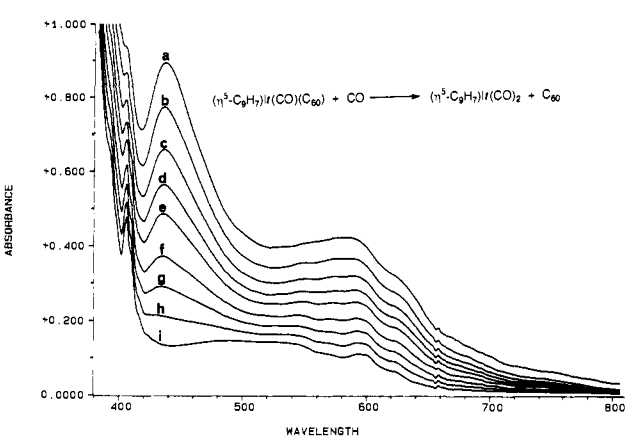
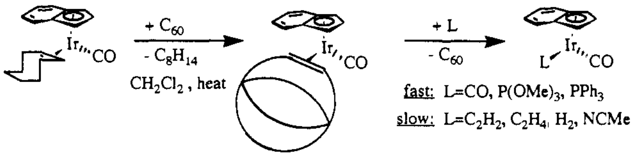


Figure 1. Absorption spectra recorded after the exposure of compound **1** in dichloromethane solution to carbon monoxide: (a) 5 s, (b) 15 s, (c) 25 s, (d) 35 s, (e) 45 s, (f) 65 s, (g) 85 s, (h) 120 s, (i) 10 min.

Scheme I



NMR spectrum of **1**, we presume that the iridium center is bound to the "double-bond site" of C_{60}, i.e., exo to the five-membered rings, as found for both the osmate ester[5b] and platinum[6a] derivatives. The CO stretching frequency of the indenyliridium compounds provides a probe of electron density at the metal center,[11] and the marked shift to higher frequency in the C_{60} derivative **1** is a good indicator of the electron-withdrawing character of C_{60} as an olefinic ligand; this was deduced previously on chemical grounds.[6a]

The cyclic voltammogram of complex **1** (CH_2Cl_2, 0.05 M $[NBu_4][PF_6]$, 100 mV/s) provides a direct indication of charge transfer upon complex formation. Two quasi-reversible reduction waves are seen at −0.75 and −1.10 V (ferrocene internal reference[12]) compared to −0.63 and −1.03 V for C_{60} under the same conditions.[13] Since the voltammogram of $(\eta^5\text{-}C_9H_7)Ir(CO)(\eta^2\text{-}C_8H_{14})$ shows no evidence of electroactivity to ca. −1.5 V, the addition of electrons to complex **1** appears to be largely localized on the C_{60} ligand. The negative shift of ca. 100 mV in the reduction potentials is consistent with a more negative C_{60} moiety after binding to the iridium center.

The visible absorption spectrum of complex **1** contains a strong band at 436 nm (ϵ ca. 8000 cm^{-1} L M^{-1}) as well as generally stronger absorption throughout the visible region compared to C_{60} alone. Changes in color of solutions of **1** provide a convenient way to monitor its susceptibility to reactions, especially those leading to displacement of C_{60} (see Scheme I). Thus, exposure of a solution of the complex to an excess of CO, $P(OMe)_3$, or PPh_3 leads to a rapid (ca. 1 min) change in color from green to the characteristic mauve of C_{60}; the known derivatives $(\eta^5\text{-}C_9H_7)Ir(CO)(L)$, which are pale yellow to colorless compounds, can be observed by their IR (ν_{CO}) bands.[11] Figure 1 shows the spectral changes for a saturated solution of CO in dichloromethane at room temperature. Under these conditions (10^{-4} M complex, ca. 0.2 M CO), the pseudo-first-order rate constant is 0.02 s^{-1}. Significantly, exposure of solutions of complex **1** to a second class of potential reactants, e.g., C_2H_4, C_2H_2, H_2, and $NCCH_3$, does not lead to any color change over the course of 5–10 min. Quantitative monitoring of the solution indicates small absorbance changes in the case of ethylene (<5% in 5 min), but it is clear that any reaction with ethylene, despite the known stability of the substitution product,[7] is more than 100 times slower than the reaction with carbon monoxide. We take these reactivity differences, in which smaller and/or more nucleophilic ligands are favored, to indicate an associative path for the substitution reaction, as has been seen for other reactions involving indenyl metal complexes.[14]

A number of interesting questions regarding the effect of metal substitution on the properties of the C_{60} framework can be formulated, and we are exploring some of these with complex **1**. Interestingly, we have not been able to observe any similar reaction with C_{70},[15] implying that C_{70} is a significantly poorer ligand.

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(12) Gagné, R. R.; Koval, C. A.; Lisensky, G. C. *Inorg. Chem.* **1980**, *19*, 2854.

(13) (a) Values of −0.61 and −1.00 V vs NHE with ferrocene as internal reference have been reported by the following: Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634. (b) Values of −0.33 and −0.73 V vs Ag/AgCl have been reported by the following: Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 1050.

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(15) UV-vis spectra clearly show that $[(\eta^5\text{-}C_5H_5)Ru(NCCH_3)_3]PF_6$ and C_{60} interact when combined in dichloromethane, presumably with release of one or more $NCCH_3$ ligands (compare ref 6a). However, no similar interaction with C_{70} (80–90% pure) is observed. Koefod, R. S.; Shapley, J. R., unpublished observations.

Multiplicity of Forms of Cyclopentanol and Other Five-Membered Rings in the Solid State

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The rapid internal motions of five-membered rings have made them a difficult subject for study by solution NMR.[2] Rapid pseudorotation at all available temperatures interconverts the envelope and twist forms and interchanges the substituent positions found on these two conformations. Solution NMR gives chemical shifts and coupling constants that are averages for all the various forms.[3] Individual conformers cannot be examined by X-ray methods, unless a single form happens to crystallize exclusively and does not undergo motion in the crystal. For the power of NMR to be brought to bear on simple five-membered rings, it will have to be done on the solid state. Variable-temperature studies with high-speed magic angle spinning and cross polarization have been able to slow conformational and other rate processes on the NMR time scale,[4] but the method has not been applied

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(1) (1) This work was supported by the National Science Foundation (Grant No. CHE-8910841) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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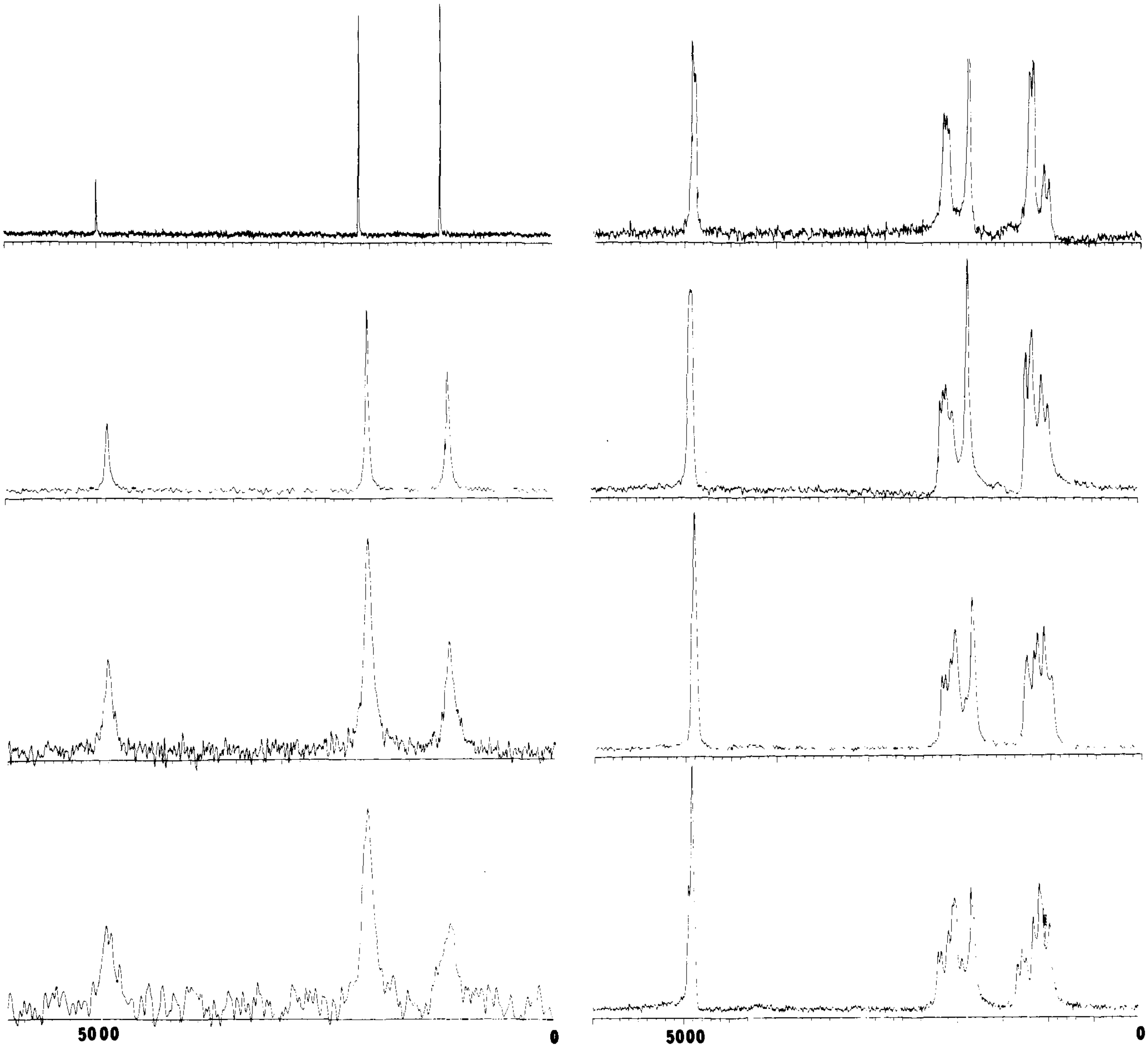

Figure 1. ^{13}C NMR spectrum of cyclopentanol at 75.428 MHz with cross polarization and magic angle spinning as a function of temperature. Left tier, top to bottom: 20, -75, -80, -85 °C. Right tier, top to bottom: -90, -100, -120, and -140 °C. The scale in hertz is arbitrary, each large tick representing 100 Hz. The fast-exchange peaks are at δ 23.9, 35.7, and 73.7.

to five-membered rings. We have found that reversible changes in the ^{13}C NMR spectrum of cyclopentanol and other five-membered rings reveal the existence of multiple forms in the solid.

The ^{13}C NMR spectrum of cyclopentanol (mp -19 °C) taken under MAS/CP conditions is shown in Figure 1 as a function of temperature. At room temperature the rapidly spinning liquid gives the normal high-resolution, isotropic, three-peak spectrum. As a solid, the sample gives an identical spectrum that begins to broaden at -75 °C.[5] Below -85 °C, each peak decoalesces into a multiplet. The resonance of C1 then consists of two equal-intensity peaks. Those of C2 and C3 each split into four peaks and, at -140 °C, seven or eight. Relative intensities change appreciably in the temperature range -90 to -140 °C. All these changes are entirely reversible.

Spectral multiplicity can come from a number of sources: different families of conformations; different positional isomers within a family; geminal isomers; hydrogen bonding between molecules to form dimers and oligomers that may not have the symmetry of the monomer; slow rotation around the C–OH bond; crystallographically different arrangements within the unit cell; multiple domains within the solid.

To our knowledge, there has been only one brief previous NMR study of cyclopentanol in the solid, and high-resolution methods were not used.[6] We have found no X-ray structure. We have sought to throw light on the observations of Figure 1 by examining other systems by the same technique. Such an approach can isolate which of the above-listed factors apply. We examined cyclohexanol (mp +25 °C) by the same procedure. For this molecule, more extensive NMR and X-ray work has been performed on the supercooled rotor solid.[7] Our high-resolution examination of cyclohexanol showed each of the peaks doubling and then splitting further into four or more peaks below -100 °C. Because cyclohexanol has only one conformational family and positional isomer, the spectral multiplicity for cyclohexanol and hence for cyclopentanol must be due in part to hydrogen-bonded forms. The

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(4) For reviews, see: Lyerla, J. R.; Yannoni, C. S.; Fyfe, C. A. *Acc. Chem. Res.* **1982**, *15*, 208–216. Fyfe, C. A. *Solid State NMR for Chemists*; C. F. C. Press: Guelph, Ontario, 1983; pp 405–419.

(5) Spectra were recorded on a Varian VXR 300 instrument with a Doty probe. Temperatures reported herein are uncalibrated and may be too low.

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low-temperature spectrum of c-C_5H_9-OD shows significant changes in peak intensity, confirming that some of the various forms result from hydrogen bonding.

We also examined sulfolane, $SO_2(CH_2)_4$ (mp +27 °C), for which X-ray results have been reported.[8] We find that each peak in the melt (C1 and C2) splits into two peaks with a ratio of about 2/1 below +10 °C. These must come from different conformers, as hydrogen bonding is not a factor. Solid cyclopentanone also gives two peaks from all but one carbon.

Cyclopentanol, cyclohexanol, and sulfolane crystallize from the liquid into plastic crystals, in which the molecules, because of their globular shapes, still retain the freedom to rotate.[9] The NMR decoalescence occurs close to the transition temperature from plastic to nonplastic forms.[10] Above coalescence, the spectrum is like that of the isotropic liquid. At the plastic to nonplastic transition temperature, the spectrum passes through a dynamic decoalescence to give a spectrum characteristic of the solid. Sulfolane and cyclopentanone in the nonplastic solid contain two distinct, probably conformational environments for each carbon. Cyclopentanol and cyclohexanol contain numerous environments for C2 and C3 brought about by hydrogen bonding. For these materials, which in general cannot give crystal structures, the NMR spectra can provide details about the forms present in the nonplastic phase.

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How Do Reaction Mechanisms Change? Appearance of Concerted Pericyclic Elimination for the Reaction of Cumyl Derivatives

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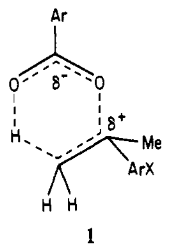
We report that destabilization of the carbocation intermediate of the stepwise solvolysis reaction of tertiary cumyl derivatives, XArC(Me)$_2$Y, by the addition of electron-withdrawing ring substituents, leads to a change in mechanism to *concerted pericyclic* elimination in which intramolecular proton transfer to the leaving group, Y = ArCO$_2$ or Cl, is concerted with C–Y bond cleavage (see **1**).



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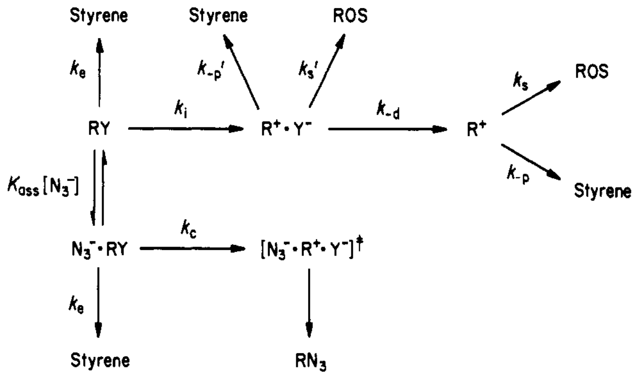
In 50:50 (v/v) trifluoroethanol/water, cumyl 4-nitrobenzoates, XArC(Me)$_2$OPNB, with $\sigma_x^+ < -0.08$, solvolyze by a stepwise S_N1 (or $D_N + A_N$)[1] mechanism through liberated carbocation intermediates that are captured by solvent with rate constants $k_s = 10^7$–10^9 s^{-1}.[2] There is very little ($\leq$1%)[3] deprotonation of the carbocation intermediate to give the corresponding α-methylstyrene (k_{-p}, Scheme I).[4] For $-0.08 \leq \sigma_x^+ \leq 0.12$, $k_s = 4 \times 10^9$–3×10^{10} s^{-1},[2] and the carbocation reacts with solvent largely before diffusional separation of the carbocation–leaving group ion pair can occur ($k_s' \approx k_{-d}$, Scheme I).[5] These reactions are accompanied by a larger amount (4–5%) of elimination, which may arise from proton abstraction by the leaving group within an ion pair (k_{-p}', Scheme I).[5-7]

Scheme I



Further destabilization of the carbocation intermediate leads to substantially larger yields of the α-methylstyrenes (Table I). The yields of α-methylstyrene for cumyl derivatives with $\sigma_x^+ \geq 0.34$ are 2–3-fold larger for the more basic pentafluorobenzoate compared with a chloride leaving group, and the fraction of elimination, f_{elim}, increases dramatically (up to 30% for 4-NO$_2$ArC(Me)$_2$OPFB or 3,5-(CF$_3$)$_2$ArC(Me)$_2$Cl) as the aromatic substituent X is made more electron withdrawing. For XArC(Me)$_2$Y with $\sigma_x^+ \geq 0.34$, the addition of 0.50 M NaN$_3$ leads to 20–30% yields of the azide adducts RN$_3$ by a preassociation mechanism (K_{ass} and k_c, Scheme I) in which azide ion provides no *assistance* to the reaction of the substrate ($k_i = k_c$).[2,8] Product analysis[4] showed that the azide adduct is formed solely at the expense of the solvent adducts ROS: the yield of α-methylstyrene is *independent* of [N$_3^-$]. This shows that solvolysis and elimination occur by *separate* pathways (k_i and k_e, Scheme I) and *not* by partitioning of a common ion pair intermediate. The reaction of the encounter complex N$_3^-$·RY to give the azide adduct RN$_3$ would be expected to lead to a decrease in the yields of *all* products formed from reaction of free RY, including any derived from intimate or "tight" ion pairs. Therefore, the independence of the yield of α-methylstyrene of [N$_3^-$] requires that elimination also occur from the complex N$_3^-$·RY, with a rate constant (k_e) equal to that for elimination from RY alone. The formation of α-methylstyrene from N$_3^-$·RY *must* be by a concerted mechanism, because the triple ion complex [N$_3^-$·R$^+$·Y$^-$] is too unstable to exist as an intermediate.[9]

The following structure–reactivity effects are consistent with the formation of α-methylstyrene from 3-F-, 4-NO$_2$-, and 3,5-(CF$_3$)$_2$-substituted cumyl pentafluorobenzoates and chlorides by *concerted* elimination at the neutral substrate (k_e, Scheme I) that occurs both in the presence and in the absence of an associated

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(3) For XArC(Me)$_2$OPNB with $\sigma_x^+ < -0.08$ it was not possible to demonstrate that the substrate was completely free of α-methylstyrene.

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(9) The estimated rate constant for collapse of [N$_3^-$·3,5-(CF$_3$)$_2$ArC(Me)$_2^+$·Cl$^-$] to give RN$_3$ is $k_{nuc} \approx 10^{19}$ s^{-1}.[2] Therefore, this species has a lifetime much shorter than the time for a single bond vibration (~10^{-13} s) so that it cannot exist as an intermediate.[2,8] Even if it were to form, then it would give only RN$_3$, because the barrier for addition of the strong nucleophile N$_3^-$ to the carbocation is much smaller than that for deprotonation to give α-methylstyrene.

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