Nucleophilic Addition Reactions with Cationic Iron π-Alkyne and Related Complexes

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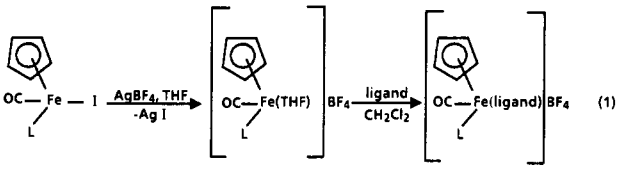
The addition of nucleophiles to unsaturated ligands activated by coordination to transition metals has proven to be useful for the preparation of new organometallic complexes and as a versatile methodology in organic synthesis.[1] Despite the considerable interest in this area, prior to our studies, addition reactions with η^2-alkyne complexes leading to (η^1-alkenyl)metal species had only been briefly studied. Chisholm and Clark had reported the addition of alkoxides to platinum–alkyne complexes.[2] Green had reported the addition of hydride to $[CpMo[P(OMe)_3]_2(\eta^2\text{-alkyne})]^+$ cations in the presence of $P(OMe)_3$ yields $CpMo[P(OMe)_3]_3(\eta^1\text{-alkenyl})$.[3] Subsequently, extensive chemistry of similar molybdenum–alkyne cations has been developed.[4] This chemistry is different from the iron chemistry reported in this Account because the alkyne is a four-electron donor in these molybdenum complexes and addition reactions generally yield η^2-alkenyl products.

The nucleophilic addition reactions carried out in our laboratories with $[CpFeCO(L)(\eta^2\text{-alkyne})]BF_4$ (Cp = cyclopentadienide; L = PPh_3, $P(OPh)_3$) complexes (alkyne acts as a two-electron donor) yield η^1-alkenyl complexes. Surprising results, such as reaction with the Cp ligand rather than the alkyne, are frequently observed. The stereochemistry of the η^1-alkenyl group formed in these reactions has been determined carefully, and isomerization reactions of this ligand are observed under certain conditions. Alkenyl complexes can also be prepared by nucleophilic addition reactions with vinylidene and η^2-allene cations. At 1 atm of CO pressure in the presence of catalytic amounts of an oxidant, these alkenyl complexes undergo CO insertion to form alkenylacyl complexes. Oxidative cleavage of the alkenyl (or alkenylacyl) group leads, overall, to a versatile route for converting alkynes into specifically substituted alkenes.

Cationic η^2-Alkyne Complexes

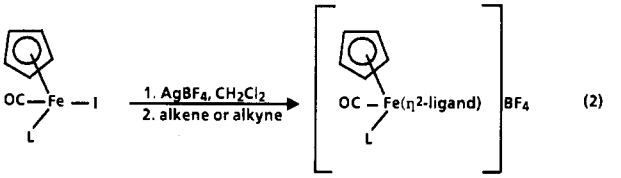
To initiate the study, a general and high-yield preparation of the unknown $[CpFeCO(L)(\eta^2\text{-alkyne})]BF_4$ (L = PPh_3, $P(OPh)_3$) complexes was needed. Only one similar complex, $[CpFe(CO)_2(\eta^2\text{-MeC}{\equiv}CH)]PF_6$, had been briefly mentioned[5] in the literature. We wanted to work with L = PPh_3, $P(OPh)_3$ complexes rather than the more extensively studied L = CO system[6] for three reasons. First, we had studied $CpFeCO(PPh_3)(\eta^1\text{-alkyl})$ complexes in detail[7] and had shown that they were stable and useful for the study of β-elimination[7c] and alkyl isomerization[7d,e] reactions. Second, the development of the chemistry of these phosphorus ligand substituted complexes is facilitated by the fact that $[CpFe(CO)_2]_2$ is not a persistent byproduct (lowering yields) as it can be in the L = CO system, especially when reactions with potential reducing reagents such as RLi or $[HBR_3]^-$ are carried out. Third, introduction of the phosphorus ligand generates an asymmetric center at iron, of potential use in both mechanistic and synthetic endeavors.

Our first efforts to prepare alkyne (also alkene) complexes are shown in eq 1.[8] This route is successful for



(1)

L = CO[8,9] and is complementary to similar exchange reactions using $[CpFe(CO)_2(\eta^2\text{-}CH_2{=}CMe_2)]^+$ developed by Rosenblum.[10] The THF adduct[11] is particularly reactive with weakly coordinating ligands if BF_3 is also introduced to coordinate the THF being displaced.[8] Unfortunately, this methodology is not successful for L = PPh_3, $P(OPh)_3$ for alkenes (with the exception of ethylene) or alkynes. Equation 2 outlines



(2)

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(11) A large-scale preparation of $[CpFe(CO)_2(THF)]BF_4$ has been reported[9a] that avoids the use of $AgBF_4$.

Daniel L. Reger was born in Texas in 1945. He received his B.S. degree from Dickinson College (1967) and his Ph.D. degree from the Massachusetts Institute of Technology (1972), working with Alan Davison. He then joined the chemistry faculty at the University of South Carolina in 1972, where he is presently Professor of Chemistry. His research interests are the synthesis and characterization of complexes containing metal–carbon bonds and complexes of early transition metals and the lanthanides.

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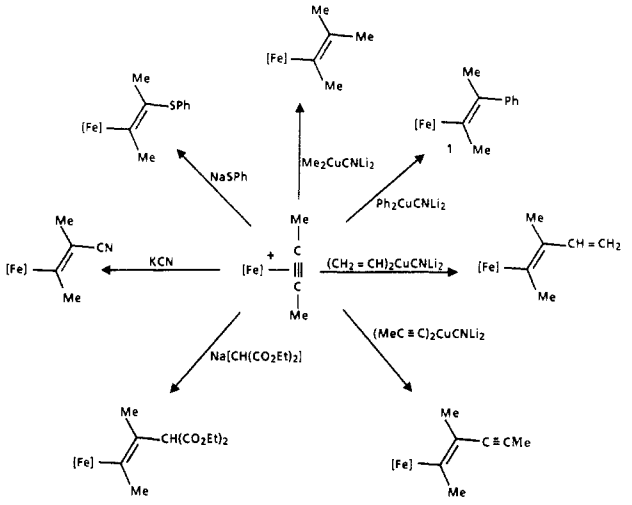
Scheme I

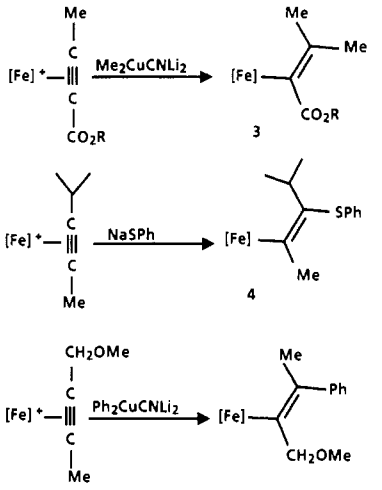


reaction conditions that avoid the presence of the THF ligand.[12,13] These reactions for L = PPh_3, $P(OPh)_3$ yield stable complexes for a wide range of alkenes and alkynes. An advantage of the $P(OPh)_3$ system is that the π-complexes are more stable, while an advantage of the L = PPh_3 system is that the products are generally easier to crystallize. For L = CO, the reaction can be complicated by the formation of $\{[CpFe(CO)_2]_2I\}BF_4$, and the reaction is very sensitive to the purity of the starting materials. Although a modification of our procedure has been published,[14] the reaction in eq 1 (possibly in the presence of BF_3) is generally a better method for preparing $[CpFe(CO)_2(ligand)]BF_4$ complexes. For L = PPh_3, $P(OPh)_3$, reaction 2 is the method of choice for all but strongly coordinating ligands. One limitation is that only internal alkyne complexes can be isolated. Presumably, terminal alkynes rearrange to vinylidene[15] complexes.

Addition Reactions with Carbon Nucleophiles and Thiophenoxide

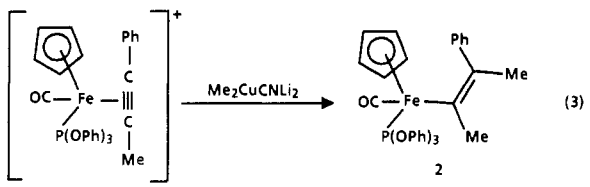
Scheme I shows a series of successful addition reactions with the 2-butyne complexes.[16] These reactions are carried out in two steps. The η^2-alkyne complex is prepared as in eq 2 and used directly for the addition reaction. Isolated yields of the alkenyliron complexes are high for the two-step procedure. Carbon nucleophiles stabilized by electron-withdrawing substituents are very successful in the reaction, but standard alkyllithium reagents (vide infra) are not. Use of the higher order cuprate reagents[17] shown in the Scheme was critical to the development of this chemistry. In our initial work in this area,[18] standard R_2CuLi reagents were used. Although in certain cases these reagents are

Scheme II



successful, yields are variable (probably dependent on exact CuI/RLi ratios) and much lower than with higher order cyanocuprate reagents. The cyanocuprate reagents also facilitate the purification procedures because only a short alumina plug filtration is needed to remove Cu residues[16] whereas column chromatography is needed with LiR_2Cu reagents.[18] The $R_2CuCNLi_2$ solutions are also easier to prepare and thus should prove to be very attractive reagents for addition reactions with other unsaturated ligands bonded to transition metals. One particularly notable reaction is the addition of the propynyl nucleophile from a cuprate reagent. Generally, in organic systems alkynylcuprate reagents are not very reactive.[19]

Scheme I shows the nucleophile adding overall trans (or anti) with respect to iron. This was the expected mode of addition because trans addition to $[CpFe(CO)_2(\eta^2\text{-alkene})]^+$ complexes had been proven earlier.[20] This point turned out to be very important (for examples of overall cis addition, see later sections) and was proven for the nucleophiles in Scheme I by the following experiments. An isomer of the product of phenyl addition, 1 (L = $P(OPh)_3$), shown in Scheme I can be prepared as shown in eq 3. The stereochemistry of the



(3)

double bond in 2 was definitely determined to be *Z* by a single-crystal X-ray analysis.[21] This defines the stereochemistry of 1 as *E*. As these isomers *do not interconvert* under the reaction conditions or isolation procedures, trans addition of the nucleophile, at least for organocuprate addition reactions, is established.

Reaction 3 and other addition reactions with this unsymmetrical alkyne complex are regioselective, with the nucleophile adding to the phenyl-substituted alkyne

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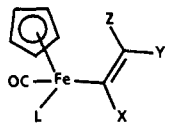
carbon atom. Scheme II shows representative reactions (the majority of the work is for L = $P(OPh)_3$) with three additional unsymmetrical alkyne complexes.[18b,22] In nearly every case, the reactions yield a single product. As mentioned above, assignment of the structural arrangement of the alkenyl ligands in these products is difficult. Initially, a combination of X-ray crystallography (e.g., complex **2**,[21] complex **3**,[18b] and a derivative of **4**[22]), isotopic labeling,[23] and variable-temperature NMR studies[16] was used. Examination of the ^{13}C NMR spectra of over 30 of the L = $P(OPh)_3$ alkenyliron complexes shows some very consistent trends in the P–C coupling constants and chemical shifts of the alkene-bound carbon atoms.[22] These trends afford two simple rules that allow complete assignment of the structure of most alkenyliron complexes in this system.

Rule 1: P–C coupling is generally observed in positions (see A) X and Y, but not at Z.

Rule 2: When X = Y or X = Z, the lower field resonance is assigned to X.



A

Although the data are more limited, these rules also hold for the L = PPh_3 system. A variety of coupling constant trends, including $^3J(PtH)$,[24a-c] $^3J(CH)$,[24d] and $^3J(WH)$,[24d] have been used to assign alkene stereochemistry of other alkenylmetal complexes, but these methods are not applicable to the tetrasubstituted alkenes reported here.

The factors controlling the regiochemistry of the additions are of considerable interest. Nucleophilic addition reactions with similar (η^2-alkene)metal complexes have been studied theoretically.[25] The origin of the activation of the alkene to nucleophilic addition was attributed to slippage of the metal along the π-bond to an intermediate resembling η^1-coordination. It was argued that electron-donor substituents on the alkene should favor slippage away from the substituent, a prediction verified experimentally.[26] For electron-acceptor substituents, a prediction was not as clear because electronic effects would favor slippage toward the substituted alkene carbon atom, but steric effects would be in the opposite direction.

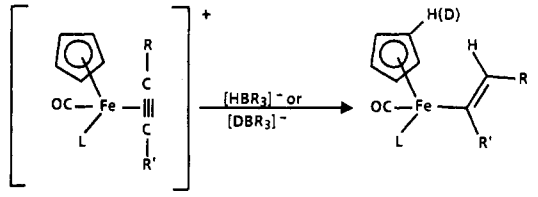
These ideas should apply to $[CpFe(CO)L(\eta^2\text{-alkyne})]^+$ complexes. For the π-donating phenyl substituent in MeC≡CPh, nucleophiles add to the alkyne carbon atom bearing this donor group as predicted by theory. The strongly electron-withdrawing ester substituent in $MeC{\equiv}CCO_2R$ does the opposite, directing the nucleophile away from the functionalized alkyne carbon atom. Similar regioselectivity to the ester-substituted case is observed with the weaker electron-withdrawing CH_2OMe substituent for the alkyne $MeC{\equiv}CCH_2OMe$. Electronic effects are clearly dominant in these two cases. Similar domination by an electron-withdrawing group has been observed in platinum chemistry.[2c] The control of regiochemistry with the $MeC{\equiv}CCHMe_2$ complex is not as clear because the reaction is not always regioselective.[22]

In order to ascertain if ground-state slippage of the alkyne can be observed, the structures of $[CpFeCO[P(OPh)_3](\eta^2\text{-alkyne})]SbF_6$ (alkyne = MeC≡CMe (**5**), PhC≡CMe (**6**)) were determined crystallographically.[27] Essentially no slippage of the alkyne ligand was observed. For the PhC≡CMe complex, **6**, the Fe–C(alkyne) distances are equal (2.14 (1) and 2.146 (9) Å), and only a slight distortion (2.165 (7) vs 2.114 (6) Å) was observed for complex **5**.

A number of functionalized alkynes have not proven useful in these reactions.[22] Thus, η^1-alkenyl complexes have not been isolated from the two-step reaction procedure for $MeC{\equiv}CSiMe_3$, $MeC{\equiv}CCH_2OSiMe_3$, MeC≡COEt, $MeC{\equiv}CNEt_2$, EtC≡CC(O)Me, and cyclooctyne. For the $SiMe_3$-substituted cases, the iron appears to induce cleavage of the silyl group. For cyclooctyne, the η^2-complex forms but reactions with nucleophilic reagents were not observed. With the other three alkynes, a cationic intermediate seems to form, but the nucleophilic addition reactions are not successful. It is likely that a lone pair on the heteroatom coordinates to iron rather than the triple bond. We have shown previously that nitrogen bonds to iron in preference to the double bond for ligands such as acrylonitrile.[12]

Reactions of Hydride and Amides: Ring Substitution Chemistry

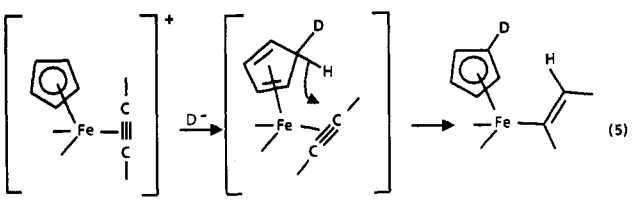
Reaction of hydride (deuteride) reagents with the η^2-alkyne cations yields products arising from overall cis addition (eq 4).[23] The stereochemistry of the double



(4)

L = PPh_3, $P(OPh)_3$; R = Me, R' = CO_2Et; R = Ph, R' = Me

bond was determined for $CpFeCO(PPh_3)[\eta^1\text{-}(E)\text{-}C(CO_2Et){=}C(H)Me]$ crystallographically.[28] As determined by a combination of ^1H, ^2H, and ^{13}C NMR experiments, if $[DBEt_3]^-$ is used in reaction 4, the deuterium label is exclusively located in the cyclopentadienyl ring, one per ring.[28] Equation 5 shows a



(5)

reasonable course for these reactions. Hydride or deuteride adds exo to the Cp ring followed by intra-

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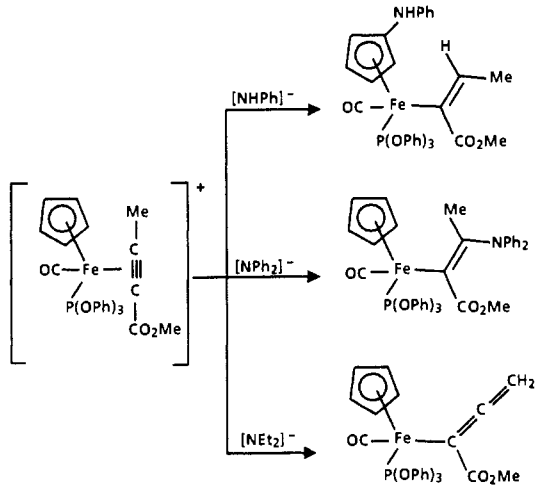
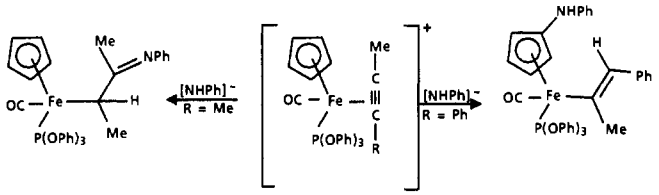
Scheme III

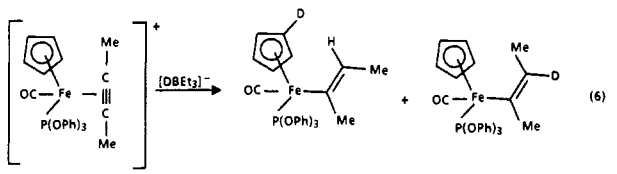


Scheme IV



molecular cis addition to the alkyne of the endo H of the cyclopentadiene ring formed in the first step.

In one case, both ring addition and alkyne addition are observed (eq 6), with the two products forming in about equal amounts.[23] Note the location of the added



deuteride for the alkyne addition product is that expected for direct trans addition. If this same reaction is carried out with Li[HB(*sec*-Bu)$_3$], only the *E* isomer forms. Thus two similar reducing reagents react quite differently.[20c]

Additional examples of ring substitution chemistry, as well as other types of reactions, are observed when amides are used as the nucleophile.[29] Schemes III and IV show reactions typical of this chemistry. Although it is not possible to predict the products, a priori, with these nucleophiles, frequently Cp ring substitution reactions are observed. Normal alkyne addition is also observed, followed by tautomerism for secondary enamine intermediates to yield imines. Cp ring substitution is also observed in reactions of MeLi with these η^2-alkyne complexes.[29] These MeLi reactions are very indiscriminate, but the ring addition product generally predominates. A similar type of Cp ring substitution reaction, where an η^2-alkyne is not involved, has been reported[30] in a reaction of a CpCo complex and MeLi.

The Cp ring substitution reactions outlined above are unique to the η^2-alkyne complexes. A wide range of nucleophiles react with alkene[6a,23] and allene[23] (vide infra) complexes in these systems to yield normal alkene

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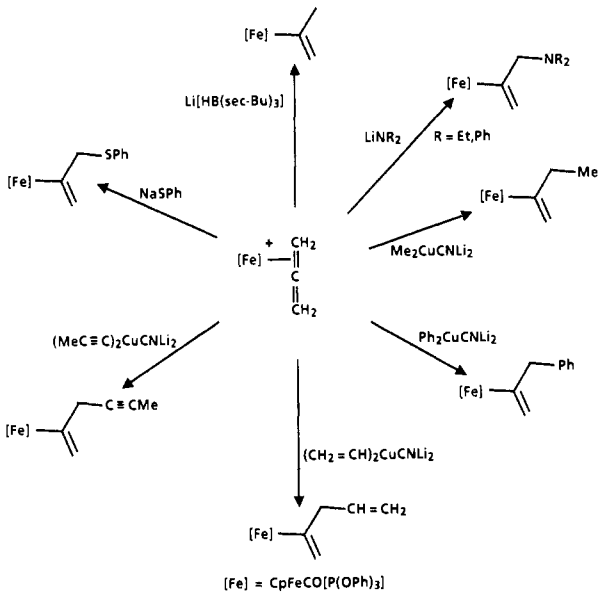
Scheme V



[Fe] = CpFeCO[P(OPh)$_3$]

addition products. The main difference for alkyne complexes is the additional π-orbital ($\pi_\perp$). This orbital has been shown to be very important in addition reactions with the d^4-molybdenum complexes noted earlier (alkyne acts as a four-electron donor), reactions that generally lead to η^2-alkenyl complexes.[4,31] The impact of this orbital for the d^6-iron complexes (alkyne acts as a two-electron donor) studied here is not as clear, although its interaction with the filled metal orbital is repulsive. In the solid-state structures of the η^2-alkyne complexes **5** and **6**, bonding to iron does not greatly perturb the alkyne.[27] The C≡C bond lengths are the same as observed in free alkynes and C≡C—R bend back angles are small, ranging from 155 (2) to 159 (1)°. Thus, the alkyne is not strongly bonded to iron. This can be observed chemically by the fact that weak ligands such as THF rapidly displace the alkyne at room temperature.

Other Routes to Alkenyliron Complexes

It had been shown earlier that CpFe(CO)$_2$(η^1-alkenyl) complexes could be prepared by addition of nucleophiles to η^2-allene complexes.[32] Starting with [CpFeCO(L)(η^2-allene)]BF$_4$ (L = PPh$_3$, P(OPh)$_3$), addition reactions such as those outlined in the previous sections of this Account would lead to terminal alkenyl complexes, complexes not available by the alkyne addition chemistry. Scheme V shows that this chemistry is very successful.[23,29] Yields are high in all reactions. Purification of the products can be effected by a simple filtration through Celite. This is important because column chromatography of most of these terminal alkenyl complexes causes a rearrangement reaction (eq 7), leading to internal alkenyl complexes.[23] The reaction also takes place in CHCl$_3$(CDCl$_3$), but not in other solvents such as hexane, benzene, CH$_2$Cl$_2$, and EtOH.

(31) (a) Allen, S. R.; Beevor, R. G.; Green, M.; Norman, N. C.; Orpen, A. G.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **1985**, 435. (b) Kreisal, F. R.; Sieber, W. J.; Hofmann, P.; Riede, J.; Wolfgruber, M. *Organometallics* **1985**, *4*, 788.

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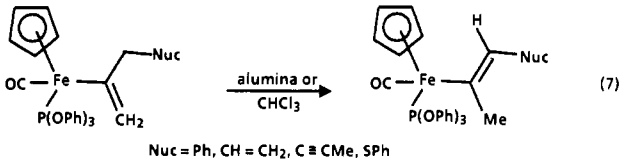
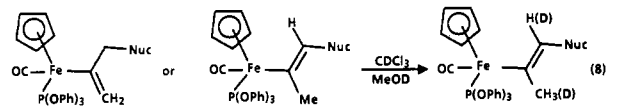


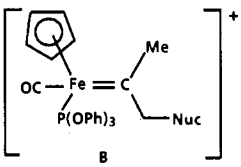
Nuc = Ph, CH = CH_2, C ≡ CMe, SPh

The *E* stereoisomer is the exclusive product in each case.

The above isomerization reactions may be acid catalyzed and, in fact, they can be induced by trace amounts of acid in Et_2O–benzene. Also, stirring either the reactants or products of eq 7 in $CDCl_3$/MeOD (but not in pure MeOD) leads to incorporation of deuterium at the α-methyl group and β-vinyl position of the internal alkenyl product (eq 8).[23] This makes the al-

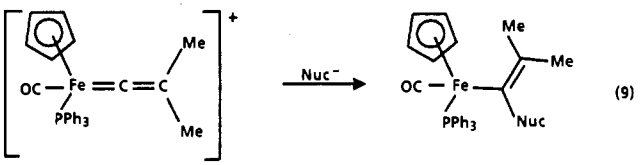


kylidene intermediate, B, an attractive intermediate in the isomerization reactions, especially since similar complexes have been prepared by this route.[33] While reasonable, other pathways are possible as evidenced by the fact that these isomerization reactions can also be catalyzed by oxidizing reagents (vide infra).



B

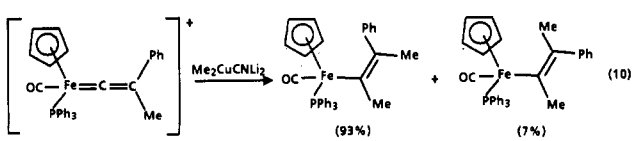
Another route to alkenyliron complexes such as those reported above is the addition of anionic nucleophiles to cationic vinylidene complexes. High-yield preparations of the requisite vinylidene complexes were well-known[34,35] and hydride addition had already been demonstrated.[35] Carbon-based nucleophiles (from $R_2CuCNLi_2$ reagents) and thiophenoxide add in good yield (eq 9).[36] Note that this chemistry differs in result



Nuc = Ph, CH = CH_2, SPh

from that outlined earlier in that the nucleophile becomes a substituent at the α-alkenyl carbon atom, whereas in the alkyne and allene addition chemistry it becomes a β-alkenyl substituent.

Addition to an unsymmetrical vinylidene complex is highly stereoselective,[36] as shown in eq 10. Presumably

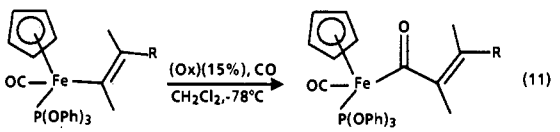


the specificity arises from the addition reaction taking place preferentially away from the bulky phenyl vinylidene substitutent.

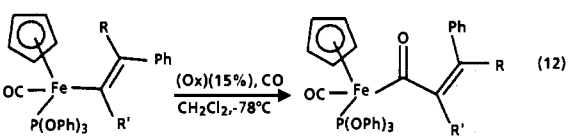
Oxidatively Induced CO Insertion and Cleavage Reactions: Synthesis of Highly Functionalized Alkenes

The many routes to alkenyliron complexes outlined above provided an opportunity for the synthesis of specifically functionalized alkenes if the alkenyl ligand could be cleaved from iron. Our goal was not only to induce a stereoselective cleavage but also to introduce additional functionality during the cleavage procedure. To accomplish this, insertion of CO into the iron–C(alkenyl) bond was desired. In addition to being of use in organic synthesis, this chemistry would also yield a large class of alkenylacyl complexes for future studies.

As expected from the work with similar alkyliron complexes,[6b] direct insertion of CO at 1 atm of pressure under a variety of conditions[37] was unsuccessful. From the work of Magnuson and Giering,[38] oxidatively induced CO insertion seemed promising. Equation 11[22,39]



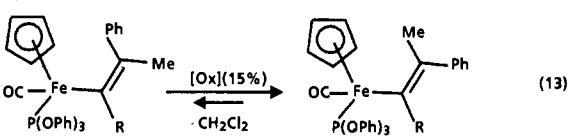
shows that alkenyl complexes will undergo CO insertion at 1 atm using ca. 15% of an oxidant ($[Cp_2Fe]^+$ in CH_2Cl_2 or Ce(IV) in a mixed CH_2Cl_2/EtOH solvent). In general, the reactions proceed with retention of the alkenyl stereochemistry. The exceptions (eq 12) are



R = R' = Me, Et; R = Me, R' = Ph; R = i-Pr, R' = Me

cases where a Ph group is trans to iron with a group other than H at the *cis*-alkenyl position. Inversion of alkenyl stereochemistry is observed in these cases except for CpFeCO[$P(OPh)_3$][η^1-(*E*)-C(CH_2OMe=C(Me)Ph]. The alkene stereochemistry of these (alkenylacyl)iron complexes was determined by a combination of X-ray crystallography, NMR,[40] and chemical methods.[22,39]

Equation 13 shows that the catalytic oxidative conditions in the absence of CO can cause double-bond isomerization reactions.[39] For R = Me the equilibrium



lies to the right, but for R = Ph an equilibrium mixture of the *Z* and *E* isomers is established in a 1:5 ratio. This reaction can thus explain the origin of the isomerization of the double bond observed in eq 12, but we have the

(33) (a) Kuo, G.-H.; Helquist, P.; Kerber, R. C. *Organometallics* **1984**, *3*, 806. (b) Kremer, K. A. M.; Kuo, G.-H.; O'Connor, E. J.; Helquist, P.; Kerber, R. C. *J. Am. Chem. Soc.* **1982**, *104*, 6119. (c) Casey, C. P.; Miles, W. H.; Tukada, H.; O'Connor, J. M. *Ibid.* **1982**, *104*, 3761.

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(35) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763.

(36) Reger, D. L.; Swift, C. A. *Organometallics* **1984**, *3*, 876.

(37) For a recent study on the carbonylation of CpFeCO(L)R complexes, see: Forschner, T. C.; Cutler, A. R. *Organometallics* **1985**, *4*, 1247.

(38) (a) Magnuson, R. H.; Zulu, S.; Tsai, W.-M.; Giering, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6887. (b) Magnuson, R. H.; Meirowitz, R.; Zulu, S.; Giering, W. P. *Ibid.* **1982**, *104*, 5790. (c) Magnuson, R. H.; Meirowitz, R.; Zulu, S. J.; Giering, W. P. *Organometallics* **1983**, *2*, 460.

(39) (a) Reger, D. L.; Mintz, E. *Organometallics* **1984**, *3*, 1759. (b) Reger, D. L.; Mintz, E.; Lebioda, L. *J. Am. Chem. Soc.* **1986**, *108*, 1940.

(40) Brunner, H.; Agrifoglio, G. *J. Organomet. Chem.* **1980**, *202*, C43.

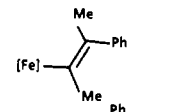
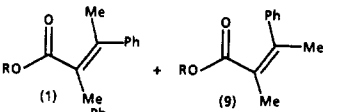
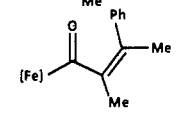
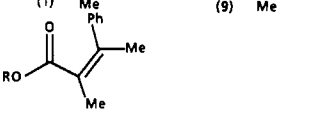
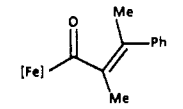
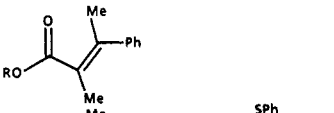
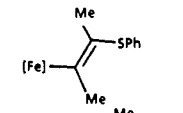
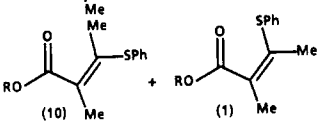
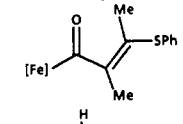
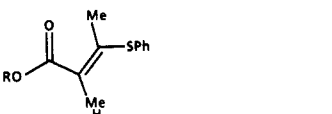
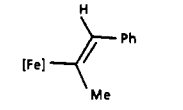
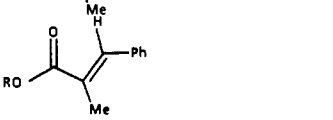
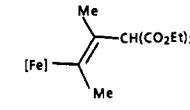
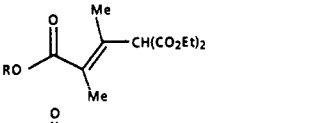
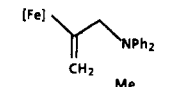
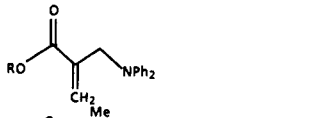
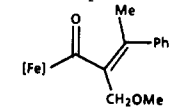
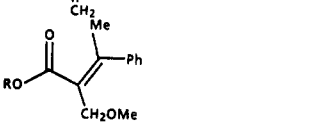
very interesting case that the acyl product isolated from the reaction is stereochemically related to the *less stable* Z-alkenyl isomer. This is analogous to Halpern's[41] asymmetric hydrogenation studies where the rate of H_2 addition determines product ratios rather than the stability of the π-alkene intermediates. For our system, either preferential CO association[42] or, more likely, kinetically favored migratory insertion of a cationic intermediate (almost certainly[42] $[CpFe(CO)_2[P(OPh)_3](\eta^1\text{-alkenyl})]^+$) related to the less stable stereoisomer determines product ratios. Note that the rearrangement reaction shown in eq 7 is also catalyzed by these oxidative conditions.

Another method to assist the CO insertion reactions is to use Lewis acid catalysts.[43] Mixing $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me)=C(Me)Ph]$ with 1 equiv of $AlCl_3$ in CH_2Cl_2 under 1 atm of CO at −78 °C produces mainly the *E*-acyl complex contaminated with a small amount of the *Z*-acyl complex. In a similar reaction, $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Et)=C(Et)Ph]$ produces the *E* and *Z* acyls in a 1:1.3 ratio.[39b] The yields in these reactions are good, but the method has not proven general for all alkenyliron complexes.

Reaction of either the alkenyl or alkenylacyl complexes with an excess of Ce(IV) (ferrocinium was used as the oxidant for case 9) in a mixed CH_2Cl_2/ROH solvent system under CO at 1 atm produces alkenyl esters in good to excellent yield; representative examples are given in Table I. The stereochemistry of the products arising from the alkenyl derivatives parallels the results in eq 11 and 12, although in two cases, small amounts of the other stereoisomer form. The cleavage reactions with alkenylacyl complexes proceed with complete retention of double-bond stereochemistry.[39b] Note in particular the *Z,E* pair in lines 2 and 3. Consistent with this result, it was not possible to reverse the insertion reaction or isomerize alkenylacyl complexes under oxidative catalytic conditions in either a CO or N_2 atmosphere.

Thus, these procedures represent new methods for the preparation of specific tetrasubstituted alkenyl esters.[44] Two of the substituents are dictated by the choice of alkyne and the third by the nucleophile employed. In general, the nucleophile can be a stabilized carbanion, a carbon-based nucleophile for which the lithium derivative can be prepared, or a heteroatom nucleophile. For additional flexibility, alkenyliron complexes can also be prepared via an iron–vinylidene route and from η^2-allene complexes. Particularly notable of this synthetic method is the observed high selectivity for the formation of a single stereoisomer, whereas the earlier methods generally give mixtures[44] (ca. 2:1 of the two stereoisomers). New methodology for di- and trisubstituted alkenyl esters is also developed.[45] Overall, the ester formation is essentially a two-step sequence. First, the η^2-alkyne complex is prepared and the nucleophile added. The second step is the oxidative cleavage. We have found the yields to be good in each step. The iron starting material, $CpFeCO[P(OPh)_3]I$, is inexpensive and can be prepared easily on a large scale. Thus, overall this chemistry outlines a unique and flexible route to (alkenylacyl)iron complexes and highly functionalized alkenes.

Table I
Synthesis of Alkenyl Esters

	Iron Starting Material[a]	Product[b]
1		
2		
3		
4		
5		
6		
7		
8		
9		

[a] [Fe] = $CpFeCO[P(OPh)_3]$. [b] In the two cases where mixtures form, the product ratios are given in parentheses.

Conclusions

High-yield synthetic routes to $[CpFeCO(L)(\eta^2\text{-alkyne})]BF_4$ (L = PPh_3, $P(OPh)_3$) complexes have been developed. These complexes will react with a wide variety of anionic nucleophiles to produce $CpFeCO(L)(\eta^1\text{-alkenyl})$ complexes. Particularly good reagents for the addition chemistry are the higher order cyanocuprates, $R_2CuCNLi_2$. With these reagents, trans addition of the nucleophile is observed. With $[HBR_3]^-$ reagents (and some amides and MeLi), generally overall cis addition of hydride takes place through a reaction pathway in which the nucleophile adds to the Cp ring followed by intramolecular transfer of the endo H atom to the alkyne. This reaction is unique for the alkyne complexes, showing that this chemistry can be quite different from addition reactions with η^2-alkene complexes. Also, careful determination of the stereochemistry of the alkenyl ligand is necessary because under certain common conditions this ligand undergoes isom-

(41) Chan, A. S. C.; Pluth, J. J.; Halpern, J. *J. Am. Chem. Soc.* **1980**, *102*, 5952.
(42) (a) Doxsee, K. M.; Grubbs, R. H.; Anson, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 7819. (b) Therien, M. J.; Trogler, W. C. *Ibid.* **1987**, *109*, 5127.
(43) (a) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272. (b) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.
(44) (a) Baboulene, M.; Sturtz, G. *J. Organomet. Chem.* **1979**, *177*, 27. (b) Slougui, N.; Rousseau, G. *Synth. Commun.* **1982**, *12*, 401. (c) Tanaka, K.; Yamagishi, N.; Tanikaga, R.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3619.
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erization reactions. Other workers preparing alkenylmetal complexes need to be aware of these potential problems. Gladysz has also discussed this point recently.[46] Alkenyliron complexes are also prepared by addition reactions with η^2-allene and vinylidene complexes.

Under catalytic oxidative conditions, these alkenyliron complexes insert CO at 1 atm, yielding CpFeCO[$P(OPh)_3$](η^1-C(O)CR=CR_2) complexes. Again, care needs to be taken in assigning double-bond stereochemistry. Retention is generally observed in the insertion reaction, but complete inversion is observed in a few (all very similar) cases. With either the alkenyl or alkenylacyl complexes, an excess of Ce(IV) in alcohol solvents gives alkenyl esters stereoselectively in good yield. Thus, overall, an alkyne is converted into a tetrasubstituted alkene (trisubstituted in certain cases) in a stereo- and regioselective process that allows extensive choice of the added nucleophile and introduces an ester functional group for further elaboration.

(46) Bodner, G. S.; Smith, D. E.; Hatton, W. G.; Heah, P. C.; Georgiou, S.; Rheingold, A. L.; Geib, S. J.; Hutchinson, J. P.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7688.

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