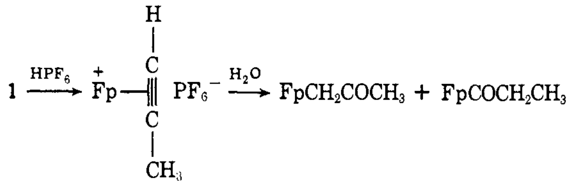


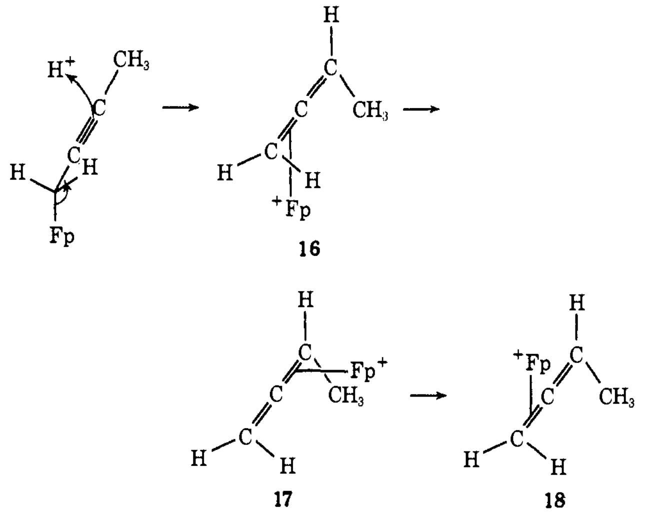
$$1 \xrightarrow{HPF_6} \overset{+}{Fp}\text{—}\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}} \;PF_6^- \xrightarrow{H_2O} FpCH_2COCH_3 + FpCOCH_2CH_3$$

13 14 15

By contrast protonation of **10** gives a cationic allene–iron complex (A) as a *single stereoisomer.*[10] Ir (KBr) 2000, 2040 cm^{-1}; nmr (CD_3NO_2) τ 3.0 (m, 1, =CH), 4.20 (s, 5, Cp), 6.8 (m, 2, $=CH_2(M)^+$), 7.70 (d, t, 3, $J = 7.0$, $J' = 3$ Hz, $=CCH_3(M)^+$).

On heating in nitromethane solution, this substance is smoothly converted to an equilibrium mixture with an isomer (B). Nmr (CD_3NO_2) τ 3.5 (m, 1, =CH), 4.25 (s, 5, Cp), 6.8 (m, 2, $=CH_2(M)^+$), 7.85 (d, t, 3, $J = 7.0, J' = 2.5$ Hz, $=CCH_3$). The reaction follows first-order kinetics, $k^{50°} = 2.03 \times 10^{-5}$ sec^{-1}, $K^{50°}_{eq}$ (B/A) = 1.95.

We interpret the high stereospecificity of the protonation reaction in terms of trans periplanar participation of the organometallic group concerted with protonation. The initial cationic allene complex is accordingly assigned structure **16**. Its conversion to the isomeric cation (**18**) represents a thermodynamically favored change to a less sterically hindered ion. Such an isomerization may take place through intermediacy of the cation (**17**), in a process closely analogous to that proposed to account for the fluxional behavior of tetracarbonyltetramethylalleneiron.[11,12]



The same mixture of isomeric cations (**16** + **18**) may also be obtained directly from methylallene in an exchange reaction with dicarbonyl cyclopentadienyl(isobutylene)iron cation. Such a reaction has previously been employed for the preparation of a number of cationic iron–olefin complexes from the free olefin.[13]

The chemistry of these allenyl–iron and cationic allene–iron complexes is being further examined.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GM-16395) and the National Science Foundation (GP 27991X).

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(10) The protonation of **10** and of the related phenylpropargyl complex has very recently been reported by D. W. Lichtenberg and A. Wojcicki, *J. Amer. Chem. Soc.*, **94**, 8271 (1972), and earlier by J. Benaim, J. Merour, and J. Roustan, *C. R. Acad. Sci., Ser. C*, **272**, 789 (1971), but neither of these authors makes reference to the stereospecificity of the reaction or to the stereochemistry of the allene salts obtained.

(11) R. Ben-Shoshan and R. Pettit, *J. Amer. Chem. Soc.*, **89**, 2231 (1967).

(12) The lower thermodynamic stability of **17** compared with **16** or **18** is in accord with our observations that the Fp(ethylene) cation is considerably more stable than the corresponding propenyl cation.

(13) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971)

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Received December 6, 1972

Additions of Nucleophiles to Metal-Activated Olefins. Synthesis of Carbon–Carbon Bonds

Sir:

The addition of simple nucleophiles to cyclobutadiene,[1] pentadienyl,[2] cyclopentadienyl,[3] hexadiene,[4] arene,[5] and cycloheptatrienyl[6] ligands coordinated to a variety of transition metals has been extensively examined.[7] By contrast, relatively few investigations of the corresponding reactions of *dihapto*olefin and acetylene ligands have been carried out and these are largely confined to platinum and palladium complexes.[1,8]

We wish to report several observations concerning the reactions of a variety of nucleophiles[9] with the readily accessible h^5-$C_5H_5Fe(CO)_2$(olefin) cations[10] and to draw attention to the potential use of these substances as stoichiometric reagents in organic synthesis.

A variety of enolate anions add readily and in moderate to good yield to the parent complex **1** affording the corresponding neutral complex.

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(1) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971.

(2) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem*,, **1**, 1 (1970); J. E. Mahler, D. E. Gibson, and R. Pettit, *J. Amer. Chem. Soc.*, **85**, 3955, 3959 (1963); M. A. Hashmi, J. D. Munro, P. L. Pauson, and J. M. Williamson, *J. Chem. Soc. A*, 240 (1967); R. J. H. Cowles, B. F. G. Johnson, P. L. Jasty, and J. Lewis, *Chem. Commun.*, 392 (1969); G. Maglio, A. Musco, R. Palumbo, and A. Sirigu, *ibid.*, 100 (1971).

(3) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959), 989 (1960); E. O. Fischer and R. D. Fischer, *Z. Naturforsch. B*, **16**, 556 (1961); E. O. Fischer and G. E. Herberich, *Chem. Ber.*, **94**, 1517 (1961); E. O. Fischer, W. Fellmann, and G. E. Herberich, *ibid.*, **95**, 2254 (1962).

(4) F. Haque, J. Miller, P. L. Pauson, and J. B. Pd. Tripathi, *J. Chem. Soc. C*, 743 (1971).

(5) (a) P. J. C. Walker and R. J. Mawby, *Inorg. Chem.*, **10**, 404 (1971); (b) G. Winkhaus, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3807 (1961); (c) I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. C*, 2257 (1967) 116, 2024 (1969); (d) P. H. Bird and M. R. Churchill, *Chem. Commun.*, 777 (1967); (e) D. Jones, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4485 (1962).

(6) (a) P. L. Pauson, G. H. Smith, and J. H. Valentine, *J. Chem. Soc. C*, 1057 (1969); (b) P. L. Pauson and K. H. Todd, *ibid.*, 2638 (1970).

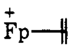
(7) A review of the reactions of electrophiles and nucleophiles with metal-coordinated olefins has been given by D. A. White, *Organometal. Chem. Rev.*, **3**, 497 (1968).

(8) J. Tsuji, *Accounts Chem. Res.*, **2**, 144 (1969); M. H. Chisholm, H. C. Clark, and L. E. Manzer, *J. Amer. Chem. Soc.*, **94**, 1532 (1972), and references cited therein.

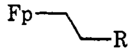
(9) The addition of several oxygen and nitrogen nucleophiles to this cation has recently been reported by: (a) L. Busetto, A. Palazzi, R. Ros, and U. Belluco, *J. Organometal. Chem.*, **25**, 207 (1970); (b) M. Graziani, L. Busetto, and A. Palazzi, *ibid.*, 26, 261 (1971).

(10) (a) W. P. Giering, M. Rosenblum, and J. Tancrede, *J. Amer. Chem. Soc.*, **94**, 7170 (1972); (b) W. P. Giering and M. Rosenblum, *Chem. Commun.*, 441 (1971); (c) M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963); (d) M. L. H. Green and P. L. I. Nagy, *J. Organometal. Chem.*, **1**, 58 (1963); (e) E. O. Fischer and K. Fichtel, *Chem. Ber.*, **94**, 1200 (1961), **95**, 2063 (1962).

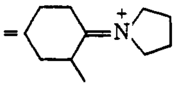
Thus, lithium diethyl malonate, lithium diethyl methylmalonate, and lithium ethyl acetoacetate, generated in tetrahydrofuran with lithium bis(trimethylsilyl)amide,[11] add smoothly at −78° to **1** yielding the adducts **2a**,[12] **2b**, and **2c** in 55, 84, and 80% yields, respectively.[13]



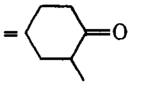
1



2a, R = CH(COOEt)$_2$
b, R = CMe(COOEt)$_2$
c, R = CH(COMe)COOEt
d, R =

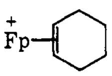


e, R =

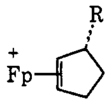


Fp = h^5-C$_5$H$_5$Fe(CO)$_2$

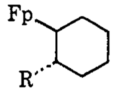
These reactions are applicable as well to cyclohexene and cyclopentene complexes **3** and **4**. Thus, **3** reacts with malonate and with acetoacetate at −78° to give the substituted cyclohexane complexes **5a**, mp 69–71°, and **5b** in 65 and 76% yields, respectively. The cyclopentene complex reacts similarly with malonate to give **6a** in 82% yield. These adducts are assigned trans stereochemistry in conformity with the generally observed stereochemical course of the additions of nucleophiles to coordinated olefins,[14] acetylenes,[15] arene,[5c,d,16] and polyenyl[6a,17] systems. On treatment with trityl cation, **6a** is transformed exclusively to the olefin complex **4b** (76%), derived from trans hydride abstraction.



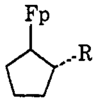
3



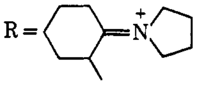
4a, R = H
b, R = CH(COOEt)$_2$



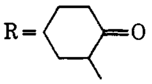
5a, R = CH(COOEt)$_2$
b, R = CH(COMe)COOEt



6a, R = CH(COOEt)$_2$
b, R =



c, R =



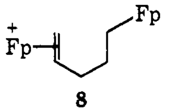
The addition reactions are not confined to those involving carbanionoid reagents, but may be effected with enamines as well.[18]

Cyclohexanone pyrrolidine enamine reacts smoothly with **1** at 0° affording the iminium salt **2d** in 80% yield and the ketone **2e**, mp 32.5–33.5° (60%), on hydrolysis. The cation **4a** is similarly alkylated by this enamine affording **6b** in 80% yield. Brief treatment with aqueous base gave the ketone **6c** in 80% yield.

A significant variant of these reactions makes use of the complex dicarbonyl h^5-cyclopentadienyl(allyl)iron (**7**) as nucleophile.

Thus, an equimolar mixture of **7** and **1** on reaction at room temperature for 4 hr in nitromethane solution gave the complex **8** in 60% yield.[19] The organometallic functions may be selectively removed or further transformed. Exposure of the complex to an acetone solution of sodium iodide for 15 min at room temperature yielded the complex **9** in 69% yield. Similarly, brief treatment of **8** with HCl in methylene chloride at room temperature afforded **10** in 56% yield. Lastly, the allylic function may be restored by treatment of **8** with triethylamine to give **11** in 31% yield (cis:trans = 1:1).

7



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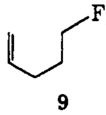

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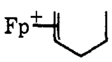

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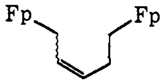
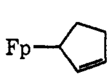
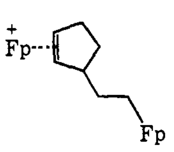


11

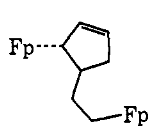
The cyclopentenyl complex **12** similarly condenses with **1** at room temperature in acetone solution, affording the adduct **13** (80%). The stereochemistry of this adduct, depicted as trans, is confirmed by its conversion with triethylamine to **14** in a process which we have shown proceeds with the stereoselective removal of an allylic proton trans to the Fp–olefin bond.[20] Treatment of **13** with sodium iodide in acetone at room temperature selectively removes the olefin-coordinated metal function affording **15** (62%).



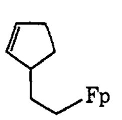
12



13



14



15

With a cationic diene acceptor a two-step condensation sequence may be achieved leading to the formation

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(11) M. W. Rathke, *J. Amer. Chem. Soc.*, **92**, 3222 (1970).

(12) All of the adducts reported herein were fully characterized by ir and nmr spectroscopy and by elemental analysis. In general the infrared spectra of adducts exhibit intense carbonyl absorptions near 1950 and 2000 cm^{-1}, characteristic of Fp–alkyl complexes, in addition to absorptions associated with the functionalities present in the alkyl ligand. Nmr spectra of the adducts show cyclopentadienyl proton absorption near τ 5.1, typical of neutral Fp–alkyl complexes.

(13) Condensation reactions with organic nucleophiles were generally run in THF solution and the products purified either by direct filtration through alumina followed by chromatography on alumina, or by quenching with water, extraction, and chromatography. Unless otherwise indicated, the neutral adducts were isolated as amber, relatively stable oils. Yields reported are those of chromatographically pure materials.

(14) A. Panunzi, A. De Renzi, and G. Parao, *J. Amer. Chem. Soc.*, **92**, 3489 (1970); J. K. Stille and R. H. Morgan, *ibid.*, **88**, 5135 (1966); M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967); C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.*, **7**, 181 (1967); J. K. Stille and D. B. Fox, *Inorg. Nucl. Chem. Lett.*, **5**, 157 (1969).

(15) M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, **94**, 1532 (1972).

(16) L. E. Dahl and W. E. Oberhansl, *Inorg. Chem.*, **4**, 629 (1965).

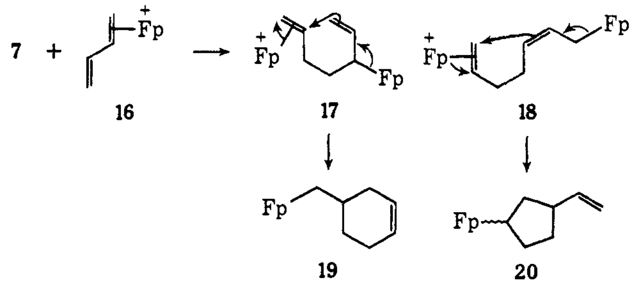
(17) M. R. Churchill and R. Mason, *Proc. Roy. Soc., Ser. A*, **279**, 191 (1964).

(18) Triphenylphosphine, triethyl phosphite, and phosphoranes also add to these complex cations to give the corresponding metallated phosphonium salts.

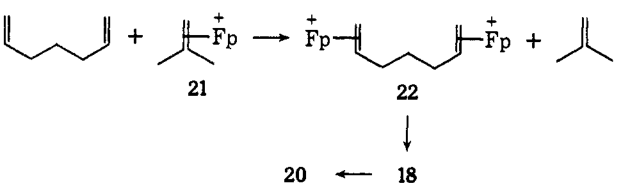
(19) These dinuclear complexes exhibit carbonyl absorption near 1950, 2000, 2030, and 2080 cm^{-1} indicative of the presence of both neutral and cationic Fp groups. The nmr spectra of these adducts show two five-proton singlet peaks near τ 5.1 and 4.3 for the two Fp groups. Primary condensations products were obtained in relatively pure form by precipitation from the reaction solution with ether, and were further purified by recrystallization from methylene chloride–ether solutions.

(20) A. Cutler, D. Ehntholt, R. W. Fish, W. P. Giering, S. Raghu, and M. Rosenblum, *J. Amer. Chem. Soc.*, **94**, 8251 (1972).

of carbocyclic rings. Thus, **7** reacts with the butadiene complex **16** to afford, after treatment with iodide, a mixture of cyclohexene and vinylcyclopentane complexes **19** and **20**, formed apparently *via* the intermediates **17** and **18** (40%).



The structure of **19** was established by independent synthesis through metallation of 4-hydroxymethylcyclohexene benzenesulfonate with the organometallic anion (Fp$^-$), while **18** and thence **20** can alternatively be obtained by exchange of the isobutylene complex (**21**)[10b] with 1,7-heptadiene, followed by treatment of the dication **22** with a molar equivalent of triethylamine.



Further elaborations and extensions of these reactions are being examined.

Acknowledgment. This work was supported by grants from the National Institutes of Health (GP-16395) and by the National Science Foundation (GP-27991-X) which are gratefully acknowledged.

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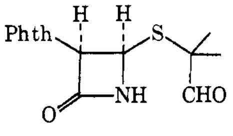
Received January 18, 1973

Removal and Displacement of the Thiazolidine Ring in Penicillin. II.[1] Selective Carbon–Sulfur Bond Cleavage

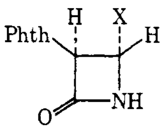
Sir:

Several methods have been reported for degrading the penicillin nucleus to monocyclic azetidin-2-ones.[2] We wish to report our progress in degrading **1**.[2a] Our studies, which extended over the past several years, have involved the reaction of **1** with chlorine. This reaction has recently been used by others to cleave the azetidine C–S bond of the penicillin nucleus.[2d] We have utilized this reagent to effect selective cleavage of the C–S bond on either side of the sulfur atom. This allows preparation of compounds **2** and **5**. In the latter case the C_4 side chain is removed while retaining the natural stereochemistry of the azetidine ring.

Direct chlorinolysis of **1**[3] as a suspension in CCl_4 using excess chlorine produced **2a**,[4,5] mp 142–144°, in nearly quantitative yield. The chloride underwent facile solvolytic displacement at room temperature. Methanol gave **2b**, mp 192–193°, and acetic acid produced **2c**, mp 187–189°. In addition to the nmr absorptions shown in Table I, **2b** and **2c** show methyl singlets at δ 3.5 and 2.2, respectively. The chloride **2a** also reacted with thiophenol in the presence of triethylamine to give **2d**, mp 212–213°. The spectral data indicate the integrity of the β-lactam and the trans relationship of the C_3 and C_4 protons in the predominant product. This method of cleaving the thioethyl side chain complements the method developed earlier in these laboratories based on displacement of the sulfone analog of **1**.[1]



1



2a, X = Cl
b, X = OCH$_3$
c, X = OAc
d, X = SPh

Table I. Spectral Characteristics[a]

Compd	δ_{H_3}, δ_{H_4}[b]		$J_{3,4}$, Hz	Lactam CO, cm^{-1}
2a	5.6	6.0[c]	1.4[d]	1800
2b	5.3	5.4	1.5[d]	1790
2c	5.4	6.2	1.5[d]	1790
2d	5.1	5.3	2.4[d]	1785
3a	5.75	5.85	6.4	1825
3b	5.70	5.75	5.6	1805
4a	6.1		6.8[e]	1830
4b	5.9			1795
5a	5.2	5.6[f]	5.0	1790
5b	5.2	5.6[f,g]	4.8	1785
6a	5.6	5.7	6.0	1800
6b	5.2	5.5	3.5	1800
7	5.6	6.0	2.4	1810

[a] All compounds show absorption at δ 7.9–8.0 in the nmr and near 1770 and 1720 cm^{-1} in the ir due to the phthalimido group; nmr spectra are run in $CDCl_3$ and ir spectra in CH_2Cl_2. [b] Assignment of the lower field signal to H_4 can be made for **2a**, **5a**, and **5b** on the basis of coupling to the NH. Otherwise, assignment is ambiguous. [c] Noticeably broadened due to weak coupling to NH. [d] The coupling constants shown are for the predominant trans isomer. [e] Observed in C_6D_6. [f] Further split by NH with $J \simeq 1$ Hz. [g] Overlapping absorptions of isomers with chlorine cis and trans to sulfur.

Sodium borohydride reduction of **1** produced the corresponding alcohol, mp 196–197°, [α]D −6°, which was acylated smoothly in methylene chloride solution by trifluoroacetic anhydride in the presence of potassium carbonate. The product **3**, mp 148–149°, [α]D −125°, shows two singlets in the ^{19}F nmr spectrum 3.28 and

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(1) Part I: J. C. Sheehan and C. A. Panetta, *J. Org. Chem.*, **38**, 940 (1973).

(2) (a) J. C. Sheehan and K. G. Brandt, *J. Amer. Chem. Soc.*, **87**, 5468 (1965); (b) D. H. R. Barton, *Chem. Commun.*, 845 (1971); (c) R. D. G. Cooper, *J. Amer. Chem. Soc.*, **94**, 1018, 1021 (1972); (d) S. Kukolja, *ibid.*, **94**, 7590 (1972), and previous communications cited therein; (e) S. Wolfe, W. S. Lee, G. Kannengiesser, and J. Ducey, *Can. J. Chem.*, **50**, 2894 (1972); (f) M. Numata, Y. Imashiro, I. Minamida, and M. Yamaoka, *Tetrahedron Lett.*, 5097 (1972), and references therein; (g) J. H. C. Naylor, M. J. Pearson, and R. Southgate, *J. Chem. Soc., Chem. Commun.*, 57 (1973), and references therein.

(3) Phth = phthalimido.

(4) Satisfactory analytical data have been obtained for all compounds unless otherwise noted.

(5) The compounds **2** are cis–trans mixtures, but the trans isomer usually constitutes >85% of the mixture.