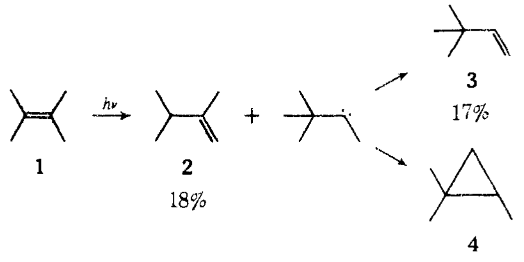
Communications to the Editor

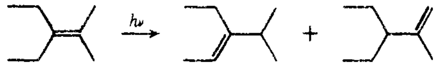
Photochemistry of Alkenes. V. [1,3]-Sigmatropic Hydrogen Shifts[1]

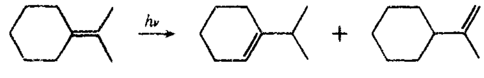
Sir:

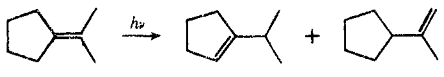
In contrast to the triplet manifold of simple alkenes, in which just one excited state (π,π^*) is clearly low lying, there are several excited states in the singlet manifold which are low lying and close in energy. Assignment of two of these as π,π^* and π,R(3s) is now widely accepted;[2,3] the presence of a π,σ^* state of similar energy has also been proposed.[3] Recent studies in these laboratories have been directed toward elucidating the *chemical* properties of these states and the effects of structure and environment on their behavior.

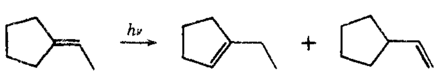
The principal photochemical processes which have been observed for simple alkenes on direct irradiation are cis ⇄ trans isomerization and [2 + 2] cycloaddition. These processes are generally attributed to the $^1(\pi,\pi^*)$ state. Recent studies from these laboratories have shown that tetrasubstituted alkenes display a competing type of behavior, as exemplified by the isomerization of **1** to a mixture of **3** and **4**, which involves a carbene intermediate and is thought to arise via the π,R(3s) Rydberg excited state.[4] We wish now to report the principal features of yet another photochemical process exhibited by alkenes on direct irradiation—1,2-positional migration of the double bond.

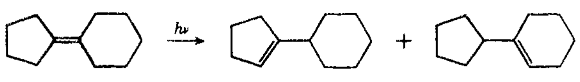

1 → **2** 18% + → **3** 17%, **4** 24%

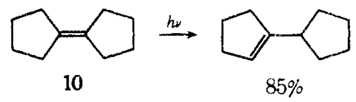

5 → 7% + 19%


6 → 26% + 22%

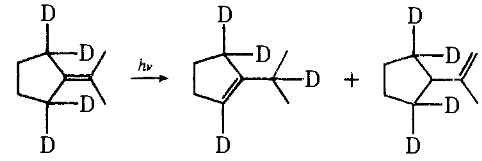

7 → **11** 83% + **12** 10%


8 → 54% + trace


9 → 83% + trace


10 → 85%

Scheme I



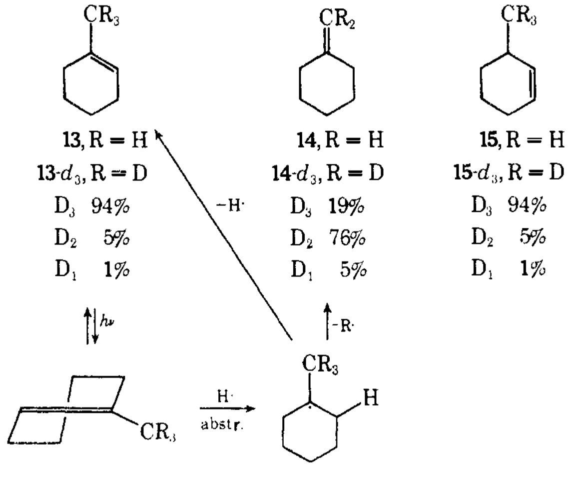
7-d_4	**11**-d_4	**12**-d_4
D_4 83	D_4 78	D_4 85
D_3 9	D_3 18	D_3 10
D_2 7	D_2 3	D_2 4
D_1 1	D_1 1	D_1 1

Thus irradiation of **1** in hydrocarbon solution affords, in addition to the carbene-derived products **3** and **4**, the positional isomer **2**.[5] Similarly, olefins **5–10** undergo positional migration of the double bond.[6] Of particular significance is the increased involvement of the double bond migration process in going from the acyclic olefin **5** to the six- and then five-membered ring analogues **6** and **7**. Indeed, as shown by olefins **7–10**, the double bond migration process strongly predominates in alkylidenecyclopentanes. Moreover, the double bond migrates preferentially into the five-membered ring.[7]

Labeling studies have indicated that the migration process is intramolecular. Irradiation of **1** in cyclohexane-d_{12} afforded the isomer **2** with no detectable incorporation of deuterium. Conversely, irradiation of **7**-d_4 afforded isomer **11**-d_4 with no significant deuterium loss (Scheme I), and the ^{1}H NMR spectrum of **11**-d_4 clearly showed the presence of deuterium in the isopropyl group. There was a significant isotope effect, with preference for migration into the ring dropping from 8.6:1 (**11:12**) in the case of **7** to 3.1:1 in the case of **7**-d_4.

The double bond migration process thus involves a [1,3]-sigmatropic shift of hydrogen.[8] The origin of the preferred migration into a five-membered ring is not clear. Likewise, the identity of the reactive excited state is uncertain. However, triplet sensitization of 3,4-dimethyl-3-hexene with *p*-xylene afforded cis ⇄ trans isomerization but no detectable migration.[9,10] Moreover, the migration process occurs even with di- and trisubstituted alkenes,[11] in contrast to other

Scheme II



13, R = H
13-d_3, R = D
D_3 94%
D_2 5%
D_1 1%

14, R = H
14-d_3, R = D
D_3 19%
D_2 76%
D_1 5%

15, R = H
15-d_3, R = D
D_3 94%
D_2 5%
D_1 1%

Rydberg-derived processes, which generally occur only in tetrasubstituted alkenes.[4] It thus appears that neither the π,π^* nor π,R(3s) state leads to migration. It is perhaps significant that σ strain in cycloalkenes and alkylidenecycloalkanes leads to low-lying $\pi \rightarrow \sigma^*$ transitions.[3] Thus the emergence of the migration process in alkylidenecyclopentanes may be due, at least in part, to the emergence of the π,σ^* state as the lowest lying singlet excited state. Work continues on identification of the excited state involved.

It must be cautioned, however, that not all light-induced positional isomerizations of alkenes involve exclusively an intramolecular hydrogen shift. Thus, although 1-methylcyclohexene (**13**) affords the positional isomers **14** and **15** on irradiation in ether or hydrocarbon solvent (13 and 6%, respectively), formation of **14** has been found to occur with substantial loss of deuterium from the labeled derivative **13**-d_3 (Scheme II). The difference in this case is almost surely associated with the now familiar tendency of cyclohexenes to undergo photoreaction via a highly strained twisted intermediate and probably involves initial cis $\rightarrow$ trans isomerization followed by hydrogen atom abstraction as shown. The partial retention of deuterium in **14**, accompanied by the formation of **15**, indicates that [1,3]-sigmatropic hydrogen shifts occur in competition with the intermolecular pathway.[12]

Acknowledgment. We are grateful to the Army Research Office for financial support.

References and Notes

(1) For part IV see H. G. Fravel, Jr., and P. J. Kropp, *J. Org. Chem.*, **40**, 2434 (1975).

(2) A. J. Merer and R. S. Mulliken, *Chem. Rev.*, **69**, 639 (1969).

(3) F. H. Watson, Jr., A. T. Armstrong, and S. P. McGlynn, *Theor. Chim. Acta*, **16**, 75 (1970); F. H. Watson, Jr., and S. P. McGlynn, *ibid.*, **21**, 309 (1971).

(4) T. R. Fields and P. J. Kropp, *J. Am. Chem. Soc.*, **96**, 7559 (1974).

(5) Irradiations were conducted on 115-ml pentane or octane solutions containing 20 mmol of olefin using a 450-W Hanovia mercury arc and quartz immersion well. Yields were determined by gas chromatographic analysis of aliquots removed from the irradiation mixture, calculated relative to an internal hydrocarbon standard, and based on consumed starting material.

(6) The expected carbene-derived products analogous to **3** and **4** were also isolated from irradiation of **5** and **6** in combined yields of 67 and 52%, respectively. Mixtures containing two or more products were isolated from irradiation of olefins **7–10** in total yields of 7, 18, 16, and 13%, respectively. These products were not identified because of their low yields and difficulties in separation. 3-Ethylcyclopentene (5%) and substantial amounts of a yellow polymer were also obtained from **8**.

(7) There was no significant change in product ratios as a function of time. Control studies showed that the disubstituted olefinic products related to **2** and **12** and the carbene-derived products from **1, 6,** and **7** are photostable under the irradiation conditions. However, the trisubstituted photoproducts related to **11** are somewhat photolabile and undergo partial reversion to the starting olefin. Thus, for example, irradiation of 1-ethylcyclopentene afforded the 3-isomer (21%) accompanied by **8** (9%).

(8) S. S. Hixson, J. C. Tausta, and J. Borovsky, *J. Am. Chem. Soc.*, **97**, 3230 (1975), have recently reported that 4-methyl-1,1,4-triphenyl-1-pentene undergoes photoisomerization to the 2-isomer via a carbene intermediate. Such a double bond migration process is not related to that reported here.

(9) By contrast, on direct irradiation the double bond migration products 3,4-dimethyl-2-hexene and 2-ethyl-3-methyl-1-pentene are formed, along with the expected carbene-derived products.[4]

(10) Similarly 2,6-dimethyl-2,6-octadiene, which undergoes double bond migration on irradiation at shorter wavelengths, exhibits only cis $\rightleftarrows$ trans isomerization on irradiation at 254 nm.

(11) For example, 3,5-dimethyl-3-heptene undergoes isomerization to the 2-isomer and 2-ethyl-4-methyl-1-hexene on irradiation in ether solution. Isomerization of 2-butene to the 1-isomer has been previously reported: H. Yamazaki and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **91**, 520 (1969).

(12) By contrast, on sensitized irradiation in hydrocarbon media **13** undergoes isomerization only to **14** via an intermolecular process; see P. J. Kropp and H. J. Krauss, *J. Am. Chem. Soc.*, **89**, 5199 (1967). This is the expected behavior in the triplet manifold, in which only the π,π^* state is available.

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Synthesis and Crystal Structure of a Novel Electron-Rich Nido Trimetallocarborane

Sir:

Recent work in these laboratories has established the ability of both borane and monocarbon carborane ligands to stabilize formal $\{C_5H_5Ni\}^{3+}$ vertices in metallocarborane polyhedra.[1-6] These studies have shown that $\{C_5H_5Ni\}$ may replace $\{CH\}$ in a heteroborane environment, with retention of the major chemical features of the polyhedral framework (including the capacity to undergo polyhedral rearrangement[7]), as previously demonstrated[8] for $\{C_5H_5Co\}$ and $\{BH\}$. We have investigated the reaction of 2-carba-*nido*-hexaborane(9), CB_5H_9, with nickelocene and report here the synthesis and x-ray crystal structure of the first trimetallocarborane containing nickel,[9] $(C_5H_5Ni)_3CB_5H_6$.

The reaction of CB_5H_9[10] with nickelocene and sodium amalgam in tetrahydrofuran afforded a mixture of products. Diamagnetic, air stable $(C_5H_5Ni)_3CB_5H_6$ (I) was isolated in low yield by column chromatography on silica gel. The mass spectrum exhibited a cutoff at m/e 448 corresponding to the $^{12}C_{16}{}^{1}H_{21}{}^{11}B_5{}^{60}Ni_3{}^{+}$ ion. Anal. Calcd: C, 43.33; H, 4.77; Ni, 39.71. Found: C, 42.70; H, 5.00; Ni, 40.32. The 60-MHz ^{1}H NMR spectrum (acetone-d_6) contained sharp singlets of relative area 2:1 at τ 4.85 and 5.07, respectively, which were assigned to the cyclopentadienyl moieties. The 80.5-MHz ^{11}B NMR spectrum contained resonances of area 1:2:2 at −78.5, −26.2, and +9.5 ppm, relative to $Et_2O \cdot BF_3$. Ambiguous NMR data and the novel electron-rich nature (vide infra) of this metallocarborane led us to determine the structure via a single-crystal x-ray diffraction study.

A well-formed green-black crystal of the compound was mounted on a Syntex P$\bar{1}$ automated diffractometer. The complex was found to crystallize in the centrosymmetric orthorhombic space group *Pnma* with unit cell dimensions $a = 7.518$ (1), $b = 14.740$ (2), and $c = 15.711$ (3) Å at 26 °C. The measured density of 1.70 (2) g cm^{-3} agreed with the calculated density of 1.692 g cm^{-3} for $Z = 4$.

A total of 1840 reflections (Mo Kα radiation) with intensities greater than three times their standard deviations was used in the solution and refinement of the structure. Conventional Patterson, Fourier, and least-squares techniques have resulted in $R = 3.16\%$, $R_w = 3.93\%$. All the hydrogen atoms were located and refined. A final difference Fourier map showed no significant features. Full details of the refinement procedure will be discussed in a subsequent publication. Table I summarizes important polyhedral bond distances and angles. The cyclopentadienyl rings were found to be planar within experimental error and showed no unusual features (average Ni–C = 2.13 (3) Å, average C–C = 1.415 (9) Å). Complex I is the first crystallographically characterized trimetallocarborane, and represents the only example of the synthesis of a trimetallocarborane by the direct insertion of three transition metal atoms into a nido carborane.

The molecular units are bisected by crystallographic mirror planes, in congruence with the molecular plane of sym-

Table I. Bond Distances (Å) and Angles (deg)

Ni6–Ni7	2.404 (1)	B2–B3	1.916 (5)
Ni6–Ni8	3.250 (1)	B2–B5	1.798 (9)
Ni6–B2	2.077 (4)	B2–B9	1.735 (6)
Ni6–B3	2.051 (4)	B3–B4	1.977 (8)
Ni6–B9	2.043 (3)		
Ni7–B3	2.070 (3)		
Ni7–B9	2.991 (5)	Ni6–Ni7–Ni8	85.07 (2)
C1–B2	1.634 (6)	Ni6–B9–Ni8	105.4 (2)
C1–B3	1.618 (5)	B9–Ni6–Ni7	84.1 (1)