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.

**Acknowledgment**. We are grateful to the National Science and Engineering Research Council and the University of Victoria for financial support. We thank R. Fernando for confirming our value of the Stern–Volmer quenching constant for $[Cr(tn)_3]^{3+}$ with hydroxide.

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

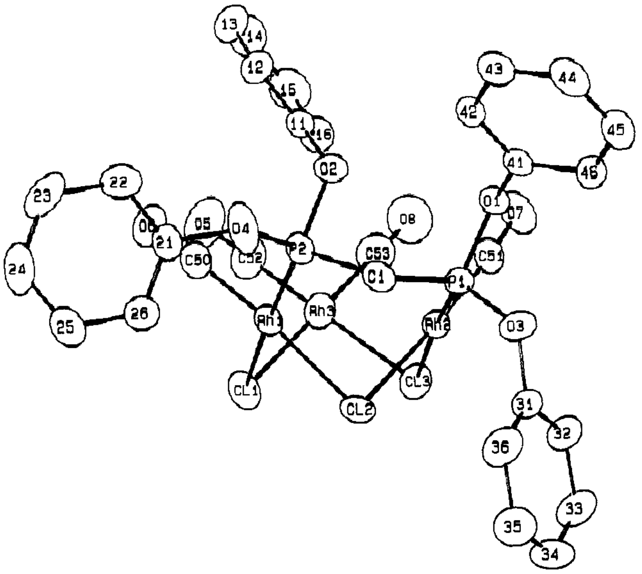

**Figure 1**. View of the structure of $[Rh_3(\mu\text{-}Cl)_3(CO)_4(\mu\text{-}dpopm)$, emphasizing the cone shape produced by the $Rh_3(\mu\text{-}Cl)_3(CO)_4(PP)$ atoms. Selected bond distances (Å) or angles (deg): Rh(1)–Cl(1) = 2.442 (1), Rh(1)–Cl(2) = 2.408 (1), Rh(1)–P(2) = 2.1742 (9), Rh(1)–C(50) = 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).

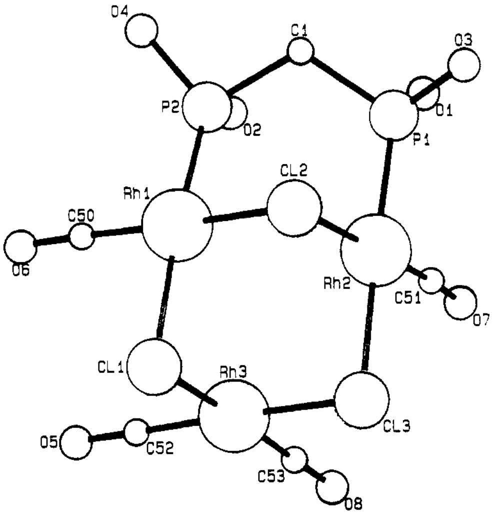

**Figure 2**. View of the structure of $[Rh_3(\mu\text{-}Cl)_3(CO)_4(\mu\text{-}dpopm)]$, emphasizing the A-frame structure of the $[Rh^1Rh^2(\mu\text{-}Cl)(CO)_2]^+$ unit.

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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(5) Spectroscopic data are as follows. NMR in $CD_2Cl_2$: $^1H$, $\delta = 3.60$ [m, 2 H, $CH_2P_2$], 7.1–7.5 [m, 20 H, $C_6H_5$]; $^{31}P$, $\delta = 149.7$ [m, $^1J(RhP) = 234$ Hz, $^2J(PP) = 78$ Hz; deceptively simple AA′XX′ multiplet; solution given gives a good fit between observed and simulated spectra but is not unique]. IR $\nu(CO)$ = 2083 (s), 2018 (vs), 1993 (m) $cm^{-1}$. Anal. Calcd for $C_{29}H_{22}Cl_3O_8P_2Rh_3$: C, 35.7; H, 2.3. Found: C, 35.8; H, 2.0.

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rhodium and also suggests a more systematic synthesis of cone-shaped trinuclear complexes, by reaction of suitable binuclear precursors with binucleating ligands *cis*-$[ML_2X_2]$, in which the anionic groups X would act as donor atoms.

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**Supplementary Material Available:** Tables of crystal data, anisotropic thermal parameters, positional parameters, bond distances, and bond angles (9 pages); a table of structure factor amplitudes (43 pages). Ordering information is given on any current masthead page.

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(6) Crystal data for **3**: fw = 975.5, monoclinic, space group $C2/c$, $a$ = 33.804 (3) Å, $b$ = 10.038 (3) Å, $c$ = 23.348 (2) Å, $\beta$ = 121.95 (1)°, $V$ = 6722.6 (7) Å$^3$, $Z$ = 8, $d_{calc}$ = 1.928 g cm$^{-3}$, Mo K$\alpha$ radiation, $\mu$ = 18.1 cm$^{-1}$, Enraf-Nonius CAD4 diffractometer, $\theta$–$2\theta$ scan method at 25 °C, quadrant of data with $1° < \theta < 30°$ measured, 10 796 unique reflections, absorption correction based on $\psi$ scans, structure solved by heavy-atom methods. Full-matrix least-squares refinement converged to $R$ = 0.032 and $R_w$ = 0.034 for 407 variables and 6098 observations with $I > 3\sigma(I)$. All H atoms were found, but refinement used calculated positions with fixed isotropic displacement parameters.

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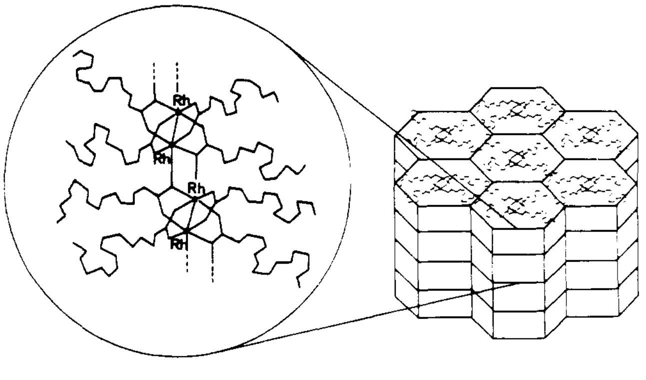
## Raman Spectroscopy as a Convenient Probe of Solid–Liquid Crystal Phase Transitions in Binuclear Rhodium(II) *n*-Alkanoates

Phase transitions from lamellar crystalline lattices to columnar liquid crystalline mesophases, shown as



have been observed for several bimetallic complexes of fatty acids.[1,2] Because of their potential as molecular materials for electronics,[3] considerable interest in this type of compound has developed, and numerous complexes have been prepared for study including those of Cu(II),[1] Rh(II),[4] and Ru(II)[5] with carboxylate ligands derived from fatty acids of varying lengths. Whereas the phase transitions of classical organic mesogens usually are followed by hot-stage polarizing microscopy, differential scanning calorimetry, and low-angle X-ray scattering, the presence in metallomesogens of heavy atoms and/or of unpaired electron density allows additional experimental techniques to be used for the characterization of their transitions into and through their various mesophases, e.g. EXAFS,[6,7] magnetic susceptibility measurements,[5,8-11] and EPR spectroscopy.[10-15] In the course of our studies[4] of the metal-metal-bonded dirhodium(II) tetrakis(*n*-alkanoates)[16] using vibrational spectroscopy, we have discovered that Raman spectroscopy is a highly sensitive probe of the phase transitions exhibited by this class of mesogens. Moreover, this probe is extremely convenient, as it has no need of an independent heat source.

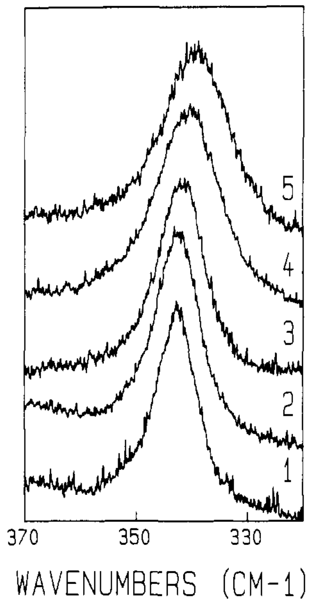


**Figure 1.** Raman spectra (514.5-nm excitation, 30 mW) of dirhodium tetrakis(hexanoate) in the 320–370-cm$^{-1}$ region as a function of the sample temperature: 1, 325 K; 2, 340 K; 3, 360 K; 4, 400 K; 5, 450 K.

Microcrystalline samples of dirhodium butyrate, hexanoate, and octanoate were prepared from dirhodium acetate by ligand exchange followed by slow recrystallization from the neat fatty acid. While investigating the Raman spectra of these complexes,

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