Copies of the final atomic parameters, bond angles, and bond distances are available.[4] The standard deviations reported were estimated from the elements in the matrix inverse. These estimated standard deviations are probably unrealistically low for several reasons. The block-diagonal method does not necessarily give correct estimates of standard deviation. Furthermore, the omission of the hydrogen atoms can cause systematic errors. The rms estimates of standard deviation based on bond distances which should be chemically equivalent are probably more realistic estimates of the actual errors. Using this approach the overall rms deviation of the light atom distances is ±0.05. This value should be considered with regard to the short C–C distance mentioned above.

A fuller discussion of the bonding in this unusual complex and the stabilization of the Ni–carbon bond will be given on completion of the structural study.

Acknowledgment. The authors are grateful to Public Health Service Research Grant No. CA12025-01 from the National Cancer Institute and to the Office of Naval Research for support of this work. A. A. S. is indebted to the National Defense Graduate Fellowship Program for a research fellowship. We acknowledge computer time donated by the Worcester Area College Computation Center and crystallographic programs made available to us by F. H. Ahmed of the National Research Council of Canada, C. K. Johnson of the Oak Ridge National Laboratory and W. N. Lipscomb of Harvard University,

Supplementary Material Available. A listing of final atomic parameters, bond angles, and bond distances will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W,, Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-5790.

(4) See paragraph at end of paper regarding supplementary material.

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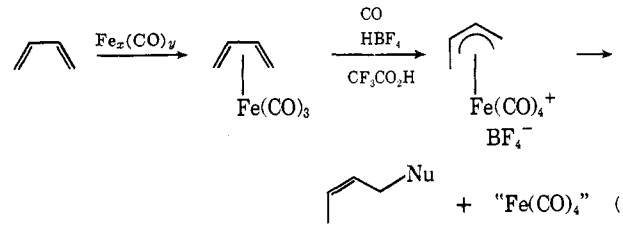
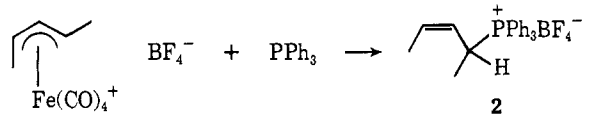
π-Allyl Iron Cations. Iron-Moderated Carbonium Ions as Organic Reagents

Sir:

We wish to report a preliminary investigation of an organometallic system which promises to be a versatile tool for the synthesis of organic species, particularly *cis*-allylphosphonium salts, from conjugated dienes. This system involves the use of π-allyliron tetracarbonyl cations, readily available in high yield from the appropriate diene iron tricarbonyl complex by protonation (HBF_4) in the presence of carbon monoxide.[1] These cationic species are subject to attack by a wide variety of nucleophiles, to give, in yields varying from 30 to 90%, the products of 1,4 addition across the diene. The overall transformation is shown in eq 1.

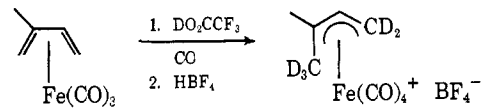


There are several features of this procedure which make it highly desirable from a synthetic standpoint. First, as shown in eq 1, the cisoid stereochemistry of the diene complex is retained in the product allyl species. Thus, this route allows the synthesis of allyl species containing cis double bonds. Even when there is a choice between the formation of a cis or a trans double bond, the cis species is favored. For example, *syn,anti*-(1,3-dimethylallyl)iron tetracarbonyl cation (**1**), prepared from *trans*-piperyleneiron tricarbonyl, gives rise to the allylphosphonium salt **2** (74%) when treated with triphenylphosphine.



1 2

Secondly, as we have shown previously,[3] it is a simple matter to obtain stereospecifically deuterium labeled allyliron cations by use of deuterated acid. This observation allows us to prepare stereospecifically labeled tetracarbonyl cations by using deuterated acid in the above preparation.[4] This fact, coupled with the stereospecificity of the nucleophilic reactions, allows the synthesis of stereospecifically labeled species in high yield. Of particular interest in this connection is the species derived from isoprene, (1,1-dimethylallyl)iron tetracarbonyl cation **3**. This species undergoes preferential



3

attack by nucleophiles at the less hindered 3 position, and the position of the label is not scrambled. Thus, this route provides a source of stereospecifically labeled isoprenyl units for use in biosynthetic studies of terpenes.

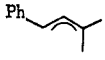
(1) These species have been previously characterized by Gibson and Vonnahme;[2a] yields in their preparation are considerably increased (to >90% in some cases) by inclusion of CO during the protonation step.[2b]

(2) (a) D. H. Gibson and R. L. Vonnahme, *J. Amer. Chem. Soc.*, **94**, 5090 (1972); (b) G. E. Emerson, Ph.D. Thesis, University of Texas, 1964; *Diss. Abstr.*, **25**, 4955 (1965).

(3) T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, **93**, 5296 (1971).

(4) Exchange can also be carried out after isolation of the tetracarbonyl cation; preparation of **3**, among other iron cations, has been reported (D. H. Gibson and R. L. Vonnahme, *J. Chem. Soc., Chem. Commun.*, 1021 (1972)) by this route. Exchange is, however, slow in the tetracarbonyl compounds ($T_{1/2} \gg 0.5$ hr) and exchange at the tricarbonyl stage[3] is much more convenient.

Table I

Allyl group of π-(allyl)Fe(CO)$_4^+BF_4^-$	Nucleophile	Product (% yield)[a]
	PPh_3	$(CH_2{=}CHCH_2PPh_3)Fe(CO)_4^+BF_4^-$
	Pyridine	$(CH_2{=}CHCH_2NC_5H_5)Fe(CO)_4^+BF_4^-$ (85)
	$CH_2{=}C(OAc)CH_3$[b]	$CH_2{=}CHCH_2CH_2COCH_3$ (8)
	$CH_3COCH_2CO_2CH_3$[c]	$CH_2{=}CHCH_2CH(CO_2CH_3)COCH_3$ (28)
	PPh_3	*cis*-$CH_3CH{=}CHCH_2PPh_3^+BF_4^-$ (74)
	PPh_3	*cis*-$CH_3CH{=}CHCH(CH_3)PPh_3^+BF_4^-$ (50)
	PPh_3	$(CH_3)_2C{=}CHCH_2PPh_3^+BF_4^-$ (74)[e]
	Pyridine	$(CH_3)_2C{=}CHCH_2NC_5H_5^+BF_4^-$ (80)[e]
	$CH_3COCHCO_2CH_3$[d]	$(CH_3)_2C{=}CHCH_2CH_2COCH_3$ (68)
		$CH_2{=}CHC(CH_3)_2CH_2COCH_3$ (17)
	$(CH_3CH_2)_2NH$	$(CH_3)_2C{=}CHCH_2N(CH_2CH_3)_2$ (28)
	$PhCH(NH_2)CH_3$	$(CH_3)_2C{=}CHCH_2NHCH(CH_3)Ph$ (28)
		$CH_2{=}CHC(CH_3)_2NHCH(CH_3)Ph$ (13)
	PPh_3	$C_6H_5CH(PPh_3)CH{=}C(CH_3)_2^+BF_4^-$

[a] Isolated. [b] Conditions: refluxed for 40 min at 90°. [c] Conditions: refluxed in acetone for 4 hr. [d] Products isolated after saponification and decarboxylation. [e] Use of stereospecifically labeled allyl cation complex leads to stereospecifically labeled isophenyl adduct.

The availability of π-allyliron tetracarbonyl cation[5] allowed us to make certain observations concerning the probable mechanism of these transformations. This species gave rise to reasonably stable olefin–iron tetracarbonyl complexes after treatment with, for example, triphenylphosphine, pyridine, or the anion of methylacetoacetate. Particularly in the case of the phosphonium and pyridinium salts, these novel organometallic species were readily isolable.[7] Some evidence (nmr) for similar intermediates was obtained in the case of species with disubstituted double bonds, but these were much less stable than the monosubstituted olefin complexes derived from the allyl species, decomposing rapidly to the uncomplexed organic moiety and (at least partially) $Fe_3(CO)_{12}$[8] at room temperature. These observations indicate that the initial attack of the nucleophile occurs on the ligand, with subsequent decomposition of the iron(0) complexes so formed, the decomposition being accelerated by increasing substitution of the double bond. As seen in Table I, nucleophilic attack in general occurs preferentially at the unsubstituted end of the coordinated allyl group.

The procedure for these alkylations is very simple. Iron salt is suspended in THF or ether and the appropriate nucleophile is added. Usually, with reasonably nucleophilic species, reaction is instantaneous as indicated by solution of the insoluble salt. Work-up is then carried out in the normal manner.

We are continuing to investigate the scope and synthetic utility of this novel reaction.

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(5) This species was prepared by treating π-allyliron tricarbonyl iodide[6] with $AgBF_4$ in the presence of CO, followed by precipitation of the cation by addition of ether.

(6) R. B. King, "Organometallic Synthesis," Vol. 1, Wiley, New York, N. Y., 1965, p 176.

(7) The physical properties of allylpyridiniumiron tetracarbonyl tetrafluoborate are: ir (CH_2Cl_2) 2100, 2032, 2012, 1996 cm^{-1} (ν_{CO}); nmr (acetone-d_6) δ 9.28 (2 H, d), 8.71 (1 H, t), and 8.22 (2 H, t), pyridine hydrogens; 5.60 (1 H, dd, J = 3.4, 13 Hz) and 4.64 (1 H, dd, J = 13, 11.5 Hz), $-CH_2^+N\ll^+$; 3.85 (1 H, mult), $-CH{=}$; and 3.03 (1 H, dd, J = 2, 12 Hz) and 2.87 (1 H, dd, J = 2, 8.5 Hz), $H_2C{=}$. *Anal.* Calcd for $C_{12}H_{10}NFeO_4BF_4$: C, 38.45; H, 2.69; N, 3.75; Fe, 14.90. Found: C, 38.42; H, 2.74; N, 3.78; Fe, 14.67. The phosphonium compounds are similar. In particular the shift of the ν_{CO} bonds to longer wavelength relative to the allyl cation (2123, 2062 cm^{-1}) indicates a reduction of the charge on the metal, and the high chemical shift of the olefinic protons indicates complexation of the olefinic moiety.

(8) (a) G. Cardaci and V. Narciso, *J. Chem. Soc., Dalton Trans.*, 2289 (1972); (b) K. Von Gustorf, M. C. Henry, and D. J. McAdoo, *Justus Liebigs Ann. Chem.*, 707, 190 (1967).

Carbon-13 Magnetic Resonance Spectroscopy and the Biosynthesis of Streptovaricin[1,2]

Sir:

The streptovaricins, rifamycins, and their derivatives have aroused considerable recent interest due to their inhibition of RNA dependent DNA polymerase (reverse transcriptase) from RNA tumor viruses, their very potent inhibition of DNA dependent RNA polymerase from *E. coli*, and their general antibacterial and antiviral properties, especially against mycobacteria.[2a,b,3]

In spite of the biological interest noted above and their remarkable ansa structures, the biosynthesis of these compounds and the related antibiotics tolypomycin and geldanamycin remains unreported. From their structures (*e.g.*, that of streptovaricin D, **1** in Figure 1) propionate and acetate seem the likely candidates as precursors for the aliphatic bridge and,

(1) Paper II in the series "Carbon-13 as a Biosynthetic Tool" [Paper I: W. M. J. Knöll, R. J. Huxtable, and K. L. Rinehart, Jr., *J. Amer. Chem. Soc.*, **95**, 2703 (1973)] and Paper X in the series "Chemistry of the Streptovaricins" [Paper IX: A. H.-J. Wang, I. C. Paul, K. L. Rinehart, Jr., and F. J. Antosz, *ibid.*, **93**, 6275 (1971)].

(2) (a) Presented at the Symposium on Ansamycin Antibiotics and their Biological Activities, Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1973, MEDI-2. Other papers in the symposium: (b) P. Sensi, *ibid.*, MEDI-1; (c) R. C. Gallo, *ibid.*, MEDI-3.

(3) Recent reviews: (a) K. L. Rinehart, Jr., *Accounts Chem. Res.*, **5**, 57 (1972); (b) W. Wehrli and M. Staehelin, *Bacteriol. Rev.*, **35**, 290 (1971).