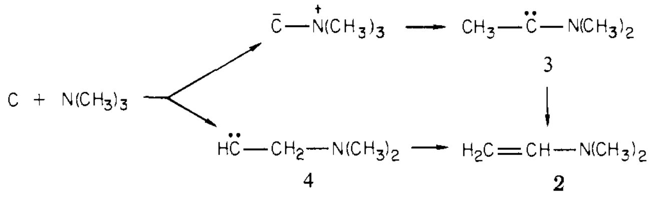
Table I. Energies of Complex 1 and Barriers to Cleavage of R′ Calculated at the UMP2/6-31G Level

reactants	energy of complex,[a] kcal/mol	barrier to cleavage of R′, kcal/mol
$C(^3P) + NH_3$	−21.4	+33.7
$C(^3P) + NH_2CH_3$	−25.8	+25.8
$C(^3P) + N(CH_3)_3$	−30.9	+30.5

[a] Energies are tabulated relative to that of reactants in each case.

deposition of carbon and substrate, the reactor was sealed off and oxygen gas was admitted at 77 K. The reactor was then allowed to warm to room temperature, and the contents were pumped out and analyzed for carbon monoxide. When this experiment was carried out using ammonia and dimethylamine as substrates, no carbon monoxide was observed among the volatile products. However, the cocondensation of carbon (82.2 mmol) with trimethylamine (86.1 mmol) followed by the addition of oxygen (21.8 mmol) gave carbon monoxide (6.4×10^{-2} mmol). Other volatile products observed were methane (8.1×10^{-2} mmol), *N*,*N*-dimethylvinylamine (**2**, 1.2 mmol), and methylisocyanide (2.7×10^{-1} mmol). The formation of **2**, which need not be a product of triplet carbon, may be rationalized as occurring during cocondensation via either carbene **3** or **4**. Likewise, methylisocyanide could be the result of cleavage during condensation or could result directly from the radical pair in eq 1. However, the carbon monoxide and methane must be generated after condensation as there is no source of oxygen until this time and any methane formed during the reaction would be pumped out.[7]

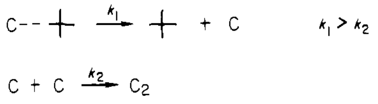


The fact that carbon monoxide is observed under these conditions constitutes strong evidence for the trapping of either triplet complex **1c** or $C(^3P)$ itself. These results are reminiscent of an earlier reaction reported by Skell and Engel[8] in which it was stated that $C(^3P)$ could be stabilized on a neopentane matrix at 77 K. Although Skell and Engel did not report the reaction of this $C(^3P)$ with oxygen, we have now observed this reaction, which confirms their postulate of the existance of $C(^3P)$ under these conditions. Thus, cocondensation of carbon (76.4 mmol) with neopentane (82.5 mmol) followed by the addition of oxygen (20.9 mmol) gave, upon warming to room temperature, carbon monoxide (4.9×10^{-2} mmol) and acetylene (1.8 mmol).

If we assume that the triplet species generated in both of these systems react quantitatively with excess oxygen to generate carbon monoxide, the amount of carbon monoxide generated should be a measure of the amount of triplet species present at any time. Thus, oxygen may be used as a titrant to measure the concentration of triplet species as a function of time. We have used this method to measure the rate of decomposition of the complex of $C(^3P)$ with both trimehtylamine and neopentane. In order to do this, carbon was condensed with substrate and the matrix was allowed to age for periods of 0, 5, 7.5, 10, and 12.5 s before adding the oxygen. The yield of carbon monoxide after each of these intervals was taken as a measure of the concentration of triplet species at that time. In both systems, the concentration of triplet species remained approximately constant over the first 5 s. This fact may be due to decay of metastable carbon species to the ground-state triplet during this time. However, the rate of decay of triplet species after this initial period revealed a significant difference between the trimethylamine and neopentane complexes of $C(^3P)$.

In the case of the carbon–trimethylamine reaction, the complex was observed to decay by clean first-order kinetics with $k = 6.3 \times 10^{-1}\ s^{-1}$ (correlation coefficient = 0.987). However, the decay of the complex between carbon and neopentane was observed to follow second-order kinetics with $k = 6.3 \times 10^{-1}\ mmol^{-1}\ s^{-1}$ (correlation coefficient = 0.975). Fitting the decay of **1c** to second-order kinetics and that of the neopentane complex to first-order kinetics was less satisfactory with correlation coefficients of 0.970 and 0.899, respectively. Thus, the complex between $C(^3P)$ and trimethylamine appears to decay by what is predominantly a first-order process which is most likely the cleavage of a methyl group shown in eq 1. The methyl radical generated in this reaction then abstracts a hydrogen from trimethylamine to generate the observed methane. The use of [UMP3/6-31G*] calculations revealed no lower energy reaction pathways for **1b** than cleavage. Thus, methyl migration to generate carbene **3** has a barrier of 50.8 kcal/mol while insertion of the carbon into an adjacent C–H bond in **1b** has a barrier of 40.8 kcal/mol.

The fact that $C(^3P)$ on neopentane disappears by a second-order process may be rationalized by assuming a very loose complex that decays by rate-determining dimerization of the carbon atom as shown in eq 2. We are currently investigating the additional chemistry of both of these interesting triplet species.



Acknowledgment. We thank the Auburn University Computation Center for a generous allotment of computer time. M.L.M. thanks Auburn University for the award of a Grant-in-Aid 82-54. D.W.M. and P.B.S. gratefully acknowledge support of the experimenal portion of this research by National Science Foundation Grant CHE-81030304.

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(6) For recent reviews of the chemistry of atomic carbon see: (a) Skell, P. S.; Havel, J.; McGlinchey, M. J. *Acc. Chem. Res.* **1973**, *6*, 97–105. (b) Mackay, C. In "Carbenes"; Moss, R. A., Jones, M., Jr., Eds.; Wiley-Interscience: New York, 1975; Vol. II, pp 1–42. (c) Shevlin, P. B. In "Reactive Intermediates"; Abramovitch, R. A., Eds.; Plenum Press: New York, 1980; Vol. I, pp 1–36.

(7) The reason for the failure of ammonia and dimethylamine to form trappable complexes is not clear. It may be that insertion into N–H bonds during cocondensation is rapid and only complexes between C and amines lacking N–H bonds are possible.

(8) Skell, P. S.; Engel, R. R. *J. Am. Chem. Soc.* **1966**, *88*, 3749.

Rates of Reversible Bond Switch with Participation of π-Bonded S^{IV} in a Protonated Thiadiazole Ring System

Yohsuke Yamamoto[†]

Department of Chemistry, Faculty of Science
The University of Tokyo
Bunkyo-ku, Tokyo 113, Japan

Kin-ya Akiba*

Department of Chemistry, Faculty of Science
Hiroshima University
Higashisenda-machi, Hiroshima 730, Japan

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The unsymmetrical nature of thiathiophthenes (**1**) and their analogues in solid state has been established by X-ray crystallographic analyses,[1] but neither the unsymmetrical nature nor any kinetic evidence of ring transformation of analogues of **1** in solution has been found in spite of a careful ^1H NMR study.[2] In a recent

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[†] Present address: Hiroshima University.

(1) (a) Gleiter, R.; Hoffmann, R. *Tetrahedron* **1968**, *24*, 5899. (b) Lozac'h, N. *Adv. Heterocycl. Chem.* **1971**, *13*, 161. (c) Hordvik, A.; Saethre, L. J. *Isr. J. Chem.* **1972**, *10*, 239. (d) Gleiter, R.; Gygax, R. *Top. Current Chem.* **1979**, *63*, 49.

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Table I. Kinetic Parameters of the Ring Transformation of 2 in Methanol-d_4[a]

run	[2]	$\frac{[\text{acid}]^b}{[2]}$	$\Delta\nu$, Hz	T_c, °C	$\Delta G^{\ddagger}_{273}$ [c,d]	$\Delta H^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [e]	k_{273} [d,f]	corr coeff
1	0.39	1.23	4.4	−4	14.7	11.2 ± 1.0	−13 ± 4	11	0.996
2	0.10	3.5	6.1	+6	14.9	11.7 ± 0.9	−12 ± 3	7	0.998
3	0.43	6.5	3.7	−7	14.7	11.1 ± 0.4	−13 ± 2	10	0.999
4	0.11	6.5	5.6	−1	14.7	11.8 ± 1.0	−11 ± 4	9	0.998
5[b]	0.11	12.8	9.5	+21	15.1	11.9 ± 1.1	−12 ± 4	5	0.996

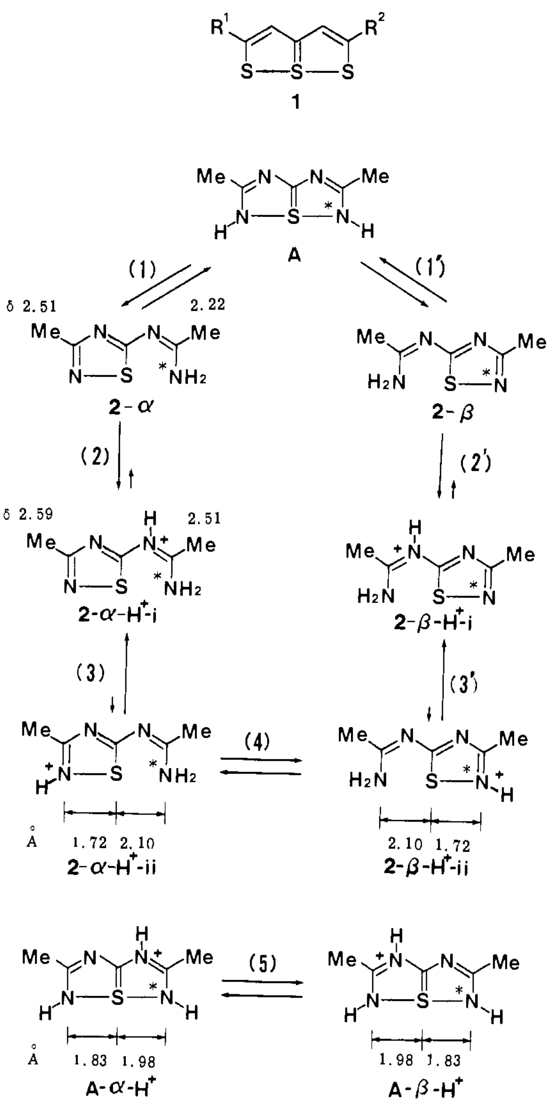
[a] For every run, spectra of methyl protons were measured at six or eight temperatures starting from around T_c down to that which gave the best separation of two peaks, usually lower by 20–30 °C from T_c. Each computer-simulated line shape was fitted to the observed one to give k_t. [b] TFA was used throughout runs 1–4 (60 MHz) and trifluoromethanesulfonic acid was used for run 5 (90 MHz). [c] kcal mol^{-1}. [d] The activation free energy ($\Delta G^{\ddagger}$) and the rate (k) were calculated according to Arrhenius equation using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ listed in the table, and the former was consistent with the value calculated from T_c within 0.2 kcal mol^{-1}. [e] eu. [f] s^{-1}.

report on the ring transformation equilibrium of a 5-((1-aminoethylidene)amino)-3-methyl-1,2,4-thiadiazole system (**2**), bond switch at π-hypervalent sulfur was invoked to rationalize the observed phenomenon.[3] Now we describe the first kinetic results for the reversible bond switch of **2** under acidic conditions by line-shape analyses of the methyl proton NMR signals.

Although the rate of ring transformation (1) is slow in neutral solution and cannot be measured by ^{1}H NMR,[3] it is greatly accelerated when an acid is added. Indeed, only one methyl signal of **2** could be observed at room temperature in the presence of various amount of trifluoroacetic acid (TFA), and a linear relationship between the chemical shift of the methyl protons of **2** and the amount of added TFA was observed until the latter reached 1 equiv (δ 2.34 with 0.1 equiv and 2.59 with 1.00 equiv in CD_2Cl_2 and CD_3OD). The chemical shift remained constant at δ 2.59 with excess TFA (up to 6 equiv) or with excess trifluoromethanesulfonic acid (13 equiv). These facts suggest that monoprotonation of **2** occurs and di- or polyprotonation does not take place.

We conclude the structure of the observed monoprotonated species in solution is **2**-α-H$^+$-i ($\equiv$ **2**-β-H$^+$-i) on the basis of the following facts: (i) pK_a of **2** was found to be 4.87 and those of 5-amino-3-phenyl-1,2,4-thiadiazole and isothiazole were reported to be 1.4 and −0.51,[4] (ii) ^{15}N NMR peaks appeared at δ 129.3 and 242.5 in the presence of 1.42 equiv of TFA at −20 °C ($CDCl_3$–CD_3CN = 3:1) under complete proton-decoupled conditions, and the former peak, the amine of the amidino group, was observed as a triplet ($^1J_{NH}$ = 92 Hz) and the latter, nitrogen 2 of the thiadiazole ring, as a singlet under nondecoupled conditions,[5] (iii) chemical shift of the amidino methyl was δ 2.51, fluctuating only very slightly according to the polarity of the solvent system, and that of the aromatic methyl was δ 2.59, when two peaks were separated at lower temperatures as above (CD_3CN and CD_3OD). These facts rule out the possibility that the observed species is A-α-H$^+$ ($\equiv$ A-β-H$^+$) (Scheme I).

Scheme I



Thus, we could determine the rate of ring transformation between **2**-α-H$^+$-i and **2**-β-H$^+$-i by lowering the temperature of methanol-d_4 solution of **2** in the presence of excess TFA as shown in Table I.[6] Even if the concentration of **2** was varied from 0.1 to 0.43 M and the ratio of TFA to **2** was varied from 1.23 to 6.5 (run 1 to 4), kinetic parameters and rates stayed constant, i.e., $\Delta G^{\ddagger}_{273}$ = 14.8 ± 0.2, $\Delta H^{\ddagger}$ = 11.6 ± 1.0 kcal mol^{-1}, $\Delta S^{\ddagger}$ = −12 ± 3 eu, k_{273} = 9 s^{-1}. Moreover, essentially the same result was obtained with large excess of trifluoromethanesulfonic acid (run 5). These facts suggest that the rate-determining step in the present system deals with the intramolecular ring transformation of the monoprotonated **2**.

The N–S–N bond length of monoprotonated **2** can be assumed as 3.82 Å (for A-α-H$^+$-i, 1.833 + 1.984)[7] and the N(2)–S length of 1,2,4-thiadiazolium ion can be estimated to be 1.72 Å on the basis of data for an isothiazolium salt.[8] Hence, the central sulfur

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(2) (a) Ingram, A. S.; Reid, D. H.; Symon, J. D. *J. Chem. Soc., Perkin Trans. 1* **1974**, 242. (b) Yamamoto, Y.; Akiba, K. *Heterocycles* **1979**, *13*, 297.

(3) (a) Akiba, K.; Kobayashi, T.; Arai, S. *J. Am. Chem. Soc.* **1979**, *101*, 5857. (b) Iwasaki, F.; Akiba, K. *Acta Crystallogr., Sect. B* **1981**, *B37*, 185.

(4) (a) Wooldridge, K. R. H. *Adv. Heterocycl. Chem.* **1973**, *4*, 16. (b) Goerdeler, J.; Fincke, A. *Chem. Ber.* **1956**, *89*, 1033.

(5) ^{15}N-labeled **2**-α was prepared from [^{15}N]ammonia [$^{15}NH_3$ (99%)] and 5-((1-ethoxyethylidene)amino)-3-methyl-1,2,4-thiadiazole in good yield and recrystallized from benzene–hexane. ^{15}N-labeled **2**-α thus prepared showed two ^{15}N NMR peaks ($CDCl_3$ at 34 °C) at δ 104.1 (t, $^1J_{NH}$ = 91 Hz) and 240.7 (s) from liquid ammonia. Thus the existence of ring transformation equilibrium in neutral solution was confirmed.

(6) Computer simulations were carried out by using a DNMR-3 program with a Hitac M-200H Computer. The program was kindly offered by Prof. M. Ōki's laboratory and is based upon one written by G. Binsch: Binsch, G. *Topics Stereochem.* **1968**, *3*, 97.

(7) (a) Akiba, K.; Arai, S.; Iwasaki, F. *Tetrahedron Lett.* **1978**, 4117. (b) Iwasaki, F.; Akiba, K. *Acta Crystallogr., Sect. B* **1981**, *B37*, 180.

(8) Hordvik, A.; Julsham, K. *Acta Chem. Scand.* **1972**, *26*, 343.

atom moves back and forth by 0.38 Å along the N–S–N line 9 times a second at 0 °C, i.e., the bond switching.

There can be several types of monoprotonated species as shown in Scheme I, however, the real entity that effects the ring transformation should be **2**-α-H^+-ii (≡ **2**-β-H^+-ii), since the N–S bond is weakened by protonation at nitrogen 2 of the ring and allows the sulfur atom to accept an electron from the unprotonated amidino nitrogen. Although an exact estimate is difficult, equilibrium ratios (**2**-α-H^+-i/**2**-α-H^+-ii) can be assumed to be in the range from $10^{3.5}$ ($10^{4.9-1.4}$) to $10^{5.4}$ ($10^{4.9+0.5}$). Thus, the real rate of ring transformation (4) should be in the range of $9 \times 10^{3.5}$ to $9 \times 10^{5.4}$ s^{-1} at 0 °C, and $\Delta G^{\ddagger}_{273}$ can be calculated to be from 8.0 to 10.3 kcal mol^{-1}. Such a low barrier of the ring transformation can be attributed to the stability of the intermediate π-sulfurane(s) and also to the essential weakness of the hypervalent N–S^{IV}–N bond.

Registry No. 2, 72212-82-9.

Supplementary Material Available: Kinetic parameters of the ring transformation of **2** in methanol-d_4 in the presence of less than 1 equiv of TFA (1 page). Ordering information is given on any current masthead page.

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(9) Partial support of this work was provided by a Grant-in-Aid for Scientific Research (No. 57430006) administered by the Ministry of Education, Science and Culture of Japanese Government.

Regioselectivity and Rearrangement upon Addition of Nucleophiles to (Diene)iron Complexes

M. F. Semmelhack* and Hanh T. M. Le

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

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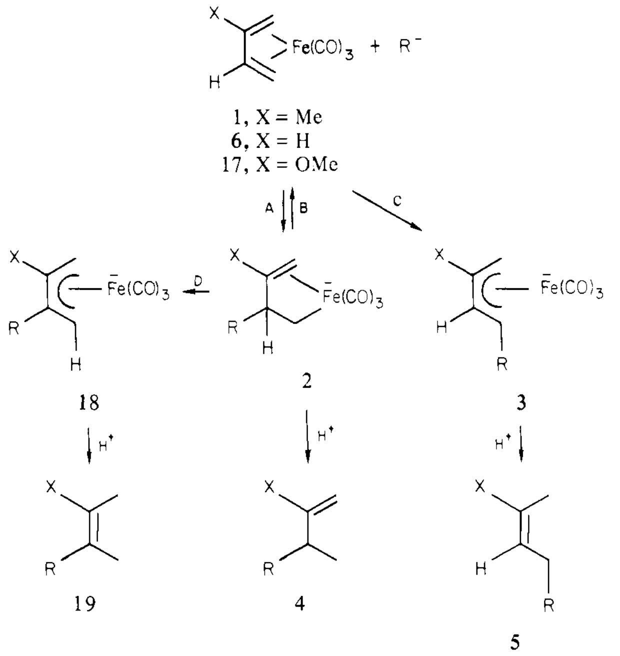
The regioselectivity in addition of nucleophiles to metal-coordinated polyene systems is of interest both for practical synthesis[1] and theory.[2,3] While the theoretical analyses assume kinetically controlled reactions, this assumption is seldom established by experiment and may often be inappropriate.[4] With η^4-1,3-diene ligands, even the simplest example (1,3-butadiene) offers two sites of attack (terminal or internal). The only published prediction suggests preferential addition at a terminal position for cationic η^4-1,3-diene complexes,[2] and a few isolated examples are in harmony.[5,6] Here we describe a systematic study of selectivity with (η^4-1,3-diene)tricarbonyiron complexes which demonstrates that kinetically controlled addition at −78 °C is strongly preferred at an unsubstituted internal position but that reversal of the initial addition can be rapid below 0 °C. Formation of the more stable η^3-allyl complexes then occurs, via nucleophile addition at a terminal position (substituted terminal preferred over unsubstituted) and, in special cases, via hydride migration (Scheme I).

Scheme I. Reaction Pathways



a, X = Me; R = CMe_2CN. b, X = Me; R = $CHPh_2$.
c, X = OMe; R = $CHPh_2$. d, X = H; R = $CHPh_2$.

Table I. Reactions of Anions with (Isoprene)tricarbonyliron[a]

entry	R^-	conditions,[a] °C/h	product ratio **4**/**5**	combined yield
1	CMe_2CN	−78/0.5	100/0	88%
2	CMe_2CN	25/2	0/100	70%
3	$CHPh_2$	−78/0.5	81/19	73%
4	$CHPh_2$	−78/2	85/15	*b*
5	$CHPh_2$	0/0.5	52/48	*b*
6	$CHPh_2$	0/2	11/89	*b*
7	$CHPh_2$	25/2	0/100	61%

[a] The anions were generated at −78 °C in THF–HMPA, and the diene complex was added slowly, on an 8–10 mmol scale. After the specified time/temperature, the mixture at −78 °C was treated with excess trifluoroacetic acid, allowed to stir for 30 min without warming, and then added to aqueous sodium bicarbonate. Isolation by the usual extraction procedures gave the crude product. The products were separated by chromatography on silver nitrate-silica gel and weighed. [b] The yield was not determined; the product ratio is the peak area ratio by analytical GLPC.

Reactions of (η^4-isoprene)tricarbonyliron (**1**) have been studied in greatest detail. While anionic intermediates of type **2** and **3** from anion addition to (η^4-1,3-cyclohexadiene)tricarbonyliron have been characterized spectroscopically,[7] for the present study we chose to analyze the product distribution (**4** and **5**)[8] after

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(1) Questions of regioselectivity have figured strongly in the development of methodology involving nucleophilic addition to the following. (a) (Alkene)metal complexes: Hegedus, L. S.; McGuire, M. A. *Organometallics* **1982**, *1*, 1175–1178 and references therein. Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122 and references therein. (b) (Allyl)palladium complexes: Trost, B. *Ibid.* **1980**, *13*, 385 and references therein. Temple, J. S.; Riediker, M.; Schwartz, J. *J. Am. Chem. Soc.* **1982**, *104*, 1310–1312. Hegedus, L. S.; Darlington, W. H.; Russell, C. E. *J. Org. Chem.* **1980**, *45*, 5193–5196. (c) (Cyclohexadienyl)iron(II) complexes: Birch, A. J. *et. al Tetrahedron, Suppl. 9* **1981**, *37*, 289 and references therein. (d) (Arene)metal complexes: Semmelhack, M. F.; Garcia, J. L.; Cortês, D.; Farina, R.; Hong, R.; Carpenter, B. K. *Organometallics* **1983**, *2*, 467–469 and references therein. Pauson, P. L. *J. Organomet. Chem.* **1980**, *200*, 207–221 and references therein.

(2) A comprehensive tabulation and general theoretical rationalization has been presented: Davies, S. G.; Green, M. L. H.; Mingos, D. M. P. *Tetrahedron* **1978**, *34*, 3047.

(3) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* **1981**, *103*, 4308–4320.

(4) For example, while the addition of nucleophiles to (η^2-1,3-diene)(cyclopentadienyl)dicarbonyliron(II) occurs at C-2 (internal), parallel additions to (η^4-1,3-diene)palladium(II) complexes are preferred at C-1 (terminal). The latter selectivity may be the result of thermodynamic control (more stable η^3-allyl product). (a) For the $CpFe(CO)_2$–diene case, see: Rosenblum, M. *Acc. Chem. Res.* **1974**, *7*, 122. (b) For the diene–Pd(II) case, see: Bäckvall, J.-E. *Ibid.* **1983**, *16*, 343. Recent results have demonstrated regiochemical equilibration during nucleophilic addition to certain (arene)chromium complexes: (a) Kundig, E. P.; Desobry, V.; Simmons, D. P. *J. Am. Chem. Soc.* **1983**, *105*, 6962–6965. (b) Ohlsson, B.; Ullenius, C. *J. Organomet. Chem.*, in press.

(5) Bottrill, M.; Green, M. *J. Chem. Soc., Dalton Trans.* **1977**, 2365.

(6) (a) Faller, J. W.; Murray, H. H.; White, D. L.; Chao, K. H. *Organometallics* **1983**, *2*, 400–409. (b) Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1977**, *99*, 4858–4860.

(7) Semmelhack, M. F.; Herndon, J. W. *J. Organomet. Chem.*, in press.

(8) For earlier examples of acid cleavage of the iron intermediates, see: Semmelhack, M. F.; Herndon, J. W. *Organometallics* **1983**, *2*, 363. The geometry of the alkenes is not always established, but a single isomer is obtained unless otherwise noted. In addition, double-bond positional isomers of **4** and **5** appear in minor amounts in certain cases. They have been characterized and included in the yields quoted for **4** and **5**.[9]

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