to eq 1 contain iodoselane **2b** [δ(^{77}Se) 370.8 ppm] as the predominant species[10] but minor amounts of the educt diselenide **1b** [δ(^{77}Se) 359.1 ppm][11] are still present. With iodine in excess, diselenide **1b** is completely consumed.

Removal of the solvent from mixtures containing **1b**, I$_2$, and **2b** proceeds with loss of iodine, and subsequent crystallization from 40/60 petroleum ether leads to purple-black crystals of the composition (R$_2$Se$_2$)$_2$I$_2$ (**4**) (R = 2,4,6-triisopropylphenyl). Crystals of **4** were orthorhombic, space group *Pbca*, and allowed a single-crystal X-ray structure determination.[12] Surprisingly, solid **4** is not an iodoselane but a very weak adduct of molecular iodine with two molecules of diselenide **1b** (Figure 1 and Table I). The diselenide molecules are related by a center of inversion in the middle of the I–I bond. The I–I bond length of **4** (2.72 Å) is comparable to that of solid I$_2$ (2.715 Å);[13] it is less elongated than in any other known adduct of selenium ligands with iodine molecules. Accordingly, the geometry of diselenide **1b** within the complex **4** appears very much like an undistorted organic diselenide, quite different from the Ph$_2$Se$_2$ moiety in complex **3**, which shows distinctly different coordination geometries of the two three-coordinated [(8-Se-3) and (10-Se-3)] selenium atoms[8] as well as a much stronger Se→I interaction (2.99 Å) and weaker I–I bonds (2.77 Å)[8] than those of **4**.

Dihalogen molecules tend to give 1:2 complexes only with very weak donors.[14] Quite typical for such adducts, the arrangement Se–I–I–Se of **4** is not far from linear (∠Se–I–I = 169.1°).

Dissolving crystals of **4** in inert solvents allows one to detect immediately an equilibrium mixture of diselenide **1b**, iodoselane **2b**, and iodine (NMR, UV); these molecules are also observed in the gas phase (EI-MS at 70 eV).

Remarkably, complex **4**, containing an iodine molecule "intercalated" weakly between two diselenide molecules, is of very similar energy compared with both the educts (diselenide **1b**/iodine) and the iodoselane species **2b** containing a covalent Se–I bond. Packing effects will contribute to make CT complex **4** (not **2b**, which predominates in solution) a stable compound in the solid state. From less bulky bis(2,3,5,6-tetramethylphenyl) diselenide (**1d**) with iodine, iodo(2,3,5,6-tetramethylphenyl)selane (**2d**), the predominant species in solution, was isolated as a pure crystalline compound.[15]

The barriers of transformation of these species into each other (eq 3) are lowest for the charge-transfer complex association/dissociation equilibria (steps i and ii are fast at all NMR time scales) and still rather low for the diselenide–diiodine dismutation (immediate equilibration according to eq 3 upon dissolving **4**).

The (low) strength of the interaction of diselenide **1b** with iodine in solid **4** [*d*(Se–I) = 3.48 Å] is quite comparable with intermolecular interactions in solid iodine or with interchain contacts in hexagonal selenium [*d*(I···I) = 3.50 Å; *d*(Se···Se) = 3.43 Å].[16,17] The solid-state structure and the reversible dismutation in solution make the diselenide **1b**/I$_2$ system the most suitable molecular model currently available for the modes of interaction between elemental selenium and elemental iodine[2,4,5] wherein catalysis of selenium crystallization (i.e. Se–Se bond breaking and bond making) is favored by iodination/deiodination via covalent and charge-transfer Se–I bonded intermediates.

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Wavelength Dependence of Unquenchable Photoaquation in the Tris(1,3-diaminopropane)chromium(III) Ion

We have discovered a wavelength dependence of product stereochemistry in [Cr(tn)$_3$]$^{3+}$ (tn = 1,3-diaminopropane) photoaquation that indicates the unquenchable photochemistry competes with vibrational relaxation. An earlier study[1] of wavelength dependence of unquenchable photoracemization yield in [Cr(phen)$_3$]$^{3+}$ was interpreted similarly, while wavelength-dependent quenching in *trans*-[Cr(en)$_2$F(NCS)]$^+$ was interpreted in terms of reaction via two quartet states.[2] All these results are important in the context of previous reports[3,4] of wavelength independence of product yields.

It is known that chromium(III) complexes may photosubstitute by two pathways,[5–8] one via the doublet state with product[9,10] forming with the doublet lifetime, the rate of the other pathway, often about 20–30% of the reaction, being faster than nanoseconds. The details of the fast pathway have not been established experimentally. It has been proposed to occur directly from a thermally equilibrated, solvent-shell-relaxed electronically excited (thexi) quartet state[11] or by surface crossing to a ground-state transition state.[12,13]

Intersystem crossing yields[14] and product yields have been observed to vary with excitation wavelength, and phosphorescence risetime lies in the picosecond or faster domain.[15,16] These features suggest the quartet route is very fast, but there is need for more information on its rate.

Previous studies[17,18] have shown that [Cr(tn)$_3$]$^{3+}$ photosubstitutes to *cis*- and *trans*-[Cr(tn)$_2$(tnH)(H$_2$O)]$^{4+}$ with quantum yield 0.15. Here, we have examined, at 20 °C, the overall quantum yields for photoaquation and the product isomer composition on irradiation into the quartet and doublet states as well as for quartet irradiation in the presence of a quencher that eliminates the

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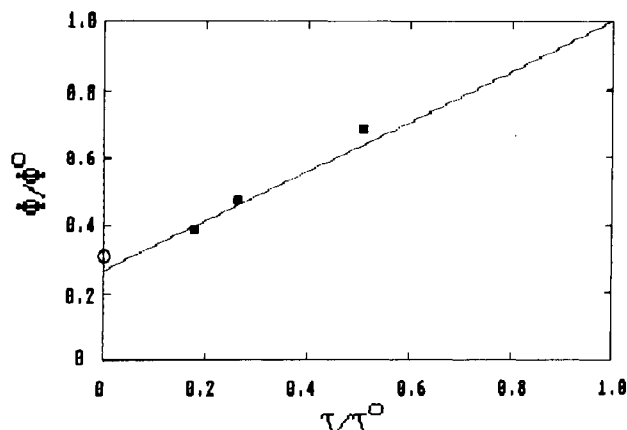
Figure 1. Hydroxide quenching of $[Cr(tn)_3]^{3+}$ photochemical yield and doublet-state lifetime. Lifetimes (τ) were measured with excitation at 337 nm and an emission wavelength of 670 nm. Photochemical quantum yields (Φ) were determined for irradiation at 488 nm with chromatographic estimation of the photoproducts. The open circle point was obtained from proton uptake and release measurements at 436 nm in solutions at pH 3 and 11. The temperature was 20–22 °C throughout. The linear regression line (open circle point not included) was forced through the point 1,1 and has intercept 0.28 ± 0.02, the proportion of unquenchable photochemistry.
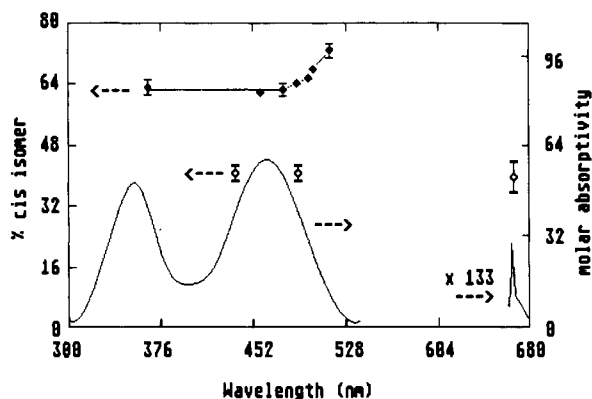
Figure 2. Absorption spectrum and percentage cis photoproduct. The temperature was 20–22 °C. Error bars shown are $\pm\sigma$; where none appear, it is because they are smaller than the size of the point plotted. Arrows indicate that spectral data are referenced to the right axis; photoproduct percentages are to the left. Key: (open diamonds) irradiation into the quartet and doublet states without quencher; (filled diamonds) irradiation into the quartet state, fully hydroxide quenched. For argon laser wavelengths, duplicate chromatograms were run on three independent photolysis experiments for a total of six results per point. At 365 nm (xenon lamp), two measurements were made.

doublet reaction pathway. The photoproduct isomer proportions were reproducibly measured ($\pm2\%$) by HPLC; thermal reactions did not interfere.

The quantum yields for irradiation at 436 nm (Xe lamp) into the quartet and at 664.8 nm (dye laser) into the doublet were 0.15 $\pm$ 0.02 and 0.16 $\pm$ 0.01, respectively. The observed similarity of quantum yields on doublet and quartet irradiation is consistent with similar reports in the literature.[3,4]

It is known, however,[10,18] that on quartet irradiation, 78% of the photoaquation occurs via the doublet state. This dominance of the doublet route is bound to obscure small wavelength effects in the 22% of "quartet" reaction.

We therefore wanted to quench "doublet" reaction without disturbing the chromatographic analysis. Hydroxide was ideal, showing only dynamic quenching as judged by the constancy of the initial emission intensity in lifetime quenching experiments. There were no changes (<1%) in the visible spectrum (350–500 nm) of the complex in 0.1 M sodium hydroxide. The linear Stern–Volmer plot has a slope of 1.3×10^5 M^{-1}; since the complex

has a doublet lifetime of 2 μs, this means the quenching is almost diffusion controlled. Hydroxide has, however, been reported in one instance to lead to reactive quenching.[19]

To check this, the quenching of the emission lifetime and photochemical yield were compared. Figure 1 shows that when the emission lifetime is completely quenched by hydroxide, 28% of the chromatographically determined photochemistry remains unquenched. A separate series of quantum yield measurements based on proton uptake and release gave 0.049 and 0.15 at pH 11 and 3, respectively, for an unquenchable yield of 33%. Finally, Gowin and Wasgestian[17] give data for the quantum yields at pH 13 and 3, which again give 28%. These results and the reasonable agreement with the laser result (22%) exclude any significant contribution from reactive quenching in this system. Our experiments in alkaline solutions also proved that thermal base-catalyzed processes did not influence the product stereochemistry over the time scale of our experiments.

Figure 2 shows the spectrum of the compound and our results on the wavelength dependence of photoproduct isomer mix at various argon ion and dye laser wavelengths. For doublet and unquenched quartet irradiations (open points) an indistinguishable percentage (40 $\pm$ 3%) cis isomer is observed. With complete doublet quenching by 0.10 M sodium hydroxide, however, a different, wavelength-dependent composition (62–73%) for the quartet mode is revealed (filled points).

The wavelength variation of the product stereochemistry shows three features. There is the percentage of cis isomer for irradiation into the doublet, there is the different, limit percentage for the fully quenched photochemistry on irradiation in the quartet bands, and finally, the quenched reaction shows an increase in percentage cis isomer as the irradiation wavelength moves through the red edge of the lowest quartet band.

The difference between the doublet and quenched quartet photostereochemistries could be evidence for direct doublet reaction. However, much photophysical[8] and photochemical evidence[6,8] is against this, so we prefer an explanation more consistent with present understanding.

The red edge effect must originate in the unusual nature of the states that absorb in the long wavelength edge of the lowest quartet band. For the closely analogous hexaammine compound, Wilson and Solomon have established[20] that the zero–zero transition occurs at 501 nm. It will be similar in our compound, and we note that, in Figure 2, the proportion of cis isomer begins its upward trend above 488 nm.

Excitation at a wavelength greater than the zero–zero value, such as 514 nm, must arise from absorption in ground-state molecules that are either vibrationally excited or in unusual solvation environments. Such molecules could reasonably give an atypical photoproduct ratio and one that diverges in step with the extent of their abnormality as excitation energy decreases. Such a model of the red edge photochemistry demands that the reaction occur on a time scale competitive with either, or both, vibrational relaxation and/or solvation sphere equilibration. Either of these models would also fit the photoracemization results[1] cited earlier.

However, these two possibilities can be distinguished here on the basis of our observations of different photostereochemistries. For normal absorption in the quartet bands, the Franck–Condon excited states have ground-state equilibrium geometry and solvation. For such wavelengths, we find a product mix which is wavelength independent but notably different from that observed for the "doublet reaction". Both from theory and from the small observed Stokes shift for phosphorescence, it is clear that the doublet state is also close to ground-state equilibrium geometry and solvation. It is therefore unreasonable to attribute the different stereochemistries found for the two states to differences in solvation. It is much more likely that the difference arises because of the specific vibrational excitation of the Franck–Condon quartet

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state. This is predicted to form with its dominant vibrational population in the e_g and a_{1g} modes.[20] In contrast, the doublet-state molecule will vibrationally equilibrate prior to reaction.

We conclude that the photochemical reaction arising from the quartet state must be competitive with vibrational relaxation and therefore occurs in a time of a few picoseconds or faster. Although the aquation is a bimolecular process, it is not required that the water molecule enter this fast, although it could. We merely require selection of a particular reaction channel on this time scale, one which influences the stereochemistry of the final product.

A further implication of this model is that the "thexi" quartet state may never be populated under solution photochemical conditions because the vibrationally excited higher levels react or decay otherwise too quickly. This is consistent with the picosecond risetime of phosphorescence, the nonfluorescence of room-temperature solutions,[21] the failure to quench quartet reaction, and the rapid formation of photoproduct from the quartet state.

We are currently exploring analogous wavelength dependencies in other chromium(III) systems with photochemistry via doublet and quartet states. In preliminary experiments, the molecule *cis*-$[Cr(tn)_2(NH_3)_2]^{3+}$ shows similar behavior.

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(21) Reference 15 presents results that may show a short-lived fluorescence from a Cr(III) complex.
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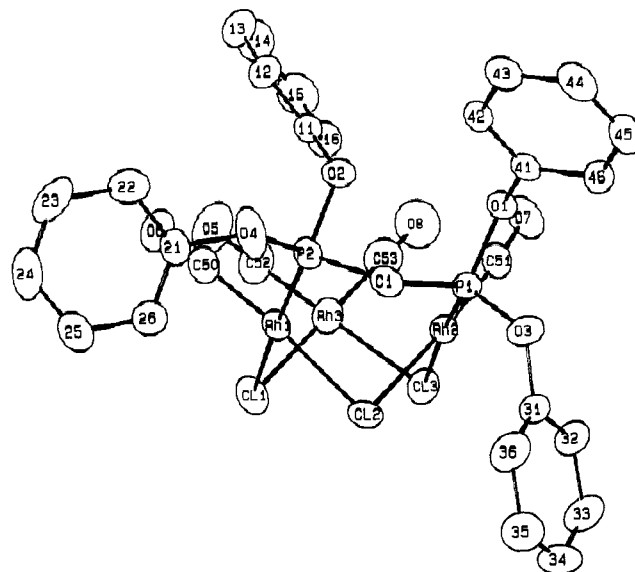Victoria, BC, Canada V8W 2Y2

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An Unusual Trirhodium Complex: Dichlorodicarbonylrhodate(I) as a Binucleating Ligand

Mague and co-workers recently reported that reaction of $MeN(PF_2)_2$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ gave an intriguing cone-shaped trinuclear rhodium complex of formula $[Rh_3(\mu\text{-}Cl)_3(\mu\text{-}PP)_3]$ (1), PP = $MeN(PF_2)_2$,[1] whereas a similar reaction of the more common bridging ligand dppm = $Ph_2PCH_2PPh_2$ is known to yield binuclear complexes, which are precursors to important "A-frame" complexes such as $[Rh_2(\mu\text{-}Cl)(CO)_2(\mu\text{-}dppm)_2]^+$ (2).[2,3] We wish to report that a similar reaction of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ with the ligand $CH_2\{P(OPh)_2\}_2$, dpopm,[4] gives another cone-shaped trinuclear complex $[Rh_3(\mu\text{-}Cl)_3(CO)_4(\mu\text{-}dpopm)]$ (3), whose structure demonstrates the close relationship between these trinuclear cone-shaped and binuclear A-frame complexes.

Reaction of a 1:1 mixture of $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ and dpopm gave a dark solution from which orange crystals of 3 slowly separated over a period of several days. The yield of 3 was ~30% based on rhodium. Since the spectroscopic data[5] did not define the structure, an X-ray structure determination was carried out.[6]

The structure is shown in Figures 1 and 2. Figure 1 shows the cone structure and emphasizes the similarity to complex 1. In particular the $Rh_3(\mu\text{-}Cl)_3$ units are very similar in 1 and 3 and in neither case is there evidence for any RhRh bonding interactions. The RhRh distances in 3 are 3.2023 (3)–3.4627 (4) Å, slightly longer than in 1 [average 3.0964 (4) Å].[1] Taking PP as

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Figure 1. View of the structure of $[Rh_3(\mu\text{-}Cl)_3(CO)_4(\mu\text{-}dpopm)$, emphasizing the cone shape produced by the $Rh_3(\mu\text{-}Cl)_3(CO)_4(PP)$ atoms. Selected bond distances (Å) or angles (deg): Rh(1)–Cl(1) = 2.442 (1), Rh(1)–Cl(2) = 2.408 (1), Rh(1)–P(2) = 2.1742 (9), Rh(1)–C(50) = 1.818 (4), Rh(3)–Cl(1) = 2.383 (1), Rh(3)–Cl(3) = 2.371 (1), Rh(3)–C(52) = 1.818 (5), Rh(3)–C(53) = 1.837 (4); Rh(1)–Cl(1)–Rh(3) = 83.71 (3), Rh(1)–Cl(2)–Rh(2) = 84.00 (4), Rh(2)–Cl(3)–Rh(3) = 92.19 (3).
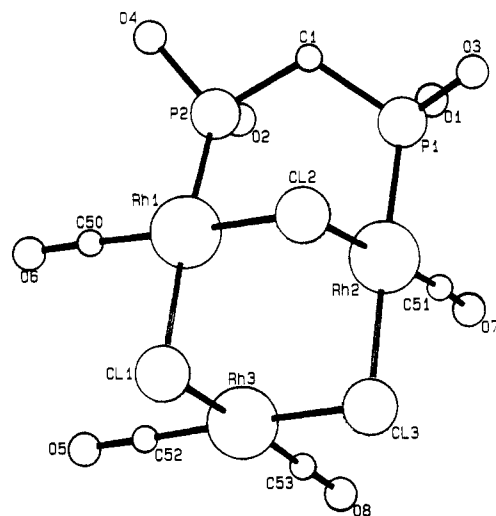
Figure 2. View of the structure of $[Rh_3(\mu\text{-}Cl)_3(CO)_4(\mu\text{-}dpopm)]$, emphasizing the A-frame structure of the $[Rh^1Rh^2(\mu\text{-}Cl)(CO)_2]^+$ unit.

a general ligand, 1 would be formed from 3 by replacement of the four carbonyl ligands by two more diphosphine ligands.

Another view of the structure 3 is shown in Figure 2. This view emphasizes the similarity to the A-frame structure 2. Complex 2 would be formed from 3 by displacement of the $[Rh^3(CO)_2Cl_2]^-$ fragment by a second diphosphine ligand. Thus 3 can also be considered as an A-frame derivative in which one of the bridging ligands of the Rh^1Rh^2 fragment is *cis*-$[Rh^3(CO)_2Cl_2]^-$, acting as a 4-electron ligand.

This work thus demonstrates the close relationship between the cone-shaped trinuclear and A-frame binuclear complexes of

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