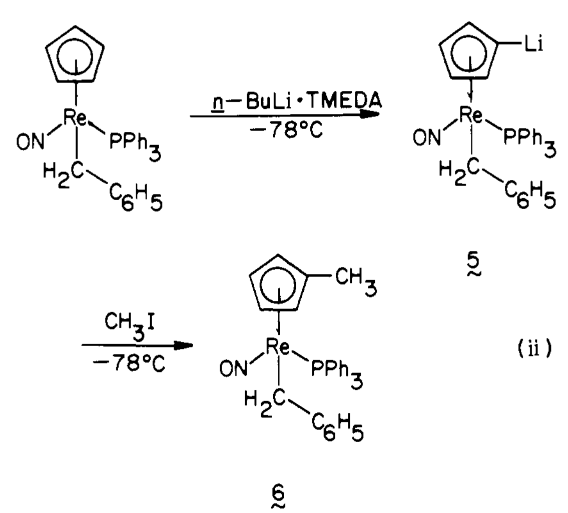
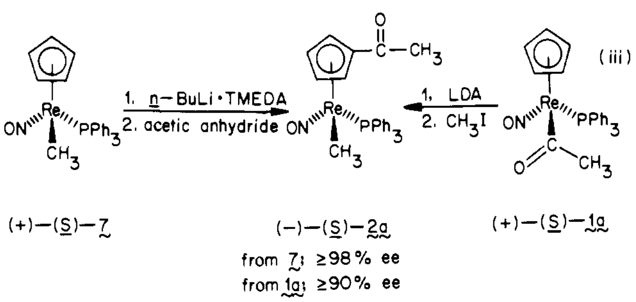


(ii)

nances of each enantiomer. With this optical purity assay available, the reaction of methyl complex **7** with *n*-BuLi·TMEDA and acetic anhydride was repeated with (+)-(*S*)-**7**, (≥98% ee, prepared from (+)-(*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$).[11] Levorotatory **2a**, ≥98% ee, was obtained. Since this transformation occurs without apparent rupture of any metal–ligand bonds, we assign the product as (−)-(*S*)-**2a** (eq iii), corresponding to retention of configuration at rhenium. Next eq i was repeated with (+)-(*S*)-**1a** (≥98% ee, also prepared from (+)-(*S*)-$[(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(CO)]^+BF_4^-$).[7] This gave (−)-(*S*)-**2a**, ≥90% ee (eq iii). Hence the rearrangement **3a** → **4a** proceeds with a high degree of *retention*.



(iii)

The above results are important in several contexts. First, migrations of $Mo\text{–}Ge(C_6H_5)_3$[3a] and $Fe\text{–}Si(CH_3)_3$[3c] to coordinated $\eta^5\text{-}C_5H_4Li$ have been previously reported. Our data indicate that such rearrangements (1) are likely to be of appreciable generality with regard to the metal and migrating ligand[6] and (2) can be intramolecular and highly stereoselective. Some conceptually related organometallic rearrangements have been recently analyzed by Hoffmann.[5] Also, note the intriguing parallel of eq i to the Wittig rearrangement,[4a] in which an alkyl ligand of an ether oxygen is α-deprotonated to $R'\bar{O}CHR$, followed by ligand′ migration to give oxygen anion $^-OCHRR'$. Finally, other cyclopentadienylmetal acyl complexes are deprotonated by LDA on the *acyl* ligand.[2] Is the contrasting chemistry of **1a** and **1c** kinetically or thermodynamically controlled? We estimate, on the basis of previously noted parallels,[7,11] that the pK_a's of the $ReCOCH_2R$ protons of **1a** and **1c** are similar to those found in amides.[12] The pK_a of $CH_3CON(CH_3)_2$ is, depending upon solvent, 31–34, and α-phenyl substitution enhances amide acidity by ca. 7 pK_a units.[12] The pK_a's of $\eta^5\text{-}C_5H_5$ C–H bonds in $(\eta^5\text{-}C_5H_5)Fe(CO)_2(R)$ complexes are in the range 29–30.[13] Hence, it is highly probable that the deprotonation of **1c** is kinetically controlled. Experiments designed to probe this point, and other aspects of the above reactions, are in progress.

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Supplementary Material Available: Table of characterization of new compounds (3 pages).[8] Ordering information is given on any current masthead page.

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Force Constants for the Cyclopropenyl Cation

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Although the unsubstituted cyclopropenyl cation ($C_3H_3^+$) has been known since the experiments of Breslow and co-workers in the late 1960s,[1] the bonds in this simplest of aromatic systems (Hückel $4n + 2$, $n = 0$) are not experimentally well characterized. We now report empirical force constants for the bonds of this ion, as derived from normal coordinate calculations applied to the fundamental vibration frequencies of $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$. The force constants for CC stretching, CH stretching, and in-plane CH bending of the cyclopropenyl cation are larger than the corresponding ones in benzene. The notably high value for the CC stretching force constant supports the value obtained in the ab initio calculation of Takada and Ohno.[2]

The precursors of the $C_3H_3^+$ and $C_3D_3^+$ ions were 3-chlorocyclopropene-d_0 and -d_3.[1c,3] The precursor of the new species, $C_3H_2D^+$, was prepared by a two-step reduction process in which perchlorocyclopropene was treated with tributyltin hydride, and the product was treated with tributyltin deuteride. For all of the cation preparations BF_3 was used as the Lewis acid. Samples for Raman spectroscopy at −50 °C were prepared in SO_2 solution, and samples for infrared spectroscopy at −196 °C were prepared as polycrystalline deposits on a cesium iodide window by a bilayer reaction technique.[4]

Table I summarizes the observed fundamental vibration frequencies and assignments for the in-plane modes of the three cations. Assignments for the out-of-plane modes, which are incomplete at the present time, are not included. The assignments of the IR bands of $C_3H_3^+$ and $C_3D_3^+$ are in reasonable agreement with the observations of Breslow et al. for Nujol mulls of the $SbCl_6^-$ salts.[1b] Except for the a_2' modes of the two ions of D_{3h} symmetry, which are neither infrared nor Raman active, and ν_9 of the $C_3H_2D^+$ ion, all of the in-plane fundamental frequencies have been observed for the three ions in one or both spectroscopies.

Normal coordinate calculations were carried out in the harmonic approximation in internal coordinate space with well-known matrix formalisms and standard computer programs.[5,6] A nonredundant set of internal coordinates [three CC stretching, three CH(D) stretching, and three CH(D) bending] were used.[7] The three simple valence force constants and four of the seven possible interaction force constants of the general valence force field were employed. Table II contains a comparison of the fitted and observed frequencies. The good quality of the fit is reflected in

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(7) Assumed bond lengths: CC, 1.398 Å; CH, 1.09 Å.[2]

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Table I. Observed Frequencies for the In-Plane Vibrational Fundamentals of $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$ (in cm^{-1})[a]

		$C_3H_3^+$		$C_3D_3^+$				$C_3H_2D^+$	
		IR	Raman	IR	Raman			IR	Raman
a_1'	ν_1		3183		2480[b]	a_1	ν_1	3175	3166[b]
	ν_2		1626		1490		ν_2	2387	2404[b]
							ν_3		1584
a_2'	ν_3						ν_4	1266	1267
							ν_5	905	923
e'	ν_4	3137	3138	2348	2349				
	ν_5	1295	1290	1250	1248	b_1	ν_7	3132	3134
	ν_6	920	927	670	675		ν_8	1289	1286
							ν_9		
							ν_{10}	720	717

[a] IR spectra were recorded on a Perkin-Elmer 580B spectrometer. Raman spectra were obtained with a Nicolet 1180-computer-assisted Spex Ramalog 5 instrument. Excitation was with the 514.5-nm line of a Coherent CR6 argon ion laser. [b] Average of Fermi resonance doublet.

Table II. Comparison of the Calculated and Observed Frequencies for $C_3H_3^+$, $C_3D_3^+$, and $C_3H_2D^+$ (in cm^{-1})

		$C_3H_3^+$		$C_3D_3^+$				$C_3H_2D^+$	
		obsd	calcd[a]	obsd	calcd			obsd	calcd
a_1'	ν_1	3183	3182	2480	2480	a_1	ν_1	3166	3169
	ν_2	1626	1633	1490	1482		ν_2	2404	2395
							ν_3	1584	1584
a_2'	ν_3		1119		909		ν_4	1267	1262
							ν_5	923	925
e'	ν_4	3138	3138	2349	2349				
	ν_5	1290	1295	1248	1243	b_1	ν_7	3134	3138
	ν_6	927	927	675	670		ν_8	1286	1290
							ν_9		1083
							ν_{10}	717	723
		av diff	2.6		3.6				4.2

[a] These modes are characterized with summed potential energy distributions in symmetry coordinate space as follows:[6] ν_1 (94 s CH str), ν_2 (94 s CCC str), ν_3 (100 s CH bd), ν_4 [95 a CH str(1), 4 a CH str(2)], ν_5 [70 a CCC str(1), 18 a CCC str(2), 7 a CH bd(1), 3 a CH bd(2)], ν_6 [85 a CH bd(1), 5 a CH bd(2), 5 a CCC str(1), 4 a CCC str(2)]. s = symmetric, a = antisymmetric, str = stretch, bd = bend; only one mode of each degenerate pair in the e′ species is characterized here.

the 2.6, 3.6, and 4.2 cm^{-1} average differences in frequencies. The fitted force constants (with statistical dispersions) for the cyclopropenyl cation are (in mdyn $Å^{-1}$ for stretch–stretch, mdyn Å rad^{-2} for bend–bend, and mdyn rad^{-1} for stretch–bend): CC str, 7.91 (17); CH str, 5.28 (02); CH bd, 0.60 (01); CC str/CC str, −0.37 (09); CC str/CH str (same C), −0.20 (03); CC str/CH str (different C), 0.19 (05); CC str/CH bd (same C), 0.16 (05).

For benzene Pulay, Fogarasi, and Boggs have used the scaled ab initio method to resolve discrepancies between various sets of empirical force constants.[8] Their preferred values are 6.578 for CC stretching, 5.176 for CH stretching, and 0.514 for CH in-plane bending. Each of the force constants in the cyclopropenyl cation is larger than the corresponding one in benzene. Adopting the customary correlation between bond strength and magnitude of force constants (e.g., CC stretching constants; saturated, acyclic hydrocarbons 4.70;[9] cyclopropane 4.29[10]), we conclude that both the CC and CH bonds are stronger in the cyclopropenyl cation than in benzene. A stronger CC bond in $C_3H_3^+$ also correlates with a shorter CC bond in cyclopropenyl cations than in benzene. For $C_3Ph_3^+$, r_{CC} = 1.373 Å and, for $C_3[N(CH_3)_2]_3^+$, r_{CC} = 1.363 Å;[11] for benzene, r_{CC} = 1.397 Å.[8] Ab initio calculations for the $C_3H_3^+$ ion also predict CC bond lengths shorter than in benzene.[2,12]

Previous work on empirical force constants for the $C_3H_3^+$ ion is limited to a Urey–Bradley force field (UBFF) derived from incomplete frequency data.[13,1b] UBFF constants have also been fitted to single-isotope vibrational assignments for $C_3Cl_3^+$ and $C_3Br_3^+$.[14] Not only are these several calculations underparameterized, but the resulting UBFF constants are not directly comparable to valence force constants. Of direct interest is Takada and Ohno's ab initio calculation (minimal basis set + C3d + CI) for the $C_3H_3^+$ ion itself, which gave 7.92 for the CC stretching force constant.[2] This surprisingly large value is now supported by our experiments.

The apparently greater CC bond strength in the cyclopropenyl cation than in benzene is remarkable in view of the lower bond order and the strained "σ" bonds in the ion. However, the positive charge on the ion should draw electrons into the bonding region of the ring, and the short CC bonds should give enhanced overlap in the delocalized π bonds,

It is well-known that force constants for stretching of CH bonds increase as the amount of s character in carbon orbitals increases in going from sp^3 in alkanes (4,9) to sp^2 in alkenes (5.1) to sp in acetylenes (5,9).[14] The dissociation energy of CH bonds also increases in this way but not as dramatically.[16] Thus, the CH bond in the cyclopropenyl cation with a force constant of about 5.3 is a strong bond with considerable sp character. A similar conclusion about the sp character of the CH bond in this ion was drawn from the large value of the ^{13}CH coupling constant in this ion[1b] and from the ab initio calculations.[2]

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Gas-Phase ^{1}H NMR Spectra and Nitrogen Inversion of Trimethylene Imine

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Gaseous trimethylene imine ($\overline{\mathrm{HN{-}CH_2{-}CH_2{-}CH_2}}$) produces ^{1}H NMR spectra indicative of an intramolecular chemical-exchange process whose characteristics are compatible with pyrimidal nitrogen inversion, In the liquid phase this process is obscured by very rapid intermolecular imine proton exchange[1] and has not been observed in cyclic imines larger than ethylene imine. Two major conclusions immediately follow from the temperature-dependent gas-phase NMR spectra shown in Figure 1: two magnetically inequivalent conformers are present in a 0.32/1.00 ratio at 30,0 °C, and the free energy for conversion between these conformers, $\Delta G^{\ddagger}$ is 17.9 (0.3) kcal/mol. These results are described more fully below and are discussed in relation to previous studies.

Trimethylene imine (Columbia Organic Chemical) and chloroform (Mallinkrodt) were degassed via five freeze–pump–thaw cycles prior to use. A gaseous sample containing 21,7 torr of trimethylene imine, 210 torr of Ar, and 15.8 torr of $CHCl_3$ (frequency and resolution reference) was prepared in a 3-cm-long 12-mm NMR tube using previously described methods.[2,3] ^{1}H

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