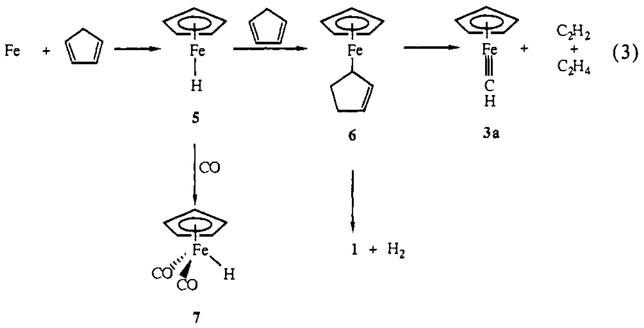
Table I. Yields of Ferrocenes in the Cocondensation of Fe Atoms, Cyclopentadiene, and Alkynes

alkyne reactant(s) (mmol) [mmol Fe][a]	product yields (mmol)
$CH_3C{\equiv}CCH_3$ (18.3) [15.4]	**1** (0.43), **2a** (0.223),[b] **2c** (0.049)[b]
$CH_3CH_2C{\equiv}CCH_2CH_3$ (17.6) [34.0]	**1** (0.31), **2b** (0.23),[b] **2d** (0.012)
$CH_3CH_2C{\equiv}CCH_3$ (17.5) [30.0]	**1** (0.25), 1,4-dimethyl-2,3-diethyl-**1** (0.42),[b] 1,4-diethyl-2,3-dimethyl-**1** (0.027)[b]
$CH_3C{\equiv}CCH_3$ (13.0), EtC≡CEt (8.8) [37.0]	**1** (0.12), **2a** (0.042),[b] 1,2-diethyl-3,4-dimethyl-**1** (0.027),[b] **2b** (0.013)[b]
$CH_3C{\equiv}CCH_3$ (12.3), C_2D_2 (17.4)[c] [25.0]	**1** (0.12), 1,2-dimethyl-**1** (0.014), trimethyl-**1** (0.009), **2a** (0.012), **2c** (0.005)
EtC≡CEt (10.6), C_2D_2 (15.0)[c] [28.0]	**1** (0.09), 1,2-diethyl-**1** (0.008), diethyl methyl-**1** (0.003), **2b** (0.012), **2d** (trace)
$CH_3C{\equiv}CH$ (11.4) [17.6]	**1** (0.349), 1,2-dimethyl-**1** (0.018), 1,3-dimethyl-**1** (0.012), trimethyl-**1** (0.009)
$CH_3C{\equiv}CH$ (13.4), C_2H_2 (13.4) [25.0]	**1** (0.247), 1,2-dimethyl-**1** (0.017), 1,3-dimethyl-**1** (0.013), trimethyl-**1** (0.011)
$HC{\equiv}CCH_2CH_3$ (19.0) [22.5]	**1** (0.713), 1,2-diethyl-**1** (0.11), 1,3-diethyl-**1** (0.076), trimethyl-**1** (trace)
C_2H_2 (21.8) [16.6]	**1** (0.513), methyl-**1** (0.034), dimethyl-**1** (trace)

[a] This value is the mmol of Fe vaporized. In all condensations 12.2 mmol of Cp–H was used. [b] These products were isolated by preparative GC and characterized by their NMR spectra. These and all other products were characterized by GC-MS and NMR spectra of product mixtures. See Supplementary Material tables. [c] Some products contained deuterium, see text.



in the present case may be a combination of the energetic reaction conditions[13] and the coordinative unsaturation about Fe which mandates the sharing of as many electrons as possible with the metal and renders these reactive intermediates kinetically accessible.

In order to gain information regrding possible high-energy gas-phase modes of reaction of Cp–H in the presence of Fe, we have carried out the reaction under conditions in which a gas-phase encounter between Cp–H and Fe is likely. Thus, when Fe is vaporized in the presence of Cp–H and the products are not condensed on the walls of the reactor but pumped directly into a trap at 77 K, C_2H_2 and C_2H_4 (in a 1.2:1 ratio) and **1** are isolated. Ball, Kafafi, Hauge, and Margrave[14] have demonstrated the formation of cyclopentadienyliron hydride, **5**, in the cocondensation of Fe atoms with Cp–H in an Ar matrix at 14 K. If we assume that **5** is an intermediate in the reaction between Cp–H and Fe under our conditions, we may postulate its reaction with Cp–H to give the η^1-cyclopentenyl complex **6** which could either go on to **1** or, under more energetic conditions,[13] cleave to C_2H_2, C_2H_4, and **3a**. That **5** is formed and has appreciable lifetime at 77 K is demonstrated by the fact that addition of CO after cocondensation of Fe and Cp–H gives cyclopentadienyldicarbonyliron hydride, **7**[15] (eq 3).

Further evidence that gas-phase metal-atom reactions occur in this system is provided by the fact that cocondensation of Fe on preformed surface of Cp–H and 2-butyne at 77 K (no hydrocarbons in the gas phase) gives only **1** and hexamethylbenzene (1:0.38 ratio) with no detectable **2a**. However, cocondensation of Fe and Cp–H onto a matrix of 2-butyne (Fe + Cp–H but no 2-butyne in gas phase) gives **1**, hexamethylbenzene, and **2a** in a 1:0.024:0.020 ratio.

The possible involvement of the acetylene, generated by the reaction in eq 3, was probed through the use of C_2D_2. When Fe, Cp-H, 2-butyne, and C_2D_2 are cocondensed, one of the products is 1,2-dimethylferrocene containing deuterium (d_0:d_1:d_2:d_3 = 0.3:15.3:43.6:40.9). Interestingly, the **2a** formed in this reaction is also labeled (d_0:d_1:d_2 = 72.7:25.6:1.6). The formation of **2a-d_1** and dimethylferrocene-d_3 in this reaction implies that some Cp—Fe≡CD, formed by a metathesis between **3a** and C_2D_2, is present.[18]

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Supplementary Material Available: Tables of NMR and mass spectral data for substituted ferrocenes (3 pages). Ordering information is given on any current masthead page.

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(15) Compound **7** was identified and quantitated by comparison of its IR spectrum[16] in methylcyclohexane with that of an authentic sample. Evaporation of solvent from the above reaction mixture gave cyclopentadienyliron dicarbonyl dimer, a known decomposition product of **7**[17] and **1** in a 0.29:1 ratio.

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A Direct Mechanism for S_N2 Nucleophilic Substitution Enhanced by Mode Selective Vibrational Excitation

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An important problem in gas-phase reaction dynamics is understanding the manner in which vibrational excitation of reactants may affect chemical reactions. This problem is of concern for both unimolecular[1-3] and bimolecular[4-11] reactions. It is well known that vibrational excitation of a diatomic reactant can enhance the reaction for A + BC → AB + C displacement with a late barrier so that the BC bond is extended at the saddlepoint.[4] For bimolecular reactions with polyatomic reactants, mode selective vibrational excitation is expected to enhance reaction if

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the mode displaces the molecular geometry to that for the saddlepoint and if the mode remains uncoupled to other modes as reactants interact.[5-11]

On first inspection, one might not expect the S_N2 nucleophilic substitution reaction to be significantly affected by mode selective

$$Cl_a^- + CH_3Cl_b \rightarrow Cl_a^-{-}CH_3Cl_b \rightarrow Cl_aCH_3{-}Cl_b^- \rightarrow Cl_aCH_3 + Cl_b^- \quad (1)$$

excitation of CH_3Cl_b. Both experimental[12] and theoretical[13] studies indicate the reaction occurs on a double well potential energy surface. The experiments have been interpreted with a model that assumes a long-lived $Cl_a^-{-}CH_3Cl_b$ cluster is formed.[14] Statistical theories are used to calculate rate constants for the cluster to dissociate to reactants $Cl_a^- + CH_3Cl_b$ or isomerize to the other cluster $CH_aCH_3{-}Cl_b^-$. Because the variational transition state[15] separating reactants and cluster has a much greater density of states (i.e., entropy) than the transition state at the saddlepoint for isomerization, statistical theories predict the cluster will preferentially dissociate to reactants. At 300 K thermal experiments are consistent with approximately one out of every 50000 clusters isomerizing.[16]

If the properties of the $Cl_a^-{-}CH_3Cl_b$ cluster are considered in more detail, it becomes less certain that CH_3Cl_b mode selective vibrational excitation will have a negligible effect on the substitution reaction. The intermolecular vibrational frequencies for the cluster are much lower than those for CH_3Cl_b.[17,18] Thus, as found for alkali association with ligands,[19,20] the $Cl_a^- + CH_3Cl_b$ intermolecular and CH_3Cl_b intramolecular vibrational motions may be significantly decoupled. Therefore, if vibrational modes in the reactant CH_3Cl_b are excited so that CH_3Cl_b attains the geometry associated with the isomerization saddlepoint as Cl_a^- collides, substitution may occur by a direct mechanism without forming either cluster. In the following, evidence is presented for such a direct mechanism.

In recent research, a global analytic potential energy function was developed[17] for reaction 1 from HF/6-31G* ab initio calculations, experimental CH_3Cl vibrational frequencies, and experimental bond dissociation energies. This analytic function is thought to give a good representation of the potential energy surface. The function reproduces the ab initio bond lengths and angles for the cluster and saddlepoint to within 0.04 Å and 0.20°, respectively. Scaled ab initio vibrational frequencies[21] for the cluster and saddlepoint are reproduced, on the average, to within 8.5%. The classical potential energy at the cluster and saddlepoint is 10.32 kcal/mol lower and 3.60 kcal/mol higher, respectively, than for the reactants.

With the above analytic potential, the classical trajectory method has been used to study the dynamics of reaction 1.[17] The trajectory calculations are performed with the general chemical dynamics computer program VENUS[22] which is an enhancement of MERCURY.[23] One hundred to 400 trajectories, with impact parameters and reactant orientations chosen randomly, are calculated for each initial condition specified by a $Cl_a^- + CH_3Cl_b$ relative translational energy E_{rel}, CH_3Cl_b normal mode energies, and a CH_3Cl_b thermal rotational energy distribution.[24] Each trajectory was followed for 20 ps.

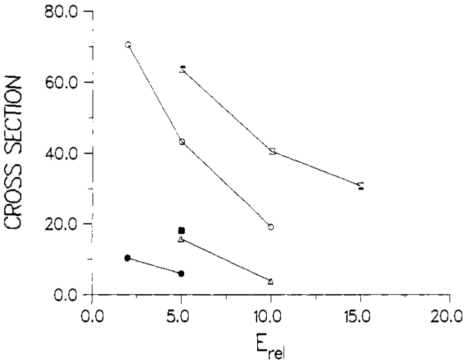

Figure 1. Reactive cross sections (Å^2) as a function of E_{rel} (kcal/mol), T_{rot}, and C–Cl stretch normal mode quantum number n: □, $n = 8$, $T_{rot} = 0$; ○, $n = 6$, $T_{rot} = 0$; Δ, $n = 4$, $T_{rot} = 0$; ■, $n = 8$, $T_{rot} = 300$ K; ●, $n = 6$, $T_{rot} = 300$ K. Each CH_3Cl_b rotation axis is excited with $RT_{rot}/2$ energy. The uncertainties in the cross sections vary from 17 to 25% for values greater than 19 Å^2 and from 32 to 57% for values less than 19 Å^2.

For vibrationally cold reactants and E_{rel} in excess of the substitution barrier, a small number of $Cl_a^-{-}CH_3Cl_b$ clusters are formed which dissociate to reactants. There are no isomerizations or substitutions. Cluster formation becomes more important as E_{rel} is decreased. At 300 K the experimental substitution cross section is estimated as 0.006 Å^2.[16,17] Observing no substitutions with vibrationally cold reactants is consistent with this value.

An attempt was made to promote substitution by exciting either the A_1 C–Cl_b stretch normal mode v_3 or the A_1 CH_3 deformation normal mode v_2, which have harmonic frequencies[25] of 744 and 1574 cm^{-1}, respectively. The motion of these modes displaces the equilibrium geometry of CH_3Cl_b to the isomerization saddlepoint geometry. For $E_{rel} \geq 2.0$ kcal/mol, no substitutions occurred by exciting v_2 and/or adding three or less quanta to v_3. However, if four or more quanta are added to v_3, backside substitution is observed. Eighty-eight percent of the substitutions are direct in that the trajectories are trapped in neither well and cross the saddlepoint only once. Only 1% of the substitution occurs via long-lived clusters. The remaining substitution trajectories are not long-lived, but cross the saddlepoint three times before reacting. In addition to these substitution trajectories, there are also trajectories which form long-lived clusters, 70% of which dissociate to reactants within 20 ps. To illustrate, for 100 trajectories with six quanta in v_3, $T_{rot} = 0$ K, trajectories. $E_{rel} = 2.0$ kcal/mol; there are 17 substitutions and 25 clusters formed. For vibrationally cold reactants, the numbers are 0 and 68, respectively, out of 400 trajectories.

Substitution cross sections, for four or more quanta in v_3, are displayed in Figure 1 as a function of E_{rel} and T_{rot}. It is seen that increasing T_{rot} greatly decreases the cross section. In contrast, the cluster formation cross sections are almost unaffected by rotational energy.[17] The significant decrease in the cross section for direct substitution upon rotational excitation is probably related to the narrow reaction path and restricted orientations required for passing over the isomerization saddlepoint. Attaining the necessary orientation may become more difficult as CH_3Cl_b is rotationally excited. Understanding the effect of rotational excitation on direct bimolecular reactions and ion–molecule reactions is an active area of research.[20,26-29]

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It is hoped that the work presented here will lead to experimental investigations of a direct mechanism for $X^- + CH_3Y \rightarrow XCH_3 + Y^-$ nucleophilic substitution. Such a mechanism may become more important as the heat of reaction becomes more exothermic. The rotational temperature dependence of the substitution cross section may provide one diagnostic for the direct mechanism.

Acknowledgment. This research was supported by the National Science Foundation. The trajectory calculations were performed, in part, at the NSF Pittsburgh Supercomputing Center.

Registry No. Cl^-, 16887-00-6; CH_3Cl, 74-87-3.

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A Shelf-Stable *syn*-Sesquinorbornatriene. An Extreme Example of a Crystallographically Determined π-Pyramidalization Angle[1]

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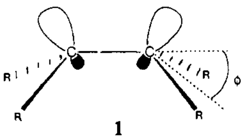
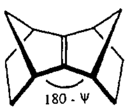
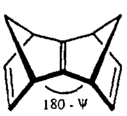
Recent research activity has added considerably to our understanding of alkene pyramidalization and to our ability to prepare molecules having olefin geometries that deviate appreciably from the norm.[3] Theoretical calculations indicate the p orbitals of C–C π bonds deformed in this manner to be transformed into hybrid orbitals that are not as well aligned for π bonding as are pure p orbitals.[4-6] Accordingly, chemical reactivity increases rapidly in proportion to the extent of structural deformation depicted in **1**. As a consequence, X-ray data have been acquired for only a select few pyramidalized alkenes whose reactivity levels are not overly intensified.[7-9]



1

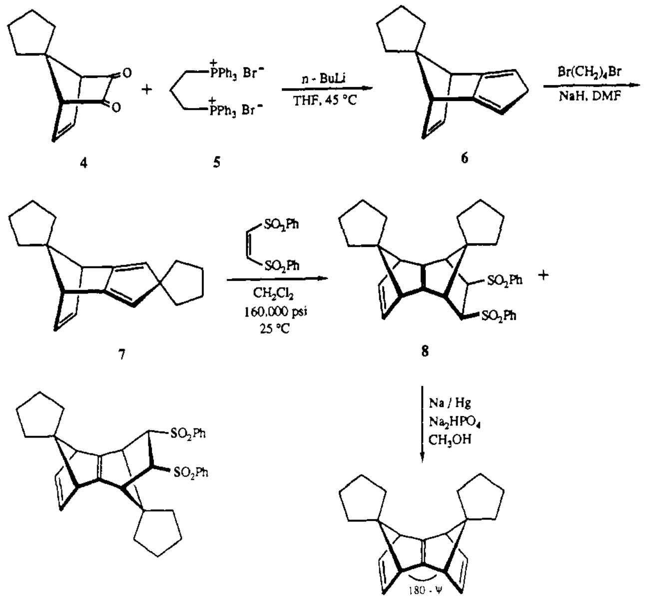


2



3

Scheme I



Our efforts in this area have been directed to *syn*-sesquinorbornene (**2**) and its dehydro analogues. Whereas derivatives of **2** experience substantial hinge-like bending in an endo direction (ψ = 16–18°),[10] introduction of a second (peripheral) double bond has the effect of enhancing the level of downward folding to approximately 21°.[11,12b] Removal of the last two protons to produce *syn*-sesquinorbornatriene (**3**) has been accomplished,[12] and certain of its spectral properties have been determined.[13] However, the high reactivity of **3** has so far precluded experimental definition of the extent of π-pyramidalization at its central double bond, conjectured to be the most extreme attainable under normal circumstances within a norbornadiene skeleton.[12]

We describe herein the preparation and crystallographic analysis of the first stable *syn*-sesquinorbornatriene (**10**). Since **3** is particularly subject to exo attack by atmospheric oxygen at its internal unsaturated linkage, approach from this face had to be sterically impeded. However, the intent was not to encumber the target molecule to such an extent that structural deformation beyond that already embodied in **3** would materialize concurrently.

To this end, bis-Wittig condensation of the known diketone **4**[14] with the double phosphonium salt **5** according to precedent[10e,15] afforded **6** (30%). This colorless oil[16] was spiroalkylated with 1,4-dibromobutane and sodium hydride in DMF[17] to give **7** (40%). Diels–Alder addition of (*Z*)-1,2-bis(phenylsulfonyl)ethylene[18] to

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(1) Part 47 of the series dealing with isodicyclopentadienes and related molecules. For part 46, see: Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics*, in press.

(2) Author to whom inquiries concerning the X-ray crystallographic analysis should be directed.

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