cl_2$. (B) First-scan cyclic voltammogram of *trans*-$Ru(dppm)_2Cl_2$. Both were taken in CH_2Cl_2 solution with a Pt-bead electrode and 0.1 M TBAH as supporting electrolyte (vs. SSCE).

Table I. Electrochemical Properties of $M^{II}(dppm)_2Cl_2$ and Related Complexes

complex	$E_{1/2}$-(M^{III}/M^{II}), V	$i_{p,a}/i_{p,c}$[a]	$E_{1/2}$- or $E_p/2$-(M^{IV}/M^{III})
trans-$Ru(dppm)_2Cl_2$[b]	0.42	0.97	1.68[d]
cis-$Ru(dppm)_2Cl_2$[b]	0.79	0.81	>1.9[d]
cis-$Ru(bpy)_2Cl_2$[b]	0.32	0.99	1.95
[*cis*-$Ru(dppm)_2(CH_3CN)Cl]PF_6$[c]	1.35	0.95	
trans-$Os(dppm)_2Cl_2$[b]	0.18	1.02	1.58[d]
cis-$Os(dppm)_2Cl_2$[b]	0.64	1.01	>1.9[d]
cis-$Os(bpy)_2Cl_2$[b]	−0.04	0.97	1.35
[*cis*-$Os(dppm)_2(CH_3CN)Cl]PF_6$[c]	+0.93	0.98	

[a] Ratio of oxidizing to reducing peak currents from cyclic voltammetry for the M^{III}/M^{II} couple. [b] Measured in CH_2Cl_2 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 CH_3CN 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*-$Ru(dppm)_2Cl_2$ in CH_2Cl_2–0.1 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*-$Ru^{III}(dppm)_2Cl_2$ 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 λ_{max} = 704 nm (CH_2Cl_2) that is characteristic of *trans*-$Ru^{III}(dppm)_2Cl_2^+$. The behavior of *cis*-$Os(dppm)_2Cl_2$ is different from the Ru analogue in that no isomerization occurs following oxidation by exhaustive electrolysis.

Comparisons between $E_{1/2}(M^{III}/M^{II})$ values for the cis isomers and for *cis*-$M(bpy)_2Cl_2$ (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 $E_{1/2}(M^{III}/M^{II})$ 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, $E_{1/2}(M^{III}/M^{II})^{cis} - E_{1/2}(M^{III}/M^{II})^{trans} = \Delta E'_{iso}$, 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 phosphorus for Os^{II} compared to that for Ru^{II}.

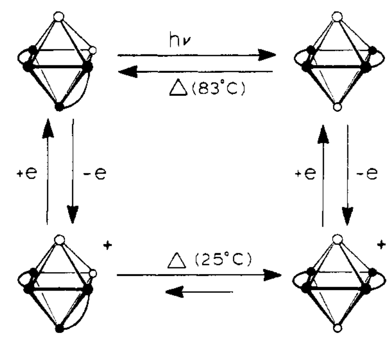


Figure 5. Scheme showing thermal, photochemical, and electrochemical interconverions in the cis–trans $Ru^{II}(dppm)_2Cl_2/Ru^{III}(dppm)_2Cl_2^+$ system.

Relative Substitution Labilities of the Cis and Trans Isomers. A cyclic voltammogram of *cis*-$Ru(dppm)_2Cl_2$ in 2:1 CH_2Cl_2–CH_3CN 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 $E_{1/2}(Ru^{III}/Ru^{II})$ for the complex $Ru^{II}(dppm)_2(CH_3CN)Cl^+$. Thus on the time scale of dissolution of *cis*-$Ru(dppm)_2Cl_2$ in the solvent the substitution reaction shown in eq 6 has gone to completion.

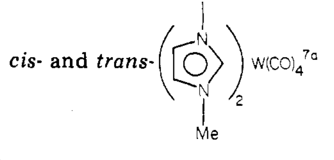
$$cis\text{-}M^{II}(dppm)_2Cl_2 + CH_3CN \rightleftharpoons cis\text{-}M^{II}(dppm)_2(CH_2CN)Cl^+ + Cl^- \quad (6)$$

For the case of *cis*-$Os^{II}(dppm)_2Cl_2$ the same substitutional chemistry occurs; however, the rate is much slower. Thus, Figure 3 (top) shows the cis osmium complex in 2:1 CH_2Cl_2–CH_3CN 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*-$M(dppm)_2Cl_2$ to react in CH_3CN–H_2O solution, followed by metathesis of the released anion for PF_6^-. 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*-$Ru(dppm)_2Cl_2$ and *cis*-$Os(dppm)_2Cl_2$ 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*-$Ru(dppm)_2Cl_2$ 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)$_2$Cl$_2$. 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 $d\pi \rightarrow d(P)$ interactions and destabilizing $d\pi \leftarrow p(Cl)$ 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 $p\pi(Cl) \rightarrow d\pi(Ru) \rightarrow d\pi(P)$ interaction as has been recognized for d^8 square-planar complexes.[11]

Upon oxidation to Ru^{III}(dppm)$_2$Cl$_2^+$ 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(NH$_3$)$_6^{3+}$.[12] It is interesting to note that irradiation of the d–d manifold in *cis*-Ru^{II}(dppm)$_2$Cl$_2$, which labilizes metal–ligand bonds, has the effect of removing an electron from a $d\pi$ 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)$_2$Cl$_2$, 38800-82-7; *cis*-Ru(dppm)$_2$Cl$_2$, 79982-54-0; *cis*-Ru(bpy)$_2$Cl$_2$, 19542-80-4; *cis*-[Ru(dppm)$_2$(CH$_3$CN)Cl](PF$_6$), 79953-54-1; *trans*-Os(dppm)$_2$Cl$_2$, 79953-55-2; *cis*-Os(dppm)$_2$Cl$_2$, 79982-55-1; *cis*-Os(bpy)$_2$Cl$_2$, 79982-56-2; *cis*-[Os(dppm)$_2$(CH$_3$CN)Cl](PF$_6$), 79953-57-4; tetra-*n*-butylammonium hexachloroosmate(IV), 58590-70-8.

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(11) Basolo, F.; Pearson, R. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; p 425.

(12) Stynes, H. C.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 2304.

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 AlCl$_3$–CH$_3$CN system has been investigated by infrared and Raman spectroscopy and by ^{35}Cl and ^{27}Al NMR spectrometry over the [CH$_3$CN]/[AlCl$_3$] molar ratio range 5.6–80. The system consists mainly of ionic complexes that share the same anion, AlCl$_4^-$. Three octahedral cations have been characterized: Al(CH$_3$CN)$_6^{3+}$, AlCl(CH$_3$CN)$_5^{2+}$, and AlCl$_2$(CH$_3$CN)$_4^+$. A new species, the Al(CH$_3$CN)$_5^{3+}$ 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, AlCl$_3$–CH$_3$CN 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 CH$_3$CN 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 AlCl$_4^-$ 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 AlCl$_3$·CH$_3$CN$_2$ is present.

Recent results obtained in our laboratories on solutions of AlBr$_3$ in CH$_3$CN[14] encouraged us to reinvestigate AlCl$_3$ in

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