

inhomogeneous components.^{9,10}

Resonance Raman spectra of CHD were obtained with excitation at 252, 266, 274, 282, and 292 nm. The absorption spectrum and Raman excitation profiles were calculated by using time-dependent wavepacket propagation techniques, and the set of excited-state parameters was adjusted to achieve the best agreement with experiment by using the methods we have described earlier.^{8a,9} The final excited state Δ 's and line widths are summarized in ref 11. Especially notable is the large homogeneous line width of 900 cm^{-1} , which corresponds to a relaxation time of ~ 10 fs.

Shown in Figure 1 is the Raman spectrum of CHD excited at 292.6 nm, ~ 500 cm^{-1} above the onset of absorption. The initial dynamics of the photoexcited molecule can be read directly from the spectrum: the ethylenic bond order inversion and flattening from C_2 symmetry to C_{2v} are evidenced by intensity in the 1578 cm^{-1} C=C stretch ($\Delta = 1.7$) and 507 cm^{-1} C=C-C=C torsion ($\Delta = 0.5$). The prominent 1321- cm^{-1} line ($\Delta = 0.8$) has been assigned as a totally symmetric (A species) wagging of the axial methylene hydrogens about an axis parallel to the C_2 symmetry axis.¹² The 948 cm^{-1} CH₂-CH₂ stretch shows a significant Δ of 0.4. Both of these modes are major components of the conrotatory ring opening reaction coordinate. The absence of B species CH₂ wag overtone intensity (data not shown) precludes any initial motion toward a pentadienyl-methylene geometry.¹³ Rapid concerted methylene CH bond rehybridization toward the shorter sp² C-H equilibrium geometry is ruled out by the absence of methylene CH stretching intensity near 2950 cm^{-1} . It is evident that excitation to the lowest allowed electronic state of CHD induces rapid barrierless motion on a trajectory toward the geometry of *all-cis*-hexatriene.

An explicit picture of the geometry changes that occur in CHD after electronic excitation can be generated by propagating a wavepacket on the experimentally derived excited-state surface. The arrows in Figure 1 present a superposition of the atomic displacements that occur along the 948- and 1321- cm^{-1} modes. The scissile C-C bond length increases by 0.1 Å and the axial CH bonds rotate 10° toward the molecular pseudoplane in the first 20 fs.¹⁴ This observation is conclusive evidence of participation of the CH₂-CH₂ group in this nominal $\pi \rightarrow \pi^*$ excitation.

In summary, this is the first direct experimental observation, to our knowledge, of the early stages of any pericyclic rearrangement. *The unique aspect of this approach is that it permits the quantitation of mode-specific, ultrafast chemical dynamics without resorting to time-resolved measurements.* This work, which is being extended to include cyclobutene and cyclooctatriene, provides new data which can be used to critically evaluate theoretical calculations of excited-state potential surfaces for pericyclic rearrangements.

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(10) (a) Grundherr, Chr. v.; Stockburger, M. *Chem. Phys. Lett.* **1973**, *22*, 253. (b) Schomacker, K. T.; Champion, P. M. *J. Chem. Phys.* **1986**, *84*, 5314.

(11) Trulson, M. O.; Dollinger, G. D.; Mathies, R. A. manuscript in preparation. Briefly, the final simulation was performed with an E_0 of 35 800 cm^{-1} , homogeneous half-width at half-maximum of 900 cm^{-1} , an electronic transition length of 0.65 Å, and displaced normal modes corresponding to the 12 strongest fundamentals (507 cm^{-1} , $\Delta = 0.54$; 557, 0.37; 750, 0.25; 948, 0.38; 1014, 0.25; 1057, 0.24; 1150, 0.35; 1237, 0.37; 1321, 0.82; 1404, 0.20; 1435, 0.09; 1578, 1.72).

(12) Normal mode assignments taken from: Di Lauro, C.; Neto, N.; Califano, S. *J. Mol. Struct.* **1969**, *3*, 219.) Those calculated in this laboratory by the QCFF/pi method, as outlined in Warshel et al. (Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* **1972**, *94*, 5612) are in qualitative agreement. However, following Carreira et al. (Carreira, L. A.; Carter, R. O.; Durig, J. R. *J. Phys. Chem.* **1973**, *59*, 812) we assign the ring breathing mode at 847 cm^{-1} and the CH₂-CH₂ stretch at 948 cm^{-1} .

(13) B species fundamental scattering is forbidden if the ground electronic state maintains C_2 symmetry. The pentadienyl-methylene structure is generated by simultaneous evolution along A and B species twist coordinates, which would give rise to B twist overtone scattering.

(14) The conversion from dimensionless Δ values to internal coordinate displacements δ in Å or radians may be found in ref 8a.

Redetermination of the Experimental Electron Deformation Density of Benzenetricarbonylchromium

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Recently Kok and Hall¹ reported a theoretical calculation of the deformation density of benzenetricarbonylchromium which was at variance with previous experimental studies,^{2,3} particularly in the region close to the metal. Stimulated by this discrepancy, we redetermined the electron density distribution in the molecule using the X-X method.⁴ In contrast to the previous experimental work, we find positions for the maxima around the chromium atom that are close to those in the theoretical calculations. The results indicate, however, that the C_{3v} symmetry assumed in the theoretical calculations is a poor approximation for the symmetry of the molecule in the crystal and that a small distortion in the geometry of a transition-metal complex in a crystal can have a significant effect on the electron deformation density around the metal.

X-ray diffraction data were collected to a $\sin \theta/\lambda = 1.0$ Å⁻¹ by using Mo K α X-radiation. Experimental details are summarized in ref 5; more detailed information has been deposited. Data collection differed from that in previous studies in two important aspects. First, each reflection was multiply measured around the scattering vector (ψ scans), and, second, the strongest reflections were measured with a lower incident X-ray intensity and rescaled. A total of 16444 intensities were measured. Equivalent reflections were averaged to give 2590 independent reflections ($R_{av} = 0.01$). Only those reflections with $I > 2.0\sigma(I)$ (2484 reflections) were used for calculation of the electron deformation density.⁵

The electron deformation density in this study agrees well with the theoretical results of Kok and Hall, at least in the sections that are available to us.¹ Figure 1 shows a comparison of the theoretical and present experimental electron deformation density in the plane of the chromium atom, one carbonyl group, and the center of the benzene ring. Four maxima can be seen around the metal, with one pointing toward the center of the benzene ring. The maxima appear sharper in the theoretical map, in spite of the fact that it has been corrected for the effects of thermal motion.⁷ The deformation density in an equivalent plane passing

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(1) Kok, R. A.; Hall, M. B. *J. Am. Chem. Soc.* **1985**, *107*, 2599-2604. The top part of Figure 1 is taken from Figure 3 of this paper, p 2602.

(2) Rees, B.; Coppens, P. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2516-2528.

(3) Troup, J. M.; Extine, M. W., unpublished results in ref 1.

(4) O'Connell, A. M.; Rae, A. I. M.; Maslen, E. N. *Acta Crystallogr.* **1966**, *21*, 208-219.

(5) Data were collected from a prismatic crystal, 0.24 \times 0.20 \times 0.33 mm, at 100 K on an Enraf-Nonius CAD-4 diffractometer using Mo K α ($\lambda = 0.71069$ Å) X-radiation. The diffraction data were measured up to θ of 46° ($\psi = 0^\circ$); in addition, reflections in the range $\theta < 20^\circ$ were measured at $\psi = \pm 15^\circ, \pm 30^\circ, \pm 45^\circ$, making a total of seven equivalents in this range. For $22^\circ < \theta < 40^\circ$ reflections were also collected at $\psi = 15^\circ$. In total 16444 reflections were measured. Data were corrected for the effects of absorption (grid point $7 \times 7 \times 11$) and averaged to give a total of 2590 unique reflections ($R_{av} = 0.012$), among which 2484 reflections were observed ($F_o > 4\sigma(F_o)$). Eighty strong reflections were measured without an attenuator at a lower X-ray source intensity and rescaled. Cell parameters were obtained by a least-squares fit to the θ values of 82 reflections. $a = 6.0328$ (6) Å, $b = 10.954$ (1) Å, $c = 6.5217$ (3) Å, $\beta = 100.675$ (4)° ($T = -173$ °C). $Z = 2$. Space group $P2_1/m$. The structure was refined by full-matrix least squares which included a secondary isotropic extinction correction ($g = 0.16$ (4) $\times 10^{-4}$). The final agreement indices were $R(F) = 0.022$, $R_w(F) = 0.027$, where $w = 1/(\sigma^2(I) + (0.01I_{rel})^2)$. Positional and thermal parameters of non-hydrogen atoms used for calculation of the deformation density maps were obtained from high-order refinement by using data with $\sin \theta/\lambda > 0.75$ Å⁻¹; the hydrogen atom coordinates were determined by moving the hydrogen atoms from their positions obtained from full data refinement along the C-H vector until the C-H distance was 1.085 Å.⁶ All the deformation density maps were calculated by using diffraction data with $\sin \theta/\lambda < 0.75$ Å⁻¹.

(6) Dunitz, J. D.; Seiler, P. *J. Am. Chem. Soc.* **1983**, *105*, 7056-7058.

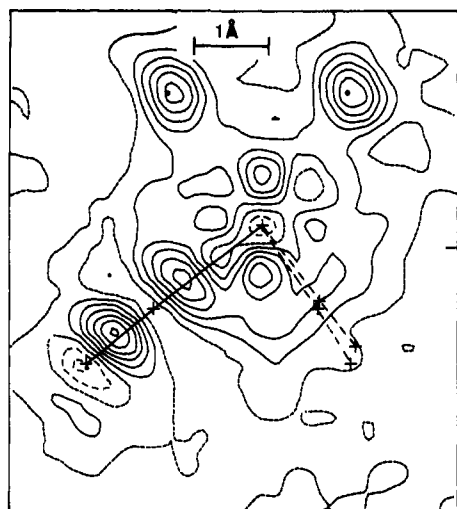
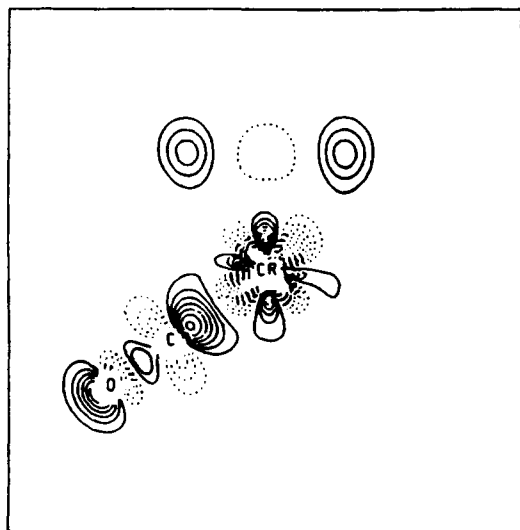


Figure 1. (Top) Theoretical electron deformation density¹ in a plane passing through the chromium atom, the center of the benzene ring, and one of the carbonyl groups. (Bottom) Experimental electron density from this study. Contour interval, $0.1 \text{ e } \text{Å}^{-3}$; negative contours dashed, zero contour dotted.

through the other independent carbonyl group is similar. The peaks in the Cr-C and C-O bonds appear to be well reproduced, but the relative peak heights are reversed in the two studies.⁸ The lone pair region on the oxygen atom is considerably weaker in this study and may be a result of a libration of the carbonyl group.⁹ Such a motion was neglected in the theoretical calculations. In all there are eight large peaks around the chromium atom, as is expected for a transition metal with six d electrons in an approximately octahedral crystal field.¹⁰

Figure 2 shows the deformation density in the plane containing the chromium atom and one of the long C-C bonds in the coordinated benzene ring. The deformation density in this plane is similar to that in the equivalent plane passing through the

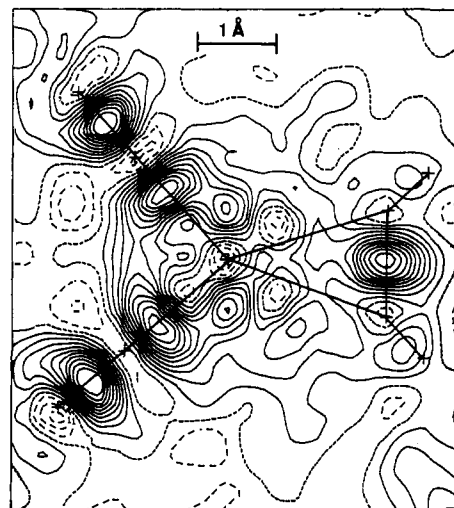


Figure 2. Electron deformation density in a plane passing through the chromium atom and a long C-C bond of the benzene ring. Two carbonyl groups lie almost in the plane. An approximate mirror plane of symmetry relates the top and bottom halves of the figure.¹¹ Contour interval, $0.05 \text{ e } \text{Å}^{-3}$.

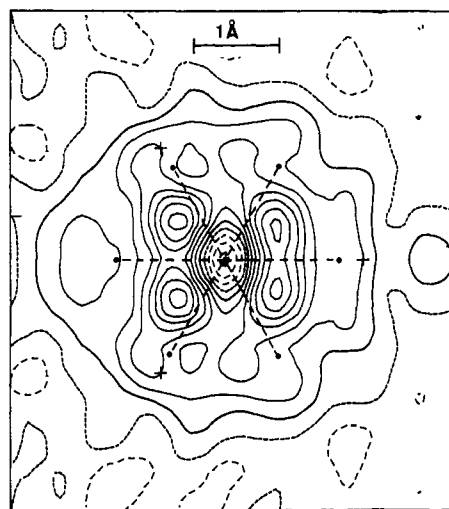


Figure 3. Electron deformation density in a plane parallel to the plane of the benzene ring passing through the chromium atom. Dashed lines connect the chromium atom to the midpoints of the C-C bonds in the benzene ring, and the carbon atoms of the three carbonyl groups are indicated by crosses. Contour interval, $0.05 \text{ e } \text{Å}^{-3}$.

chromium atoms and the other independent long C-C bond. They are both characterized by two regions of negative deformation density between the metal and the C-C bonds, which can be attributed to donation of electron density from a d orbital on the metal into the carbon p orbitals on benzene.

The molecules of benzenetricarbonylchromium do not take full advantage of the C_{3v} symmetry available to them on crystallization but lie on mirror planes of symmetry in the crystal.⁵ In order to see whether the electron density exhibited a local 3-fold axis of symmetry around the molecule, we calculated the deformation density in a plane parallel to the plane of the benzene ring passing through the chromium atom. The result is given in Figure 3 and shows four peaks around the metal with heights of $0.35 \text{ e } \text{Å}^{-3}$. The expected $3m$ symmetry of the map is broken, even far from the crystallographic mirror plane.¹² Closer inspection of the bond angles in the molecule revealed significant deviations from idealized symmetry not seen in the bond distances, which within their respective standard deviations satisfy a 3-fold axis of sym-

(7) The effect of thermal motion on the electron deformation density has been discussed by: Breitenstein, M.; Dannöhl, H.; Meyer, H.; Schweig, A.; Seeger, R.; Seeger, U.; Zittlau, W. *Int. Rev. Phys. Chem.* **1983**, *3*, 335-391.

(8) This was also seen for $\text{Cr}(\text{CO})_6$. Experimental: Rees, B.; Mitschler, A. *J. Am. Chem. Soc.* **1976**, *98*, 7918-7924. Theory: Sherwood, D. E., Jr.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93-100.

(9) Coppens, P.; Dam, J.; Harkema, S.; Feil, D.; Feld, R.; Lehmann, M. S.; Goddard, R.; Krüger, C.; Hellner, E.; Johansen, H.; Larsen, F. K.; Koetzle, T. F.; McMullan, R. K.; Maslen, E. N.; Stevens, E. D. *Acta Crystallogr., Sect. A* **1984**, *440*, 184-195.

(10) Toriumi, K.; Saito, Y. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 28-81.

(11) Since the two halves are symmetry independent, the agreement between them gives a measure of the accuracy of the map. This appears to be one contour line, or $0.05 \text{ e } \text{Å}^{-3}$.

(12) Rees has pointed out that the error in the deformation density is higher close to a symmetry element. Rees, B. *Acta Crystallogr., Sect. A* **1976**, *432*, 483-488.

metry. Most significant are the differences in the angles D-Cr-CO, where D is the center of the benzene ring (123.7 (1)°, 127.8 (1)°, and 127.8 (1)°). The benzene ring is thus bent toward one carbonyl group while the symmetry-imposed mirror plane of symmetry is maintained.

The reason for this is unclear. As an 18-electron complex, benzenetricarbonylchromium should not be subject to a second-order Jahn-Teller distortion.¹³ There are no intermolecular distances between non-hydrogen atoms of less than 3.0 Å, so packing effects do not appear to be the cause, though this cannot be ruled out. In any case, it does seem that the bending of the benzene ring toward one carbonyl group has a noticeable effect on the deformation density around the chromium atom.¹⁴

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Supplementary Material Available: Table I, crystal data and details of data collection; Tables II and III, atomic coordinates and thermal parameters for full data and high-order refinements; Table IV, interatomic distances and angles; Figure 1, molecular structure, and Figures 2-9, selected sections through the electron deformation density (8 pages); Table V, observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

(13) Engleman, R. *The Jahn-Teller Effect in Molecules and Crystals*; Wiley-Interscience: New York, 1972.

(14) A referee has pointed out that such effects could be caused by anharmonic thermal motion of the chromium atom. The atom has, however, a small mean-square displacement ($U_{eq} = 0.009 \text{ \AA}^2$) and its thermal parameter is almost isotropic.

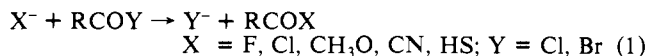
Intermediates and Transition States in Chloride Ion/Acyl Chloride Displacement Reactions

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In our previous gas-phase studies on reaction kinetics of nucleophilic substitution reactions at acyl halides, eq 1, we concluded



that the loose ion-neutral cluster is the global minimum along the reaction coordinate and that there is a sizable barrier separating the reactant and product clusters.¹ We also suggested for the case of a degenerate chloride exchange reaction, that the trivalent adduct is very likely a transition state rather than an intermediate in the corresponding displacement reaction.¹

Since then, at least, two theoretical studies dealing with this problem have appeared.^{2,3} We report here additional experimental evidence showing that the loose cluster ion does indeed exist in the gas phase as a stable species and that there is a sizable barrier to the exchange of the two chlorines in the ion-neutral cluster, $CF_3COCl \cdot Cl^-$.

(1) (a) Asubiojo, O. I.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3715. (b) Brauman, J. I. In *Kinetics of Ion-Molecule Reactions*, Ausloos, P., Ed.; Plenum: New York, 1979; pp 153-164. (c) Asubiojo, O. I. Ph.D. Thesis, Stanford University, 1977. (d) Dodd, J. A. Ph.D. Thesis, Stanford University, 1985.

(2) Klass, G.; Sheldon, J. C.; Bowie, J. H. *Aust. J. Chem.* **1982**, *35*, 2471.

(3) Dewar, M. J. S.; Storch, D. M. *J. Chem. Soc., Chem. Commun.* **1985**, 94.

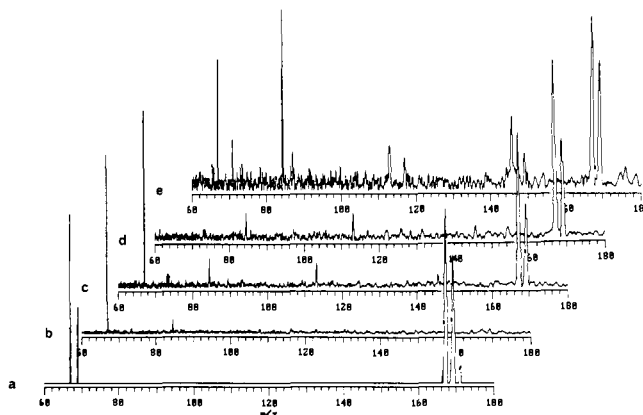


Figure 1. (a) 500 ms, 30 scans: $CH_3OH \cdot Cl^-$ (m/z 67, 69) and $CF_3COCl \cdot Cl^-$ (m/z 167, 169, 171). (b) 500 ms, preceded by an ion sweep out pulse (1-amu window centered at 67 amu), 50 scans. (c) 800 ms, 300 scans. (d) 800 ms, preceded by a second ion sweep out pulse (6-amu window centered at 169 amu), 300 scans. (e) 1100 ms, 1000 scans. In (b)–(e) the peak at m/z 84 is an artifact arising from 217.5-kHz noise. The signal-to-noise ratio becomes worse at longer delay times due to ion loss which reduces the ion abundance. The high-voltage ion ejection pulse also degrades the S/N ratio.

By analogy with solution-phase chemistry,^{4,5} it is generally believed that a tetrahedral adduct is also a stable species in carbonyl addition reactions in the gas phase.⁶ Some theoretical studies do show that such tetrahedral species are stable in the gas phase and are formed with small or no activation barriers from the separated anionic nucleophile and carbonyl compound.^{7,8} Sheldon found three stable clusters/adducts formed from CH_3O^- and acetone at STO-3G level of calculation, with the tetrahedral adduct being the most stable.⁹

In most experimental gas-phase studies, initial nucleophilic attack at carbonyl carbon could only be inferred from the products generated; in the relatively few instances when the adducts were detected, no definite structure could be assigned for them from available experimental information.¹⁰ In cluster ions formed by the addition of a solvated alkoxide anion to carbonyl compounds containing acidic α -hydrogens, a structure corresponding to an enolate anion solvated by an alcohol molecule is assigned.² Bartmess and co-workers put the adducts formed from addition of carbanions to carbonyl groups higher in energy than the corresponding ion-neutral loose complexes, leaving the question whether the tetrahedral adducts are transition state or stable

(4) In some cases salts of tetrahedral adducts have been isolated. See: (a) Fodor, G.; Letourneau, F.; Mandova, N. *Can. J. Chem.* **1970**, *48*, 1465. (b) Woodward, R. B. *Pure Appl. Chem.* **1964**, *9*, 49. (c) Zaugg, H. E.; Popenick, V.; Michaels, R. J. *J. Am. Chem. Soc.* **1964**, *86*, 1339. (d) Swarts, F. *Bull. Soc. Chim. Belg.* **1926**, *35*, 414. (e) Adickes, F. *Chem. Ber.* **1925**, *58B*, 1992. (f) For a broad spectrum of other examples, see references cited in ref 5b and 6f.

(5) (a) Fraenkel, G.; Watson, D. *J. Am. Chem. Soc.* **1975**, *97*, 231. (b) Guthrie, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 588. (c) Satchell, D. P. N.; Satchell, R. S. In *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Interscience: London, 1969.

(6) (a) McDonald, R. N.; Chowdhury, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4123. (b) DePuy, C. H.; Grabowski, J. J.; Bierbaum, V. M.; Ingemann, S.; Nibbering, N. M. M. *J. Am. Chem. Soc.* **1985**, *107*, 1093. (c) Nibbering, N. M. M. In *Kinetics of Ion-Molecule Reaction*; Ausloos, P., Ed.; Plenum: New York, 1979; pp 172-177. (d) José, S. M.; Riveros, J. M. *Nouv. J. Chim.* **1977**, *1*, 113. (e) Faigle, J. F. G.; Isolani, P. C.; Riveros, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 2049. (f) Bowie, J. H.; Williams, B. D. *Aust. J. Chem.* **1974**, *27*, 1923.

(7) (a) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517. (b) Weiner, S. J.; Singh, U. C.; Kollman, P. A. *J. Am. Chem. Soc.* **1985**, *107*, 2219. (c) Sheldon, J. C.; Bowie, J. H.; Hayes, R. N. *Nouv. J. Chim.* **1984**, *8*, 79. (d) Williams, I. H.; Spangler, D.; Maggiora, G. M.; Schowen, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 7831. (e) Bürgi, H. B.; Dunitz, J. D.; Lehn, J. M.; Wipff, G. *Tetrahedron* **1974**, *30*, 1563.

(8) For addition of neutral nucleophiles, see: Williams, I. H.; Spangler, D.; Maggiora, G. M.; Schowen, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 7717.

(9) Sheldon, J. C. *Aust. J. Chem.* **1981**, *34*, 1189.

(10) See, for example: (a) Klass, G.; Sheldon, J. C.; Bowie, J. H. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1337. (b) Dottore, M. F.; Bowie, J. H. *Ibid.* **1982**, 283.