of the product of reaction of **3** with PF_5 as a complex rather than salt **5**. Further work is under way to investigate the reactions of **7** with nucleophiles as a way to obtain new sulfur(VI) compounds.

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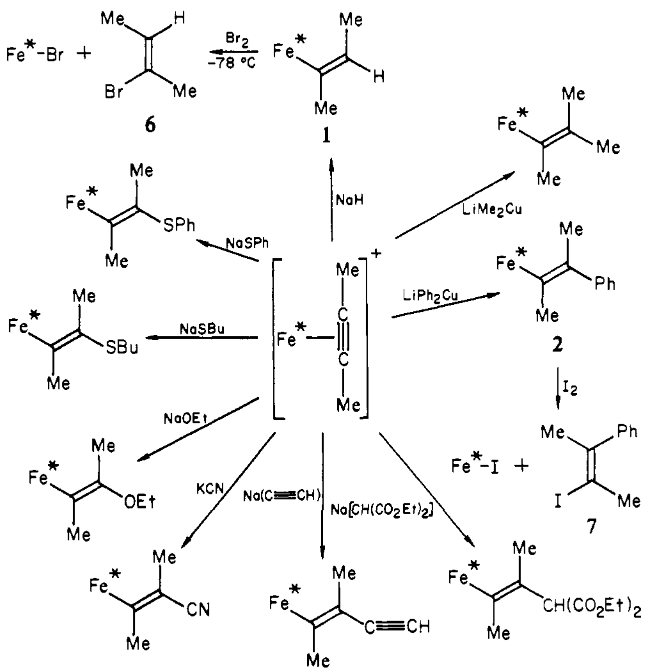
Versatile Preparation of Highly Functionalized σ-Alkenyl Complexes of Cyclopentadienyliron. A New Route to Substituted Alkenes

Sir:

We have recently reported a general synthetic route to $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-alkyne})]BF_4$ complexes and briefly outlined their reduction with borohydride reagents to yield alkenyl complexes.[1] We now report that a wide variety of nucleophiles will react with these cationic π-alkyne[2] complexes to yield new substituted alkenyl complexes. This represents a different and more versatile route to alkenyl complexes than "insertion" of an alkyne into a metal–hydride bond.[3] The nucleophiles add trans to the metal, and alkenyl products in which the more bulky β substituent is cis to the iron undergo a cis–trans isomerization reaction above room temperature. Importantly, the alkenyl group can be cleaved from the metal with retention of stereochemistry. Thus, the sequence coordination of the alkyne to iron, addition of a nucleophile to the alkyne, and cleavage of the alkenyl group with halogen, represent a new route to specifically substituted alkenes that offers wide flexibility in control of the alkene substituents.

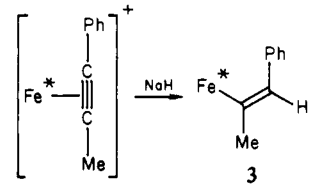
Shown in Scheme I are a number of these new addition reactions for the 2-butyne complex. Although these reactions can be carried out on the isolated pure π complex,[4] a more convenient and higher yield procedure is to use the crude product remaining after solvent evaporation of the filtered reaction mixture used to prepare the alkyne complex.[5] Yields are generally high, and the new alkenyl complexes[6] are thermally stable and only slowly decompose in solution when exposed to air. Because of the many types of reagents represented in Scheme I and the large variety of internal alkynes that will coordinate to the iron, this chemistry represents a very flexible route to many substituted iron–alkenyl complexes.

Scheme I



Fe* = CpFe(CO)(PPh₃)

As shown in Scheme I, the stereochemistry of the products is that which arises from trans addition of the nucleophile. Trans addition of nucleophiles to $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^2\text{-alkene})]^+$ complexes has been shown previously.[7] Proof of trans addition with these alkyne complexes was made with ^1H nuclear Overhauser effect (NOE) enhancement experiments[8] with **1** and **2** (see Scheme I) and the product shown in reaction **1**. Thus, irradiation of the vinyl hydrogen atom resonance for **1** and the phenyl resonance for **2** leads to ca. a 20% enhancement of *both* methyl resonances, a result consistent only with the stereochemistries shown. For the product of reaction **1**, irradiation of the vinyl hydrogen atom resonance leads to a 20% enhancement of the methyl resonance whereas irradiation of the phenyl resonance produces no enhancement of the methyl resonance. It should be noted that reaction **1** is regioselective as only one product was obtained. We assigned structure **3** on the basis of the characteristic downfield shift of the vinyl hydrogen atom NMR resonance α to a phenyl substituent[9] (at δ 6.20 in $CDCl_3$; for comparison in compound **1**, the vinyl hydrogen atom resonates at δ 5.40) and on the small[10] (0.8 Hz) coupling constant between the methyl and



3 (1)

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[1] Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73–84.

[2] Complexes of terminal alkynes cannot be prepared in this system, presumably because of the formation of vinylidene complexes; see: Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763–7765. Boland, B. E.; Fam, S. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *172*, C29–C32. Bruce, M. I.; Willis, R. C. *Aust. J. Chem.* **1979**, *32*, 1471–1485.

[3] (a) Reichel, P. M.; Malzahn, D. C. *Inorg. Chim. Acta* **1979**, *36*, 267–268. (b) Schwartz, J.; Labinger, J. A. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 333–340.

[4] In a typical reaction, a THF (30 mL) solution of $[(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(\eta^2\text{-2-butyne})]BF_4$ (1.0 g, 2.0 mmol) was cooled to −78 °C and treated with $LiCu(CH_3)_2$ (2.0 mmol) in THF (10 mL). The reaction was allowed to warm to room temperature, the solvent evaporated, the residue extracted with CH_2Cl_2, and this solution placed on an alumina chromatography column. Elution with hexane–CH_2Cl_2 (3:2 v/v) developed a single red band which was collected and the solvent evaporated. The residue was dissolved in toluene (10 mL) and treated with hexane (10 mL). Cooling overnight at −10 °C yielded red crystals which were collected and dried (0.95 g, 97%). For the KCN, NaOEt, NaSPh, and NaSBu reactions, carefully dried methanol was used as the solvent. For the other reactions, THF was used as the solvent.

[5] The η^2-alkyne complexes are best prepared by adding cooled (below −20 °C) CH_2Cl_2 to an equimolar mixture of Fe*-I and $AgBF_4$ followed by addition of 1.1 equiv of the alkyne. After the mixture is warmed to room temperature, it is filtered (using filter-aid) and the solvent evaporated. The appropriate solvent is then added and the nucleophilic addition reaction carried out as above. The yield for this two-step sequence for the 2-butyne complex and $LiMe_2Cu$ is 96%.

[6] Complete characterization (IR, ^1H and ^{13}C NMR, and melting-point data) and analytical figures have been obtained on all of the alkenyl complexes reported in this paper.

[7] (a) Nicholas, K. M.; Rosan, A. M. *J. Organomet. Chem.* **1975**, *84*, 351–356. (b) Sanders, A.; Magatti, C. V.; Giering, W. P. *J. Am. Chem. Soc.* **1974**, *96*, 1610–1611. (c) Wong, P. K.; Madhavaro, M.; Marten, D. F.; Rosenblum, M. *Ibid.* **1977**, *99*, 2823–2824.

[8] (a) Noggle, J. H.; Schirmer, E. R. "The Nuclear Overhauser Effect"; Academic Press: New York, *1971*. (b) Bell, R. A.; Saunders, J. K. *Top. Stereochem.* **1973**, *7*, 1–92. (c) All NOE experiments were carried out in carefully degassed CS_2 or $CDCl_3$ solutions.

[9] Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. "Spectrometric Identification of Organic Compounds", 3rd ed.; Wiley: New York, 1974; p 223.

[10] Geminal CH_3–H coupling for compound **1** is 6.0 Hz.

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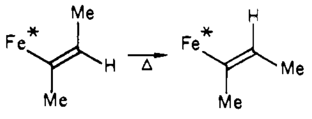
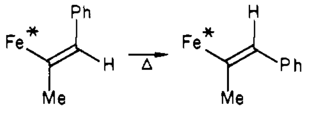
vinyl hydrogen atoms (also see the cleavage reactions and the NOE results on complex **5** outlined below).

Both compounds **1** and **3** have the larger β substituent cis to the iron. Heating either compound in toluene solution at ca. 40 °C for 15 min causes isomerization to the presumably more stable isomers **4** and **5** (eq 2 and 3). Again, ^{1}H NOE enhancement experiments proved the stereochemistry of the products. For example, with **5**, irradiation of the vinyl hydrogen atom resonance now leads to no enhancement of the methyl resonances whereas irradiation of the phenyl resonance leads to a 22% enhancement of the methyl resonance. Note that the methyl–vinyl hydrogen coupling remains small (1.4 Hz) as expected for this isomer. Bergman has reported an analogous (probably base catalyzed) isomerization for a nickel–alkenyl complex.[11] Further investigations of these isomerization reactions are under way at present.



1 **4** (2)



3 **5** (3)

That these alkenyl complexes can be useful in the synthesis of alkenes is demonstrated by the fact that the alkenyl group can be cleaved by halogens with retention of stereochemistry. As shown in Scheme I, reaction of **1** with Br$_2$[12] at −78 °C in Et$_2$O yields **6**[13] and of **2** with I$_2$[12] in warm CS$_2$ yields **7**.[14] Cleavage of **3** and **5** with Br$_2$[15] and **4**[16] and **5**[17] with I$_2$ also proceeds with retention of stereochemistry. Isolated yields of alkenes in these small-scale reactions are good (60–78%), and the Fe*-X complex is isolated nearly quantitatively. Note for the two compounds (**1** and **3**) undergoing the cis–trans isomerization reaction that either alkene isomer can be cleaved free of contamination of the other. Because the iron starting material for this chemistry, Fe*-X (X = I, Br), is inexpensive and easy to prepare on a large scale[18] (and is recovered in the last step), the reactions outlined here represent a new and potentially powerful method for preparing specifically substituted alkenes from internal alkynes, a method different in approach and result from zirconium[3b] or copper chemistry.[19] Complete development of this method for the synthesis of alkenes is under way at present.

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[11] Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410–4412.

[12] The Br$_2$ cleavage reactions were carried out by cooling an Et$_2$O solution of the complex to −78 °C followed by the dropwise addition of 1 equiv of Br$_2$ in Et$_2$O, and the resultant solution was stirred cold for 2 h. The I$_2$ cleavage reactions were carried out by dropwise addition of 1 equiv of I$_2$ in CS$_2$ to a CS$_2$ solution of the complex heated to 35 °C. To either reaction is added degassed H$_2$O, the water layer is extracted with ether, the organic extracts were combined and dried over MgSO$_4$, and the filtered solution was flash evaporated into a liquid nitrogen cooled trap at low pressure. The organic compound is isolated by evaporation of the solvent from the warmed solution in the trap (60–78% yield), and they were identified by comparison of IR and ^{1}H NMR data with literature values as noted. The Fe*-X complex (X = Br, I) was isolated by a brief chromatography on alumina, eluting with CH$_2$Cl$_2$, of the remaining residue after the flash evaporation. Note that up to the step of the flash evaporation the solutions need moderate protection from oxygen.

[13] Vidal, M.; Vincens, M.; Arnaud, P. *Bull. Soc. Chim. Fr.* **1972**, 665–681.

[14] Stereochemistry assigned by ^{1}H NOE enhancement experiments. ^{13}C and ^{1}H NMR data are also consistent with the formulation.

[15] Klein, J.; Levene, R. *Tetrahedron Lett.* **1974**, 2935–2938.

[16] Matter, A. E.; Pascual, C.; Pretsch, E.; Pross, A.; Simon, W.; Sternhell, S. *Tetrahedron* **1969**, *25*, 2023–2034.

[17] Heck, R. F.; Schoenberg, A.; Bantoletti, I. J. *Org. Chem.* **1974**, *39*, 3318–3326.

[18] (a) King, R. B. In "Organometallic Synthesis"; Eisch, J. J., King, R. B., Ed.; Academic Press: New York, 1965; Vol. I., p 114. (b) Reichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1977**, *5*, 1177–1181. (c) Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chem. Acta* **1969**, *3*, 346–350.

[19] (a) Jukes, A. E. *Adv. Organomet. Chem.* **1974**, *12*, 215–323. (b) Posner, G. H. *Org. React.* (N.Y.) **1972**, *19*, 1–113.

Arene–Metal Complexes in Organic Synthesis. Synthesis of Acorenone and Acorenone B

Sir:

The development of synthesis strategies for the generation of a quaternary carbon, especially a spirocyclic ring system with good control over the stereochemistry, continues to be a challenge to organic synthesis. Among spirocyclic natural products, the spiro[4.5]decane system has been studied often because of many examples in nature and interesting elements of stereochemistry. Acorenone (**1**) and acorenone B (**2**) are members of this class of sesquiterpenes and have been synthesized by several research groups.[1] In common with most previous syntheses of spirosesquiterpenes,[2] the strategy in these efforts involved the formation of *gem*-disubstituted monocyclic ring systems and then construction of the second ring. We have reported a new approach to the formation of spiro[4.5]decenones which appears particularly attractive as the basis of a simple synthesis of the acorenones.[3]

Acorenone and acorenone B have the common structural feature of a spiro ring formed from a 2-substituted cyclohexenone and 1,3-dialkylcyclopentane. There are three centers of chirality, the carbons bearing the methyl and isopropyl groups and the spiro carbon. Our strategy (Scheme I) relies on the activating and meta-directing effects of the chromium tricarbonyl group[4] to introduce the spirocyclopentane unit by nucleophilic addition to an anisole derivative (**3**). It employs the specific exo addition to coordinated arenes[5,6] to control the configuration at the spiro carbon. Hydrogenation of an *exo*-methylene unit is proposed to introduce the cis relationship of the two alkyl groups. The execution of this strategy is outlined in Schemes II–IV, showing all isolated intermediates.

As outlined in Scheme II, the chromium complex **3** was prepared in 95% yield by heating *o*-methylanisole and chromium hexacarbonyl in dioxane at reflux with an air condenser.[5,7] Complex **3** was easily crystallized (mp 71–72 °C) and has been prepared on a 70-g scale. The first crucial bond is formed by reaction of **3** with the cyanohydrin acetal anion **4**[8] followed by oxidation with excess iodine. Treatment with aqueous acid and then base converted the cyanohydrin acetal to a ketone unit,[8] effecting formal nucleophilic substitution for hydrogen by an acyl group. The reaction produced isomer **5** (90–95% yield) contaminated by a trace (<3%) of a positional isomer.[9] The 4-carbon side chain required for cyclization (in **7**) was obtained by addition

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[1] (a) G. L. Lange, E. E. Neidert, W. J. Orrom, and D. J. Wallace, *Can. J. Chem.*, **56**, 1628 (1978); (b) W. Oppolzer, K. K. Mahalanabis, and K. Battig, *Helv. Chim. Acta*, **60**, 2388 (1977); (c) M. Desaro and J-P. Bachmann, *J. Chem. Soc., Chem. Commun.*, 203 (1978); (d) H. Wolf, M. Kolleck, and W. Rascher, *Chem. Ber.*, **109**, 2805 (1976); (e) B. M. Trost, K. Hiroi, and N. Holy, *J. Am. Chem. Soc.*, **97**, 5873 (1975); (f) J. F. Ruppert, M. A. Avery, and J. D. White, *J. Chem. Soc., Chem. Commun.*, 978 (1976).

[2] (a) J. A. Marshall, S. F. Brady, and N. H. Anderson, *Fortschr. Chem. Org. Naturst.*, **31**, 283 (1974); (b) A. A. Krapcho, *Synthesis*, 77 (1978).

[3] M. F. Semmelhack, J. J. Harrison, and Y. Thebtaranonth, *J. Org. Chem.*, 44, 3275 (1979).

[4] M. F. Semmelhack and G. Clark, *J. Am. Chem. Soc.*, **99**, 1675 (1977).

[5] M. F. Semmelhack, H. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, *J. Am. Chem. Soc.*, **101**, 3535 (1979).

[6] For a general discussion of nucleophilic addition to coordinated π systems, see: S. G. Davies, M. L. H. Green, and D. M. P. Mingos, *Tetrahedron*, 34, 3047 (1978).

[7] B. Nichols and M. C. Whiting, *J. Chem. Soc.*, 551 (1959).

[8] The cyanohydrin acetal was prepared from isobutyroaldehyde and used according to the method of G. Stork and L. Maldonado, *J. Am. Chem. Soc.*, **93**, 5286 (1971).

[9] Compound **5** was obtained in high purity by careful fractional distillation, 77% yield.

0002-7863/80/1502-5924$01.00/0