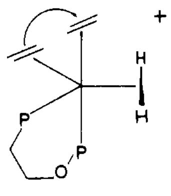
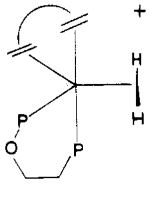


9a



9b

rotamer shown in **9a**, with both H atoms in the equatorial plane, should be favored, as is known to be the case for olefins.[11] In the case of olefins, the π^* orbital of the ligand can orient the olefin, but in the case of H_2, it is proposed that the σ^* orbital plays an analogous role. It can be seen that the equatorial cod C=C group and the H_2 molecule share d orbitals with Ph_2PR in **9a** but with the better π-acceptor Ph_2POR in **9b**. The former is preferred, as discussed for the case of olefins by Hoffmann et al.[12] A further advantage of **9a** is the presence of the more electronegative Ph_2POR group in the axial rather than the equatorial position, which is known to be preferred.[13]

It should be noted that **9a** may be an intermediate with free rotation of the H_2 around the M-H_2 axis, rather than a transition state, in view of the recent isolation of an η^2-H_2 complex, $[W(CO)_3(PCy_3)_2(\eta^2\text{-}H_2)]$.[14] As expected on the basis of the ideas presented above (but not on simple steric grounds), the orientation of the H_2 molecule in the tungsten complex is approximately parallel with the P-W-P axis, as shown by neutron diffraction.[15]

The formation of the product shown in eq 4 is also consistent with this idea since pyridine seems to be slightly more electron donating than PCy_3,[16] but as previously mentioned, this reaction could be easily under steric control.

We conclude that the addition of H_2 to a metal complex can be directed by the electronic effect of the ligands. We propose that the σ and σ^* orbitals of H_2 can play the same role as the π and π^* orbitals of olefins in orienting the molecule on the metal and that arguments[12] successfully applied to olefins can be extended to cover the case of H_2. It would have been interesting to compare these results with those for olefin addition to the same complex. Unfortunately, there was no reaction between $[Ir(cod)(L_2)]^+$ and maleic anhydride or TCNE. We have rationalized the observed direction of addition in terms of competition for metal d electrons in a proposed trigonal-bipyramidal transition state. Clearly, further examples are required before the generality of these ideas can be completely assessed.

Experimental Section

All complexes were prepared by using standard inert-atmosphere, Schlenk tube techniques. CH_2Cl_2 was distilled from CaH_2 and Et_2O from Na/Ph_2CO before use. ^1H NMR spectra were recorded on a Brucker 270-MHz instrument and ^{31}P NMR spectra on a Varian CFT-20.

(Diphenylphosphino)ethyl diphenylphosphinite (pop) was prepared by the method of ref 8, except that the product was chromatographed on alumina with benzene as eluent and stored as a standard solution in benzene under N_2. The ^{31}P NMR spectrum of the product was identical with that reported in ref 8.

(1,5-Cyclooctadiene)((diphenylphosphino)ethyl diphenylphosphinite)iridium(I) Tetrafluoroborate. To a solution of $[Ir(cod)(MeCN)_2]BF_4$ (0.47 g, 1 mmol) in CH_2Cl_2 (20 mL) at -78 °C was added dropwise pop (1 mmol) in benzene (5 mL). The red solution was stirred at -78 °C (30 min) and then at room temperature (1 h). The volume of the solution was reduced to 5 mL in vacuo and the product isolated with Et_2O, washed with Et_2O, and dried in vacuo. Anal. Calcd for $C_{34}H_{36}IrP_2OF_4B\cdot{}^1/_2CH_2Cl_2$: C, 49.07; H, 4.42; P, 7.34. Found: C, 48.99; H, 4.80; P, 7.45.

Dihydrido(1,5-cyclooctadiene)((diphenylphosphino)ethyl diphenylphosphinite)iridium(III) Tetrafluoroborate. A solution of $[Ir(cod)(pop)]BF_4$ in dichloromethane (for ^1H NMR, 30 mg in 0.4 mL of CD_2Cl_2; for ^{31}P NMR, 100 mg in 1.5 mL of CH_2Cl_2) was treated with H_2, and the spectra observed in Table I were observed. The configuration was determined as **8a** by ^{31}P decoupling the ^1H spectrum and using frequencies determined in the ^{31}P NMR experiment.

Registry No. **7**, 87556-62-5; **8**, 87567-00-8; pop, 32309-62-9; H_2, 1333-74-0.

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Mechanical Spectroscopy of Organometallic Complexes: Assignment of the Spectrum of $C_6H_6Cr(CO)_3$ to Ring Rotation

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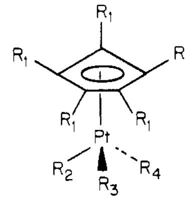
Recently we reported preliminary studies[1] of the mechanical spectra of six cyclopentadienylplatinum(IV) alkyl complexes of the type $CpPtR_1R_2R_3$ (**1-6**), where $R_1R_2R_3$ were combinations of methyl, ethyl, and acyl groups. The experiments[2,3] consisted of subjecting a rigid piece of polystyrene,[4] in which the complex was dissolved, to a mechanical displacement and allowing it to return to its rest position. The damping of the resultant vibration is dependent upon the degree to which the energy imparted by the initial displacement is dissipated. If the molecules of the sample undergo molecular motion(s) that can interact with the mechanical motion of the matrix, then it may be possible to bring the two into resonance. This was achieved by varying the temperature of the sample (thus changing the molecular dynamics) and keeping the frequency of the mechanical motion approximately constant. Resonance causes an increase in the rate of damping and results in a peak in the tan δ^1 vs. temperature plot. The presence of a platinum complex gave a peak in the spectrum, at a temperature that depended upon the set of alkyl ligands in the $PtR_1R_2R_3$ tripod.



1: $R_1 = H, R_2 = R_3 = R_4 = CH_3$
2: $R_1 = H, R_2 = R_3 = CH_3, R_4 = C(O)CH_3$
3: $R_1 = H, R_2 = R_3 = C_2H_5, R_4 = C(O)CH_3$
4: $R_1 = H, R_2 = R_3 = C_2H_5, R_4 = CH_3$
5: $R_1 = H, R_2 = CH_3, R_3 = C_2H_5, R_4 = C(O)CH_3$
6: $R_1 = C_6H_5, R_2 = R_4 = CH_3$

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[4] Polystyrene has a low background tan δ and thus presents a broad window in the desired ranges of temperature and frequency.

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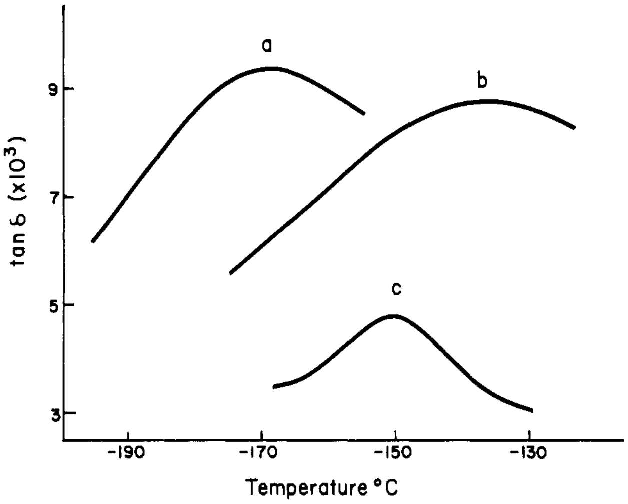
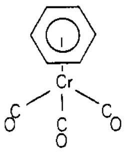


Figure 1. Temperature dependence of tan δ (vibrating reed) for (a) $C_6H_6Cr(CO)_2PPh_2$ (in polystyrene) at 740 Hz, (b) $C_6H_6Cr(CO)_3$ at 706 Hz, and (c) $C_6H_6Cr(CO)_2PPh_3$ at 891 Hz.

By the application of different frequencies of vibration the temperature dependence of the absorption was measured and used to determine an activation energy. Only the Cp ligand was common to complexes **1–5**, and no peak was observed for **6**, consistent with the postulate that its four phenyl rings would lock the ring in the matrix. Thus, the peaks were assigned to rotation of the Cp ring about the ring–metal axis. On the basis of this assignment the variations in the activation energies for the different complexes were successfully interpreted in terms of the relative steric interactions between the alkyl substituents on the platinum atom and the Cp ring.[1]

Interest in the rotation of aromatic organic rings attached to metals is as old as ferrocene chemistry itself,[5] and many techniques have been used to study the phenomenon.[6] Mechanical spectroscopy appears to be a very promising technique with which to examine ring rotation in solid or liquid complexes imbedded in polystyrene, a matrix which would be expected to be fairly isotropic and constant from sample to sample. Although the evidence strongly supports the assignment of the resonances observed for the platinum complexes to ring rotation, it does not conclusively eliminate whole-molecule tumbling or rotation of the $PtR_1R_2R_3$ tripod segment as possible sources of the absorption. Because of the potential usefulness of the technique we have conducted further experiments, which, it is hoped, unambiguously settle the question.

The mechanical spectra of a variety of (arene)tricarbonylchromium and substituted ferrocene complexes have been measured[7] and have shown peaks.[8] While the peaks appear at different temperatures, they all have intensities and peak shapes that are very similar to those observed for complexes **1–5**. Thus the phenomenon appears to be a general one and not one restricted to the platinum compounds alone.



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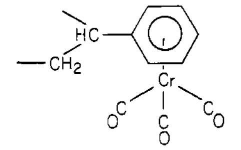

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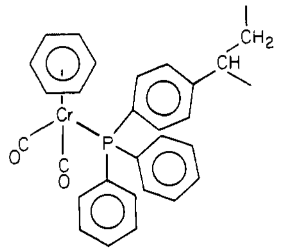

9

The mechanical spectrum of $C_6H_6Cr(CO)_3$ (**7**) is shown in Figure 1. When $Cr(CO)_6$ was examined, no peak was observed. Although this is a negative result, one would expect $Cr(CO)_6$ to give a peak if the phenomenon responsible for the peak observed for **7** was due to resonance of whole-molecule rotation with the mechanical motion. Compact complexes such as **7** and $Cr(CO)_6$ may be tumbling in the polystyrene matrix; however, these and other observations below are consistent with the conclusion that rotation of the C_6H_6 ring is the cause of the peak.

The mechanical spectrum of $C_6H_6Cr(CO)_2PPh_3$ gives a peak that is shown in Figure 1. Neither PPh_3 nor $Cr(CO)_5PPh_3$ gave an absorption in their mechanical spectrum. This tends to rule out the possibility that the peak observed for $C_6H_6Cr(CO)_2PPh_3$ was due to the presence of PPh_3 or the Cr–PPh_3 segment. In addition, inclusion of the bulky PPh_3 group would be expected to lock the $Cr(CO)_2PPh_3$ tripod in the matrix. Thus, observation of a peak tends to rule out rotation of the metal–tripod segment as the cause of the peak in the mechanical spectrum.

The $Cr(CO)_3$ residue was attached to the phenyl rings of polystyrene in varying concentrations.[9] Thus, the (arene)$Cr(CO)_3$ complex produced, **8**, was attached to the polymer backbone via the arene ring. This prevents its rotation about the ring–metal axis. No peak was observed in the mechanical spectrum. It seems unlikely that the presence of a substituent on the arene ring could substantially hinder the metal–tripod rotation. The complex $C_6H_5C_2H_5Cr(CO)_3$ and other (arene)$Cr(CO)_3$ complexes with substituents gave strong absorptions in their mechanical spectrum.[7] Thus, the absence of a peak for **8** is consistent with the postulate that ring rotation is responsible for the peaks observed for the other complexes. Finally, polystyrene, in which about 6.3% of the phenyl rings had been substituted with the diphenylphosphide group,[10] was reacted with $C_6H_6Cr(CO)_2THF$ prepared by photolysis of the tricarbonyl.[11] This resulted in the attachment of the C_6H_6-$Cr(CO)_2$ segment to the polymer backbone, **9**, via the phosphine ligand. Linkage of the metal tripod to the polymer in

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(7) The following complexes have shown peaks in their mechanical spectra: ferrocene; acetyl-, benzoyl-, (hydroxymethyl)-, vinyl-, *n*-butyl-, 1,1′bis(hydroxymethyl)-, 1,1′-diacetyl-, 1,1′-dimethyl-, and decamethylferrocene; ferrocenecarboxaldehyde; ferrocenylacetic acid, ferrocenecarboxylic acid; -1,1′-dicarboxylic acid; arylchromium tricarbonyl, where aryl = benzene, toluene, *o*-, *m*-, and *p*-xylene, mesitylene, hexamethylbenzene, and ethyl-, methoxy-, fluoro-, chloro-, and bromobenzene; (benzene)(phosphine)chromium dicarbonyl, where phosphine = PPh_3, PMe_2Ph, and $P(n\text{-}Bu)_3$; cyclopentadienylmanganese tricarbonyl; cyclopentadienyliron dicarbonyl halide, where halide = bromide and iodide.

(8) The activation energies found for these compounds will be reported and discussed in subsequent publications.

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this way would be expected to prevent both whole-molecule tumbling and metal–tripod rotation. The mechanical spectrum of the sample is shown in Figure 1. The observed peak appears to be the most conclusive evidence for the assignment of the phenomenon responsible for the absorption in the mechanical spectrum of organometallic complexes containing arene or Cp ligands to rotation of the ring about the ring–metal axis.

Acknowledgment. This work was supprted by grants from the National Science and Engineering Research Council of Canada and the Quebec Department of Education.

Registry No. 7, 12082-08-5; $C_6H_6Cr(CO)_2PPh_3$, 12278-67-0; $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5PPh_3$, 14917-12-5; PPh_3, 603-35-0; $C_6H_5C_2H_5Cr(CO)_3$, 12203-31-5; polystyrene, 9003-53-6.

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Thermal Decomposition of the Pentacyanoaquoferrate(II) Ion in Aqueous Solution

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A wide number of substitution[1-8] and electron-transfer[9-11] reactions involving the pentacyanoaquoferrate(II) ion, $Fe(CN)_5H_2O^{3-}$, have been investigated. This species is known to be the primary product of the thermal and photochemical decomposition of hexacyanoferrate(II), a reaction that ultimately can lead to a variety of products, depending mostly on pH and air content of the medium.[12,13]

$Fe(CN)_5H_2O^{3-}$ is known to be susceptible to autoxidation and dimerization processes; however, these can be put under control if air is rigorously excluded and work is carried out in sufficiently dilute solutions, respectively.[14] An additional complication relates to the thermal decomposition of the complex, which is known to be significant in aged solutions. The nature of this last reaction is not well understood; previous studies throw some light on this question, but the working material is known to be a complex mixture of monomeric and polymeric species.[15] The availability of a cleaner method of generating the monomeric aquo ion[16] calls for a reinvestigation of the stoichiometry, as well as of the kinetic and mechanistic aspects of the decomposition reaction, which is important in its own right, as well as helpful in controlling the properties of solutions containing $Fe(CN)_5H_2O^{3-}$.

Experimental Section

Solutions of $Fe(CN)_5H_2O^{3-}$ (5×10^{-5}–10^{-3} M) were prepared from solid $Na_3Fe(CN)_5NH_3 \cdot 3H_2O$, which was synthesized by conventional procedures.[17] Doubly distilled and deoxygenated water was used, and analytical grade reagents were employed in the control of pH and ionic strength (NaCl). A slight excess of ascorbic acid was also added to prevent oxidation of $Fe(CN)_5H_2O^{3-}$.

Measurements were initiated about 10 min after the dissolution of the solid; this time allowed the complete aquation of the $Fe(CN)_5NH_3^{3-}$ ion to proceed, the transfer of the solution (syringe techniques were used), and adequate thermostating of the spectrophotometric cell. Most of the work was carried out by measuring the decay of the 440-nm absorption of the pentacyanoaquoferrate(II) ion with a Shimadzu UV-210A double-beam spectrophotometer. A pseudo-first-order rate constant, k_{obsd} (s^{-1}) was obtained from the linear plot of ln ($A_t - A_\infty$) vs. time, where A_t is the measured absorbance at time t. At least two measurements were made in every case, and measured k_{obsd} were accurate to within approximately 5%. Temperature and ionic strength dependence of k_{obsd} were determined within the ranges of 20–50 °C (±0.1 °C) and 0.1–1 M, respectively, with a concentration of the reactant ion c of 5×10^{-5} M. pH was varied in the range 4–7.

At intermediate concentrations of the aquo complex (ca. 2×10^{-4} M), dispersion effects were operative, due to the slow formation of a colloidal precipitate; although the final A_t values were most probably affected by some error, the linear plots were well-behaved up to 3 half-lives and led to slightly lower numerical k_{obsd} values compared to those obtained with diluted solutions. At higher concentrations (ca. 10^{-3} M), no decay of the 440-nm band was observed; instead, a continuous shift of the maximum to lower wavelengths as well as an increase in absorbance was seen in the successive spectra, while the solution became cloudy. After several hours, a white precipitate was formed, which turned blue if air was allowed to enter the reaction medium.

The buildup of Fe^{2+} was followed either by adding 1,10-phenanthroline (phen) initially to the reaction medium or by treating periodically extracted aliquots of the reacting mixture with the same reagent. In both cases, the graph of A_t (absorbance at 510 nm, maximum of $Fe(phen)_3^{2+}$) vs. t showed an S-shaped behavior, although the induction period was in fact very short (about 3–4 min). Neglecting the first points, the plot of ln ($A_\infty - A_t$) vs. t was linear, with an essentially equal numerical value of k_{obsd} compared to that obtained from the decay at 440 nm. The treatment of kinetic data based on the growth of $Fe(CN)_6^{4-}$ concentration did not lead to well-behaved linear plots, probably because of overlapping spectra or dispersion effects.

A search for significant concentrations of reaction intermediates was made by adding ethylenediamine (about 1 half-life after initiating the reaction) under oxidizing conditions in an alkaline medium; this test has been successfully used in the identification of $Fe(CN)_4en^{2-}$, which turns red when oxidized to the diimine complex $Fe(CN)_4diim^{2-}$ (diim = NH=CH—CH=NH), and could be indicative of the presence of $Fe(CN)_4(H_2O)_2^{2-}$ in our solutions.[18] Alternatively, neutral $Fe(CN)_2(H_2O)_4$ was investigated by treating the reacting solution with phen in the presence of chloroform at different times. In both cases negative results were obtained.

Results and Discussion

The stoichiometry of the thermal decomposition reaction conformed to eq 1, as shown by concentration changes of the

$$Fe(CN)_5H_2O^{3-} \rightarrow {}^{5}/_{6}Fe(CN)_6^{4-} + {}^{1}/_{6}Fe^{2+} + H_2O \tag{1}$$

reactant anion as well as those for both products of the reaction. A set of successive spectra shows that the decay of the peak centered at 440 nm is accompanied by the appearance

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