chromatography (Al_2O_3 containing 5% of water, hexane) and sublimation (50–65 °C/0.1 torr), was achieved in 39% yield by simple dehydrogenation with DDQ. The structural assignment of **4** as a Dewar heptalene was made by elemental analysis[10] together with the spectral data,[14] compared with those of 8-cyanoheptafulvene.[15]

On thermolysis, **4** undergoes quantitative isomerization to **3**[16] with first-order kinetics in the temperature range 391–413 K (by ^1H NMR monitoring in toluene-d_8).[17] From an Arrhenius plot ($r = 0.9967$) of the data, the activation parameters $\Delta H^\ddagger = 32.3 \pm 1.3$ kcal/mol, $\Delta S^\ddagger = 2.0 \pm 3.2$ eu, $E_a = 33.1 \pm 1.3$ kcal/mol, and $\log A = 13.8 \pm 0.7$ are obtained. The activation energy for the ring opening of **4** is substantially higher than those of Dewar benzene (E_a = 23.0 kcal/mol)[1b] and bicyclo[4.2.0]octa-2,4,7-triene (E_a = 18.8 kcal/mol)[18] yet smaller than those of **2** (E_a = 36.7 kcal/mol)[5] and naphtho[1,8]bicyclo[3.2.0]hepta-2,6-diene (**13**) (E_a = 39.3 kcal/mol).[19] Since the strain energy imposed on a central σ bond in the bicyclo[3.2.0]heptane skeleton of **4** seems to be smaller than those of **2** and **13**, the lower value observed for the thermally allowed isomerization of **4** may be interpreted in terms of transition-state aromaticity (Evans' principle).[20] Thus, the transition state for **4** → **3** is isoconjugate with Hückel azulenocyclobutadiene and would be stabilized to some extent.

In the photochemical behavior of **4**, there are several aspects worthy of comment. While **4** is quite stable under irradiation using a 450-W high-pressure Hg lamp through Pyrex for 5.5 h in a degassed mixture of methylcyclohexane and isopentane (1:1 v/v) at 0 °C, isomerization of **4** to **3** takes place readily upon irradiation with either a 450-W high- or low-pressure Hg lamp (2537 Å) through quartz within 2 h. The wavelength dependence[21] observed in the isomerization of **4** is further confirmed by the following experiments. Irradiation of **4** with a 450-W high-pressure Hg lamp through a Corning 9863 (λ 240–400 nm) in the same solvent affords **3** within 2 h whereas the same irradiation through a Corning 5847 (λ 300–400 nm) does not give any detectable amount of **3** for 5 h.[22] These experiments suggest that the photoisomerization of **4** takes place via an upper excited singlet state.[23] Further study on the photochemical behavior of **4** is in progress.

Registry No. 3, 87306-22-7; **4**, 87306-21-6; **5**, 930-60-9; **6**, 87306-23-8; **7**, 87306-24-9; **8**, 87306-25-0; **9**, 87306-27-2; **10**, 87306-26-1; **11**, 87306-29-4; **12**, 87306-28-3.

---

(14) Compound **4**: red needles, mp 99.5–100.5 °C under argon; MS, m/z 179 (M^+, 13%), 153 ($M^+ - CN$, 100%); IR (KBr) ν_{CN} 2200 cm^{-1}; UV/vis (cyclohexane) λ_{max} (nm) ($\log \epsilon$) 230 (4.13), 270 (sh, 3.80), 347 (4.11), 361 (4.19), 380 (3.98), 436 (2.64), 466 (2.67), 504 (2.61), 546 (2.43), 598 (2.08), 658 (1.37); ^1H NMR ($CDCl_3$, 100 MHz) δ 6.41 (dm, 1 H, J = 11.1 Hz), 6.15 (dd, 1 H, J = 2.7, 0.4 Hz), 5.86–6.06 (m, 5 H), 3.78 (d, 1 H, J = 2.9 Hz), 3.69 (bs, 1 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 51.1, 52.9, 100.9, 118.2, 125.8, 130.1, 131.1, 133.1, 133.4, 135.0, 141.1, 152.2, 156.8.

(15) Oda, M.; Kitahara, Y. *Chem. Commun.* **1969**, 352.

(16) Compound **3**: brown crystals, mp 33.5–35.0 °C under argon; MS, m/z 179 (M^+, 41%), 153 ($M^+ - CN$, 100%), 128 (azulene cation, 36%); IR (KBr) ν_{CN} 2202 cm^{-1}; UV/vis (cyclohexane) λ_{max} (nm) ($\log \epsilon$) 267 (4.34), 362 (3.69), long tailing up to 740 nm; ^1H NMR ($CDCl_3$, 100 MHz) δ 5.86–6.38 (m, 6 H), 5.70 (d, 1 H, J = 10.3 Hz), 5.20–5.44 (m, 2 H); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 109.6, 117.8, 127.8, 130.9, 131.3, 131.5, 131.7, 135.3, 135.4, 135.9, 136.7, 138.0, 145.5.

(17) A solution of **4** in toluene-d_8 was degassed and sealed in vacuo in an NMR tube. The tube was immersed in a thermostated and stirred oil bath. The tube was removed at appropriate intervals and immediately cooled to room temperature. The disappearance of **4** and the appearance of **3** were monitored by NMR integration. First-order rate constants are $k^{413.8} = 1.76 \times 10^{-4}\ s^{-1}$, $k^{403.3} = 5.83 \times 10^{-5}\ s^{-1}$, $k^{395.7} = 2.43 \times 10^{-5}\ s^{-1}$, and $k^{391.8} = 1.94 \times 10^{-5}\ s^{-1}$.

(18) Vogel, E.; Kiefer, H.; Roth, W. R. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 442.

(19) Turro, N. J.; Ramamurthy, V.; Pagni, R. M.; Butcher, J. A., Jr. *J. Org. Chem.* **1977**, *42*, 92.

(20) Dewar, M. J. S. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 761. Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2932.

(21) Turro, N. J.; Ramamurthy, V.; Cherry, W.; Farnett, W. *Chem. Rev.* **1978**, *78*, 125.

(22) Compound **3** is stable under the same irradiation conditions.

(23) No photochemical reaction could be observed when **4** was irradiated in an acetone solution.

Photoaddition of Alkyl Halides to Olefins Catalyzed by Copper(I) Complexes

Michiharu Mitani,* Isao Kato, and Kikuhiko Koyama

Department of Synthetic Chemistry
Faculty of Engineering, Shinshu University
Wakasato, Nagano 380, Japan

Received July 1, 1983

While highiy activated halogen compounds such as CCl_4, CCl_3CN, $CHBr_3$, etc. have been known to add to olefins under promotion of some transition metals or complexes to give 1:1 adducts,[1] the addition of rather unactivated halogen compounds such as dichloromethane and aromatic or alkyl monohalogen compounds to olefins is difficult. We recently reported that cuprous chloride promotes the addition of unactivated halogen compounds to olefins under UV irradiation in Me_2SO solution.[2] However, under these conditions alkyl monohalogen compounds gave 1:1 adducts with olefins only in low yields. In the present communication we report a major improvement in this metal-catalyzed photochemistry, which now promises to be a synthetically useful new carbon–carbon bond-forming process.

As a working hypothesis for the mechanism of these reactions, we proposed a pathway in which Cu(I) reductively cleaves carbon–halogen bonds of halocarbons under assistance of UV irradiation to generate Cu(II) or Cu(III) intermediates. If so, some ligands may be expected to stabilize the copper intermediate in the high oxidation state and promote the addition of alkyl halides to olefins. Effects of ligands upon the CuCl-catalyzed photochemical addition of dichloromethane to ethyl acrylate were initially investigated. In the presence of tripenylphosphine, bipyridyl, *o*-phenanthroline, triethylamine, triethyl phosphite, and dimethyl sulfide as ligands, ethyl 2,4-dichlorobutylate (**1**), the expected 1:1 adduct, was produced only in yields of 1, trace, 0, 3, 6, and 0%, respectively, and the Michaelis–Arbuzov type product **2** was obtained as the major product in the case of triethyl phosphite. On the other hand, tri-*n*-butylphosphine as the ligand gave **1** in 95% yield and was proved to be generally suitble as the ligand for such CuCl-catalyzed addition reactions. The ultraviolet absorption spectrum of the CuCl–$(n\text{-Bu})_3P$ complex in THF showed two peaks at 251.0 and 290.5 nm. By irradiation using a low-pressure Hg lamp corresponding to the absorption band at 251.0 nm on a solution consisting of THF (20 ml), *n*-butylbromide (8 mmol), acrylonitrile (4 mmol), CuCl (0.4 mmol), and $(n\text{-Bu})_3P$ (1.2 mmol), 2-bromoheptanonitrile (**3**) was produced in 62% yield. On the other hand, irradiation by a medium-pressure Hg lamp corresponding to the absorption band at 290.5 nm afforded **3** in 30% yield. Effects of ratios of $(n\text{-Bu})_3P$ to CuCl were investigated, and the optimized ratio was determined to be 3 equiv. Thus, addition reactions of alkyl halides to olefins were performed using a low-pressure Hg lamp in the presence of 3 equiv of $(n\text{-Bu})_3P$ relative to CuCl catalyst at ambient temperature. The results are shown in Table I. **3** and **4** were produced in yields 3 and 3.5 times higher than obtained previously in Me_2SO solution without added phosphine.[2] While primary, secondary, and tertiary alkyl bromides gave the 1:1 adducts with acrylonitrile in comparable yields, alkyl chloride did not produce the 1:1 adduct. CuBr as catalyst gave adducts in yields comparable with or a little higher than obtained with CuCl as catalyst. For investigation of effects of temperature on the addition reaction, a THF solution containing 1,3-dibromopropane, ethyl acrylate, CuBr, and $(n\text{-Bu})_3P$ was irradiated using a high-pressure Hg lamp at −50 °C, room temperature, and 50 °C to afford **5** in yields of 80, 54 and 32%,

---

(1) Asscher, M.; Vofsi, D. *J. Chem. Soc.* **1963**, 1881, 3921. Murai, S.; Tsutsumi, S. *J. Org. Chem.* **1966**, *31*, 3000. Burton, D. J.; Kehoe, L. J. *Tetrahedron Lett.* **1966**, 5163; *J. Org. Chem.* **1970**, *35*, 1339; **1971**, *36*, 2596. Susuki, T.; Tsuju, J. *Tetrahedron Lett.* **1968**, 913; *J. Org. Chem.* **1970**, *35*, 2982. Mori, Y.; Tsuji, J. *Tetrahedron* **1972**, *28*, 29. Matsumoto, H.; Nikaido, N.; Nagai, Y. *J. Org. Chem.* **1976**, *41*, 396. Boutevin, B.; Dongala, E. B. *Tetrahedron Lett.* **1977**, *4315*.

(2) Mitani, M.; Nakayama, M.; Koyama, K. *Tetrahedron Lett.* **1980**, *21*, 4457.

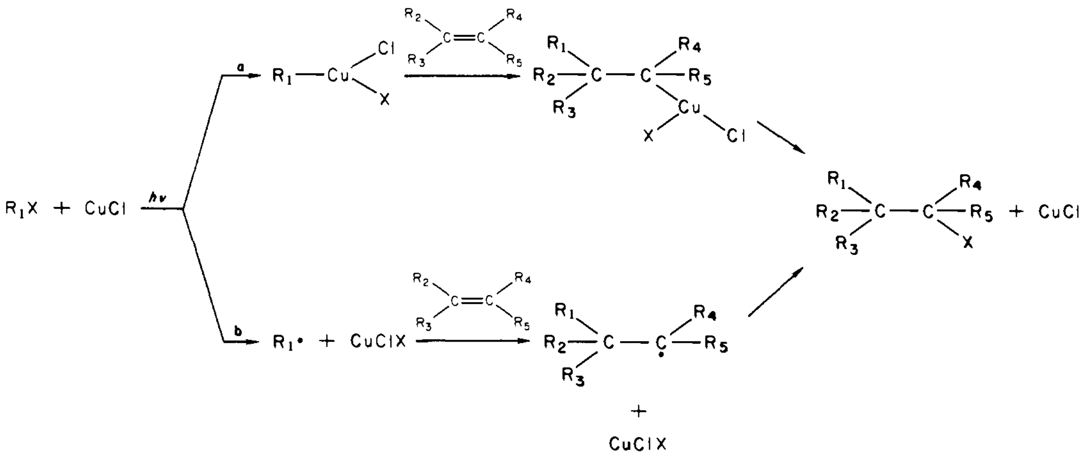
0002-7863/83/1505-6719$01.50/0

Table I. Cu(I)-Catalyzed Photoaddition of Alkyl Halides to Olefins[a]

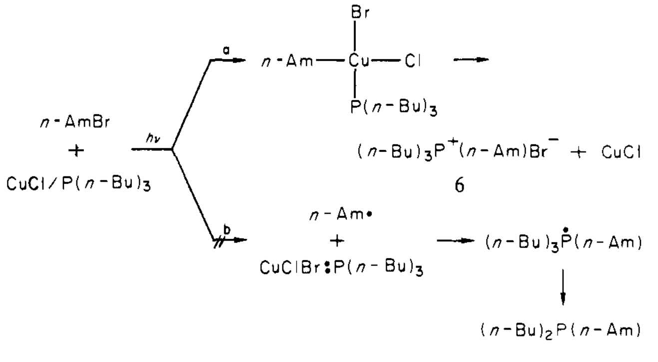
run	alkyl halide	X in CuX	olefin	1:1 adduct[b]	yield, %[c]
1	$CH_3(CH_2)_3Br$	Cl	$CH_2{=}CHCN$	$CH_3(CH_2)_4CHBrCN$, 3	62
2	$CH_3(CH_2)_3Br$	Br	$CH_2{=}CHCN$	3	61
3	$CH_3(CH_2)_3Br$	Cl	$CH_2{=}CHCOOEt$	$CH_3(CH_2)_4CHBrCOOEt$	55
4	c-$C_6H_{11}Br$	Cl	$CH_2{=}CHCN$	c-$C_6H_{11}CH_2CHBrCN$	65
5	c-$C_6H_{11}Br$	Cl	$CH_2{=}CHCOOEt$	c-$C_6H_{11}CH_2CHBrCOOEt$, 4	53
6	$(CH_3)_3CBr$	Cl	$CH_2{=}CHCN$	$(CH_3)_3CCH_2CHBrCN$	50
7	$Br(CH_2)_4Br$	Cl	$CH_2{=}CHCN$	$Br(CH_2)_5CHBrCN$	64
8	$Br(CH_2)_3Br$	Cl	$CH_2{=}CHCN$	$Br(CH_2)_4CHBrCN$	64
9	$Br(CH_2)_3Br$	Br	$CH_2{=}CHCN$	$Br(CH_2)_4CHBrCN$	70
10	$Br(CH_2)_3Br$	Br	$CH_2{=}CHCOOEt$	$Br(CH_2)_4CHBrCOOEt$, 5	54
11	$Br(CH_2)_3Br$	Br	$CH_2{=}CHCOOEt$	5	54[d]
12	$Br(CH_2)_3Br$	Br	$CH_2{=}CHCOOEt$	5	52[e]
13	$Br(CH_2)_3Br$	Cl	$CH_2{=}CHCOMe$	$Br(CH_2)_4CHBrCOMe$	35
14	$Br(CH_2)_3Br$	Br	$CH_2{=}CHCOMe$	$Br(CH_2)_4CHBrCOMe$	45
15	$Br(CH_2)_3Br$	Br	$CH_2{=}C(Me)CN$	$Br(CH_2)_4C(Me)BrCN$	73
16	$Br(CH_2)_3Br$	Br	$CH_2{=}C(Me)COOEt$	$Br(CH_2)_4C(Me)BrCOOEt$	50
17	$Br(CH_2)_3Br$	Br	$CH_2{=}C(COOEt)CH_2COOEt$	$Br(CH_2)_4C(COOEt)BrCH_2COOEt$	57
18	$Br(CH_2)_3Br$	Br	diethyl maleate	$Br(CH_2)_3CH(COOEt)CHBrCOOEt$	70
19	$Br(CH_2)_2Br$	Cl	$CH_2{=}CHCN$	$Br(CH_2)_3CHBrCN$	6
20	$Br(CH_2)_2COOEt$	Cl	$CH_2{=}CHCN$	$EtOOC(CH_2)_3CHBrCN$	60
21	$CH_3(CH_2)_3Cl$	Cl	$CH_2{=}CHCN$	$CH_3(CH_2)_4CHClCN$	0

[a] A solution consisting of THF (20 mL), CuX (0.4 mmol), $(n\text{-Bu})_3P$ (1.2 mmol), halogen compound (8 mmol), and olefin (4 mmol) was irradiated by a low-pressure Hg lamp (75 W) for 20 h at room temperature. [b] All products showed satisfactory spectral data (NMR, IR, MS). [c] Determined by VPC method. [d] *tert*-Butylcatechol (0.8 mmol) was added. [e] Hydroquinone (0.8 mmol) was added.

Scheme I



Scheme II



respectively. Thus, the addition reaction seems to proceed more effectively at lower reaction temperatures.

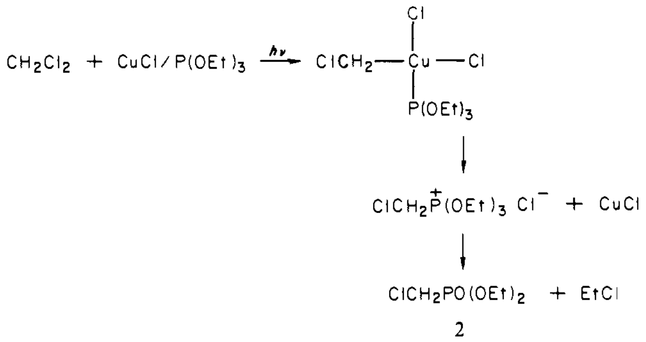
Concerning the mechanism of this Cu(I)-catalyzed photoaddition reaction, we have proposed that the initial step of the reaction is reductive cleavage of carbon–halogen bonds of halogen compounds by CuCl under photostimulation.[2] It, however, has remained to be solved if CuCl cleaves carbon–halogen bonds by an overall two-electron change to generate a Cu(III) species (Scheme I, path a) or by an overall one-electron change to generate a carbon radical and Cu(II) species (Scheme I, path b). In order to clarify this mechanistic point, a THF solution containing *n*-amyl bromide, $(n\text{-Bu})_3P$, and CuCl was irradiated at ambient temperature in the absence of olefin. If the overall two-electron change mechanism is operative, production of the phosphonium salt **6** may be expected by reductive elimination following formation of the Cu(III) complex as shown in path a of Scheme II.[3] On the other hand, homolytic displacement products from $(n\text{-Bu})_3P$ (i.e., $n\text{-Bu}_2PAm\text{-}n$, $n\text{-Am}_2PBu\text{-}n$, and/or $n\text{-Am}_3P$) may be produced if the carbon–halogen bond is cleaved following an overall one-electron change pathway (Scheme II, path b).[4] In fact, irradiation resulted in the production of **6** in 50% yield while homolytic displacement products could not be detected. **6** was not produced in a dark reaction or in a photochemical reaction in the absence of CuCl catalyst. Moreover, the intervention of the radical species also seems excluded since the presence of radical inhibitors (*tert*-butylcatechol and hydroquinone) did not disturb the addition reaction (Table I, run 11 and 12). Thus, it seems reasonable to assume that the overall two-electron change mechanism (path a), in which halogen compounds oxidatively add to the Cu(I) compound under photoirradiation to generate Cu(III) intermediates, is operative. Furthermore, **2** obtained by photoirradiation of a dichloromethane solution containing CuCl, $(EtO)_3P$, and ethyl

---

[3] As the mechanism of the reaction of aryl halides with Pd(0)–triarylphosphine complexes to afford phosphonium salts, the two-electron oxidative-addition pathway to generate intermediately the aryl–Pd(II) complexes followed by the reductive-elimination reaction has been proposed. Ziegler, C. B., Jr.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

[4] Bentrude, W. G.; Hansen, E. R.; Khan, W. A.; Min, T. B.; Rogers, P. E. *J. Am. Chem. Soc.* **1973**, *95*, 2286.

Scheme III



acrylate may also be explained reasonably by a similar two electron oxidative addition–reductive elimination pathway (Scheme III). **2** was not obtained without assistance of photoirradiation or in a photochemical reaction without CuCl catalyst. The reactions of Scheme II and III further suggest that pathway a and not b of Scheme I is involved in copper(I)-catalyzed photoaddition of alkyl halides to olefins.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research (No. 56550606) from the Ministry of Education, for which we are grateful.

Registry No. $CH_3(CH_2)_3Br$, 109-65-9; c-$C_6H_{11}Br$, 108-85-0; $(CH_3)_3CBr$, 507-19-7; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_2COOEt$, 539-74-2; $CH_3(CH_2)_3Cl$, 109-69-3; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}CHCOOEt$, 140-88-5; $CH_2{=}CHCOMe$, 78-94-4; $CH_2{=}C(Me)CN$, 126-98-7; $CH_2{=}C(Me)COOEt$, 97-63-2; $CH_2{=}C(COOEt)CH_2COOEt$, 2409-52-1; *cis*-CH(COOEt)=CH(COOEt), 141-05-9; CuCl, 7758-89-6; CuBr, 7787-70-4; $(n\text{-}Bu)_3P$, 998-40-3; $CH_3(CH_2)_4CHBrCN$, 38799-37-0; $CH_3(CH_2)_4CHBrCOOEt$, 5333-88-0; c-$C_6H_{11}CH_2CHBrCN$, 87319-36-6; c-$C_6H_{11}CH_2CHBrCOOEt$, 77100-90-4; $(CH_3)_3CCH_2CHBrCN$, 87319-37-7; $Br(CH_2)_5CHBrCN$, 87319-38-8; $Br(CH_2)_4CHBrCN$, 87319-39-9; $Br(CH_2)_4CHBrCOOEt$, 29512-97-8; $Br(CH_2)_4CHBrCOMe$, 87319-40-2; $Br(CH_2)_4C(Me)BrCN$, 87319-41-3; $Br(CH_2)_4C(Me)BrCOOEt$, 87319-42-4; $Br(CH_2)_4C(COOEt)BrCH_2COOEt$, 87319-43-5; $Br(CH_2)_3CH(COOEt)CHBrCOOEt$, 87319-44-6; $Br(CH_2)_3CHBrCN$, 87319-45-7; $EtOOC(CH_2)3CHBrCN$, 87319-46-8.

Enantioselective Cyclopropane Synthesis Using the Chiral Carbene Complexes ($S_{Fe}S_C$)- and ($R_{Fe}S_C$)-$(C_5H_5)(CO)(Ph_2R^*P)Fe{=}CHCH_3^+$ (R^* = (*S*)-2-Methylbutyl). Role of Metal vs. Ligand Chirality in the Optical Induction

M. Brookhart,* D. Timmers, J. R. Tucker, and
G. D. Williams

Department of Chemistry
University of North Carolina
Chapel Hill, North Carolina 27514

G. Ronald Husk

U.S. Army Research Office
Research Triangle Park, North Carolina 27709

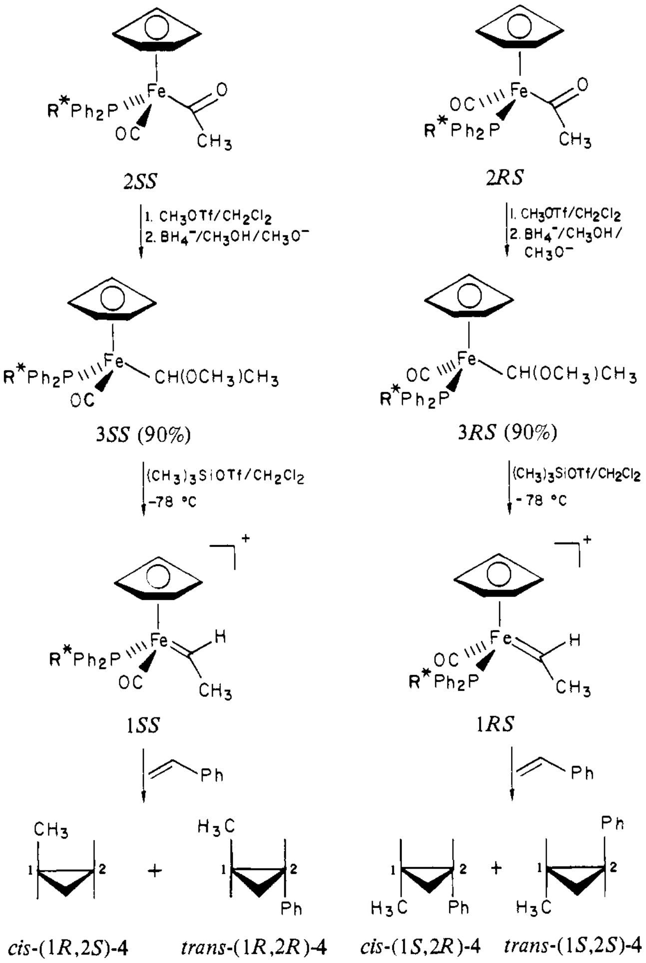
Henri Brunner and Benedikt Hammer

Institut fur Anorganische Chemie
Universitat Regensburg
D-8400 Regensburg, FRG

Received April 29, 1983

Transfer of the carbene ligand from optically active transition-metal carbene complexes to alkenes represents a potentially useful and general method for the enantioselective synthesis of cyclopropanes;[1-7] however, few practical systems have been reported. Recently, synthetic utility has been demonstrated for preparation of cyclopropanes from the reactions of alkenes with electrophilic, cationic carbene complexes of the general structure $Cp(CO)_2Fe{=}CRR'^+$ (R = R′ = H;[8] R = H, R′ = aryl;[9] R = H, R′ = CH_3;[10-12] R = R′ = CH_3[13]). We report here the in situ

Scheme I



---

[1] Bosnich, B., Fryzuk, M. D. "Topics in Inorganic and Organometallic Stereochemistry"; Geoffroy, G. L., Ed.; Interscience: New York, 1981; Vol. 12 of "Topics in Stereochemistry", pp 119–154.

[2] Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151–206.

[3] (a) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1975**, 1707. (b) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Ibid.* **1977**, 2599. (c) Moser, W. R. *J. Am. Chem. Soc.* **1969**, *91*, 1135. (d) Nozaki, H., Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655.

[4] (a) Nakamura, A.; Konishi, A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem Soc.* **1978**, *100*, 3443. (b) Nakamura, A.; Konishi, A.; Tsujitani, R.; Kudo, M.; Otsuka, S. *Ibid.* **1978**, *100*, 3449; and earlier papers. (c) Aratani, T.; Yoneyoshi, Y.; Nagase, T. *Tetrahedron Lett.* **1982**, 685.

[5] Davison, A.; Krusell, W. C.; Michaelson, R. C. *J. Organomet. Chem.* **1974**, *72*, C7.

[6] Flood, T. C.; Disanti, F. J., Miles, D. L. *Inorg. Chem.* **1976**, *15*, 1910.

[7] Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.

[8] (a) Brandt, S.; Helquist, P. *J. Am. Chem. Soc.* **1979**, *101*, 6473. (b) Jolly, P. W.; Pettit, R. *Ibid.* **1966**, *88*, 5044.

[9] (a) Brookhart, M.; Humphrey, B. H.; Kratzer, H.; Nelson, G. O. *J. Am. Chem. Soc.* **1980**, *102*, 7802. (b) Nelson, G. O.; Brookhart, M. *Ibid.* **1977**, *99*, 6099.

[10] (a) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1981**, *103*, 979. (b) Brookhart, M.; Tucker, J. R.; Husk, G. R. *Ibid.* **1983**, *105*, 258. (c) If one assumes styrene attack over triphenylphosphine (which we regard as unlikely on the basis of Gladysz's results) then also mechanistically consistent is synclinal reacting via front-side closure or anticlinal reacting via backside closure.

[11] Kremer, K. A. M.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 1862.

0002-7863/83/1505-6721$01.50/0