134 Organometallics 1984, 3, 134-140

Nucleophilic Addition Reactions with Iron η^2-Alkyne Derivatives. Synthesis and Investigation of CpFeCO(L)(η^1-alkenyl) (L = PPh_3, $P(OPh)_3$) Complexes

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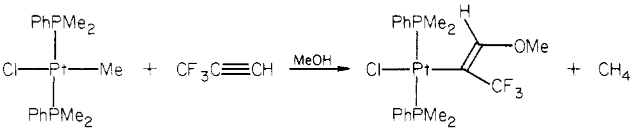
The reaction of $[CpFeCO(L)(\eta^2\text{-alkyne})]BF_4$ (L = PPh_3, $P(OPh)_3$) complexes with a variety of nucleophilic reagents leads to a large family of CpFeCO(L)(η^1-alkenyl) derivatives. Carbon-based nucleophiles are generally best delivered from $R_2Cu(CN)Li_2$ type reagents and include R = Me, Ph, $CH{=}CH_2$, and $C{\equiv}CMe$. The latter two reagents react with $[CpFeCO[P(OPh)_3](THF)]BF_4$ to yield the η^1-alkenyl or η^1-alkynyl complex, respectively. The reagents $Na[CH(CO_2Et)_2]$, KCN (or better R_4NCN), and NaSPh are also successful in the alkyne addition reactions. All of the nucleophiles add trans. The $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)Nuc]$ complexes show dynamic NMR behavior. At low temperatures, two rotamers of the alkenyl group about the Fe–C(alkenyl) bond are observed and these equilibrate near ambient temperature. Rotamers are not observed for L = PPh_3 complexes or for complexes prepared from unsymmetrical alkynes. Isomerization of the double bond for certain η^1-alkenyl complexes is also observed.

Introduction

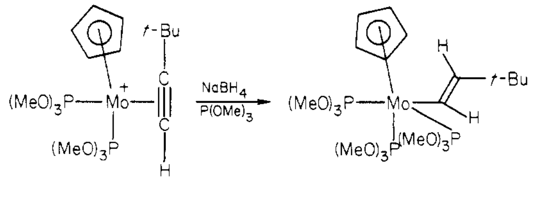
Coordination of an alkene to a neutral or cationic transition-metal complex generally activates the alkene toward nucleophilic addition reactions that lead in many cases to alkylmetal products.[1] The reasons for this activation by the metal is the topic of a recent theoretical paper.[2] These reactions have been shown to take place by trans addition of the nucleophile to the alkene[3] and are frequently regioselective for cases of unsymmetrical alkenes.[4]

In contrast to these extensive investigations, only a few analogous reactions with η^2-alkyne complexes, reactions that lead to alkenylmetal complexes, have been reported. As part of the extensive study of Pt–carbene complexes formed from reactions of Pt(II) complexes with alkynes in alcohol solvents, Chisholm and Clark report a few preparations of Pt–alkenyl complexes that almost certainly form from this type of reaction.[5] In the case shown in eq 1, overall trans addition of the nucleophile was established by NMR coupling constant arguments.[5c]



(1)

A 16-electron molybdenum η^2-alkyne complex reacts with hydride in the presence of excess phosphite ligand as shown in eq 2.[6] The E configuration of the alkenyl group was assigned initially on the basis of NMR coupling constant data and has been subsequently verified by crystallographic techniques. Similar reactions carried out in the absence of added ligand lead to η^2-alkenyl products.[7]



(2)

We have reported that $[CpFeCO(L)(\eta^2\text{-alkyne})]^+$ cations [L = CO, PPh_3, $P(OPh)_3$] will react with a variety of nucleophiles. Our initial report was for hydride as the nucleophile with symmetrical alkynes.[8] The stereochemistry of the addition was not assigned. This point is complicated and is the topic of separate publications.[9] In this initial work, we found that the reactions for the cases where L = PPh_3 and $P(OPh)_3$ gave both higher yields and more stable products. Subsequently, in preliminary form, it was demonstrated that many types of nucleophiles were successful in the addition reaction for the L = PPh_3 case.[10] Overall trans addition of the nucleophiles was assigned on the basis of ^1H nuclear Overhouser effect (NOE) enhancement experiments. This point was more definitively proven by our report[11] on the syntheses of both the Z and E isomers of $CpFeCO[P(OPh)_3][\eta^1\text{-}C(Me){=}C(Ph)Me]$ with the structure of the Z isomer being verified crystallographically. We report here full details on the synthesis and characterization of this family of molecules. Many types of nucleophiles have been shown to add to the η^2-alkyne ligands. The use of higher order organocuprate reagents in these reactions is presented. For $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)Nuc]$ complexes (Nuc = added nucleophile), two rotamers of the alkenyl group can be observed by NMR at low temperatures. This has allowed us to prove the alkene stereochemistry of all complexes. In contrast, the NOE technique has not proven general. We also discuss the isomerization of the alkenyl

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(1) (a) Wong, P. K.; Madhavaro, M.; Marten, D. F.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 2823. (b) Reger, D. L. *Inorg. Chem.* **1975**, *14*, 660.

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

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

(4) Lennon, P.; Rosan, A. M.; Rosenblum, M. *J. Am. Chem. Soc.* **1977**, *99*, 8426.

(5) (a) Chisholm, M. H.; Clark, H. C. *Inorg. Chem.* **1971**, *10*, 2557. (b) Chisholm, M. H.; Clark, H. C. *J. Am. Chem. Soc.* **1972**, *94*, 1532. (c) Chisholm, M. H.; Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1972**, *11*, 1269.

(6) (a) Bottrill, M.; Green, M. *J. Am. Chem. Soc.* **1977**, *99*, 5795. (b) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Bottrill, M.; Green, M.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1983**, 927.

(7) (a) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1267. (b) Davidson, J. L.; Murray, I. E. P.; Preston, P. N.; Russo, M. V.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1981**, 1059. (c) Davidson, J. L.; Vasapool, G.; Manojlovic-Muir, L.; Muir, K. W. *Ibid.* **1982**, 1025. (d) Allen, S. R.; Green, M.; Orpen, A. G.; Williams, I. D. *Ibid.* **1982**, 826.

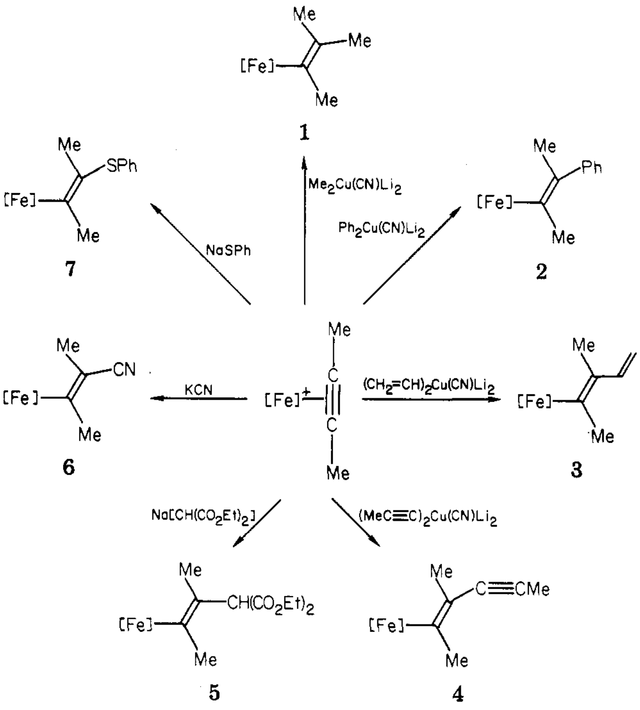
(8) (a) Reger, D. L.; Coleman, C. J.; McElligott, P. J. *J. Organomet. Chem.* **1979**, *171*, 73. (b) Reger, D. L.; Coleman, C. J. *Inorg. Chem.* **1979**, *18*, 3155.

(9) (a) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710. (b) Reger, D. L.; Belmore, K. A., unpublished results.

(10) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923.

(11) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.

Scheme I

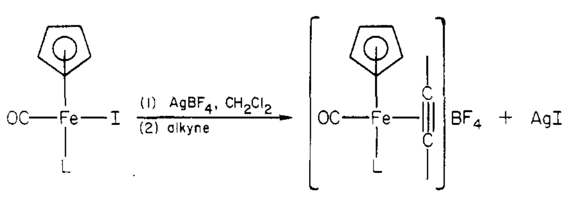


[Fe] = CpFeCO(L); a, L = P(OPh)$_3$; b, L = PPh$_3$

ligand in certain of these molecules.

Results and Discussion

Synthesis of Complexes. The iron alkenyl complexes reported here are prepared by nucleophilic addition reactions with cationic η^2-alkyne complexes. These cations are prepared as shown in eq 3. Although most of the

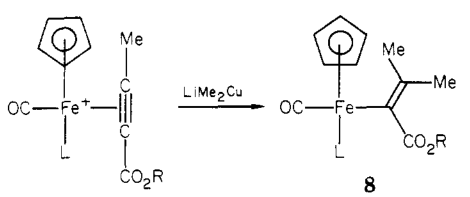


(3)

L = PPh$_3$, P(OPh)$_3$

η^2-alkyne complexes used here have been isolated in pure form by us previously[8] (only internal alkynes are successful), in the work reported here the CH$_2$Cl$_2$ solutions are simply filtered to remove the AgI and the solvent is evaporated to leave a fluffy solid of the η^2-alkyne complex. These solids are generally used in the addition reactions directly, and thus the yields (which generally range from 70 to 90%) reported in the experimental are for the two-step process. For frequently used cations, such as [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF$_4$, the solid can be prepared on a large scale and stored under nitrogen at 0 °C for use as needed.

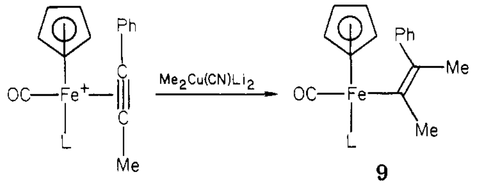
Scheme I shows that many different types of nucleophilic reagents will react with the η^2-butyne cation for both L = P(OPh)$_3$ and PPh$_3$. Two unsymmetrical alkynes have been studied to date. Equation 4 shows the addition re-



8

(4)

action for an ester-substituted alkyne. The regiochemistry of this reaction for L = PPh$_3$ and R = Et has previously been assigned by using crystallographic means.[12] For the methyl addition reaction with L = P(OPh)$_3$, the reaction is not completely regioselective with small amounts of CpFeCO[P(OPh)$_3$][η^1-(*Z*)-C(Me)=C(CO$_2$R)Me] also forming. Equation 5 shows the product of the addition reaction with phenylmethylacetylene. In this case, both the regio and stereochemistry of the product [L = P(OPh)$_3$] have been determined crystallographically.[11]



9

(5)

The use of higher order mixed organocuprate reagents, recently reported by Lipshutz,[13] offer substantial advantages in most of these reactions. In our earlier communication (L = PPh$_3$), standard LiR$_2$Cu type cuprate reagents were employed. Although the LiPh$_2$Cu reaction with [CpFeCO(PPh$_3$)(η^2-MeC≡CMe)]$^+$ and the reaction shown in eq 4 are readily reproducible, yields for the other addition reactions have proven variable. For example, in the LiPh$_2$Cu reaction with [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]$^+$ yields ranging from 25 to 69% have been observed (four runs). This represents one of the better cases. For the LiMe$_2$Cu reaction with this same cation, yields were less than 10%. Changing to the R$_2$Cu(CN)Li$_2$ reagents greatly improves the yields in these reactions and also simplifies both reaction procedures and product isolations. The main advantage in carrying out the reactions is that CuCN is commercially available in pure form and reacts with 2 equiv of MeLi or PhLi at −60 °C. The reactions are initiated at −78 °C and appear to go to completion at this temperature. Although warming these solutions to room temperature followed by solvent evaporation turns these brown solutions green, extraction with CH$_2$Cl$_2$ followed by filtration using a small plug of alumina generally yields pure products. With use of these methods, yields of 81–93% of **1** and **2** have been routinely observed. With the LiR$_2$Cu reagents, the reactions turn black during the workup and column chromatography is necessary to effect purification.

In the (CH$_2$=CH)$_2$Cu(CN)Li$_2$ reaction [L = P(OPh)$_3$], some displacement of the alkyne is observed to produce CpFeCO[P(OPh)$_3$](η^1-CH=CH$_2$) (**10**). These two products can be easily separated by column chromatography (although some isomerization of **3a** takes place, vide infra). The formation of compound **10** in this reaction is extremely interesting because we had previously observed that the reaction of [CpFeCO[P(OPh)$_3$](THF)]BF$_4$ and (CH$_2$=CH)Li failed to yield this product. We then carried out the reaction shown in eq 6 to prepare this complex directly.

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(6)

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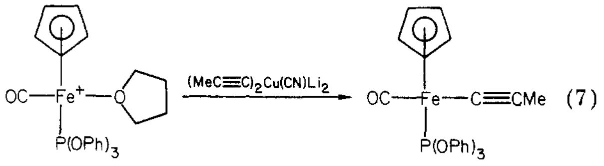
[12] Reger, D. L.; McElligott, P. J.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1982**, *1*, 443.

[13] Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 2305.

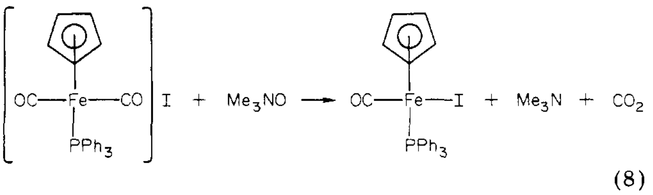
As shown in eq 7, CpFeCO[P(OPh)$_3$](η^1-C≡CMe) (**11**) forms readily by using these cyanocuprate reagents. An analogous reaction with Li(MeC≡C)$_2$Cu failed because the I$^-$ in the solution of this reagent (formed from CuI and MeC≡CLi) added to the iron more rapidly than the alkynyl group. A small amount of CpFeCO[P(OPh)$_3$]CN does form in the cyanocuprate reaction but is easily separated from **11** on a short alumina column. A similar direct reaction with MeC≡CLi yields only trace amounts of **11**. This reaction and the addition reaction of the propynyl group to the 2-butyne cation to produce **4a** (Scheme I) are particularly interesting because in organic systems alkynylcuprate reagents are generaly not very reactive.[14]



11

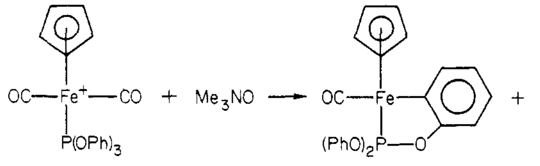
Of the other nucleophilies used, Na[CH(CO$_2$Et)$_2$] and NaSPh add readily in yields of 80–86%. The NaSPh reaction is particularly convenient because it can be carried out in CH$_2$Cl$_2$, the solvent in which the η^2-alkyne complex is formed (eq 3). With the exception of KCN, all of the other reactions are carried out in THF. As noted earlier, this necessitates evaporation of the CH$_2$Cl$_2$ after reaction 3 and the THF must be introduced at −78 °C to prevent displacement of the η^2-alkyne ligand. The KCN reaction is carried out in methanol and considerable displacement of the alkyne takes place. This problem can be solved by using R$_4$NCN reagents in CH$_2$Cl$_2$. The reaction with NaOPh seems to proceed in good yield but the product is unstable, decomposing upon attempted purification on alumina.

In comparing the chemistry of the L = PPh$_3$ vs. the L = P(OPh)$_3$ system, the latter is generally superior. Of primary importance is the fact that the η^2-alkyne complexes are more stable for L = P(OPh)$_3$. One has to be careful not to heat the η^2-alkyne complexes for L = PPh$_3$ for any extended period of time, and it is best to carry out the nucleophilic addition reaction immediately after the cation is prepared. Another important difference was that CpFeCO[P(OPh)$_3$]I forms from CpFe(CO)$_2$I and P(OPh)$_3$ in 80% yield whereas CpFeCO(PPh$_3$)I forms using PPh$_3$ in only 35–45%. Also formed in this latter reaction is [CpFe(CO)$_2$(PPh$_3$)]I in 55–60% yield. We have recently been able to convert this cationic byproduct to the desired product quantitatively by using the procedure shown in eq 8. Thus this advantage for the L = P(OPh)$_3$ system is no longer as important. An advantage for the L = PPh$_3$ system is that the final alkenyl products are generally easier to crystallize. The alkenyl complexes for L = P(OPh)$_3$ are extremely soluble, even in hexane, and are generally isolated as oils.



(8)

Reaction 8 encouraged us to try to prepare η^2-alkyne complexes directly from the appropriate [CpFe(CO)$_2$(L)]BF$_4$ complex, thus avoiding the AgBF$_4$ needed in eq 3. For L = P(OPh)$_3$, eq 9 shows the results of such a reaction (the results are the same with or without the addition of ethylene or an alkyne). This is not an unexpected result in that we have shown earlier[8b] that the same ortho-metalated product is obtained in a reaction of CpFeCO[P(OPh)$_3$]I, AgBF$_4$, and Et$_2$NH. Addition of HBF$_4$ to **12** in the presence of an alkyne also failed. The Me$_3$NO reaction for L = PPh$_3$ did not yield any characterizable product.



12

$[NMe_3H]^+ + CO_2$ (9)

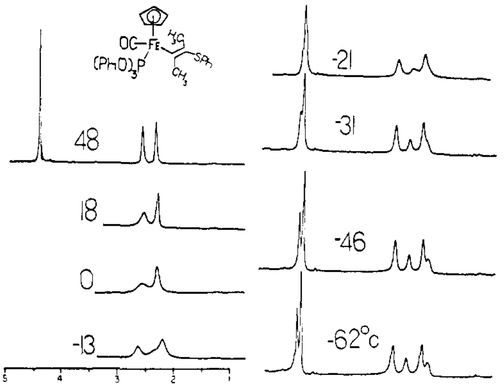
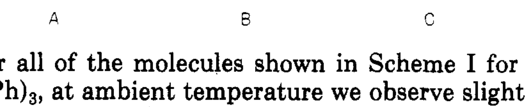


Figure 1. Variable-temperature ^{1}H NMR data for CpFeCO[P(OPh)$_3$][η^1-(*E*)-CMe=C(Me)SPh] in the region of the Cp and Me group resonances taken at 90 MHz.

Observation of Alkenyl Rotamers. For the three alkenyl complexes that we have investigated crystallographically, two orientations of the alkenyl group have been observed. Both CpFeCO(PPh$_3$)[η^1-C(CO$_2$Et)=CMe$_2$] (**8b**) and CpFeCO[P(OPh)$_3$][η^1-(*Z*)-C(Me)=C(Ph)Me] (**9a**) are found in orientation A whereas CpFeCO(PPh$_3$)[η^1-(*E*)-C(CO$_2$Et)=C(H)Me][9a] is found in orientation B. The third possible orientation, C, seems unreasonable because of the unfavorable steric interactions of the alkenyl ligand with the large Cp ligand.



For all of the molecules shown in Scheme I for L = P(OPh)$_3$, at ambient temperature we observe slight line broadening in the ^{1}H NMR spectra for one of the alkenyl methyl group resonances. Variable-temperature NMR studies show that both alkenyl methyl resonances and the Cp resonance for each molecule split into two resonances, in a ratio of about 2:1 at low temperature. Figure 1 shows the data for CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)SPh]. We interpret these data as being due to a dynamic process involving rotamers A and B. At low temperatures, both rotamers are observed. As the temperature increases, the two rotamers equilibrate on the NMR time scale via rotation about the Fe–C(alkenyl) bond. It is interesting to note that in all cases the more deshielded of the Me resonances in the high-temperature spectra splits into two resonances at low temperature that are nearly 1 ppm apart.

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[14] Normant, J. F.; Alexakis, A. *Synthesis* 1981, 841.

One would expect the magnetic environment on the $P(OPh)_3$ side of the molecule to be quite different from the CO side, and this is reflected in the large chemical shift difference.

The onset of line broadening, starting from low temperatures, is in the range of −25 °C (**5a**) to −50 °C (**6a**) for all of these molecules. Thus the barrier to rotation is not greatly influenced by the substituent trans to the iron. For molecule **7a**, computer simulation of the data shown in Figure 1 yields the following activation parameters for this process: $\Delta G^{\ddagger} = 13.4$ kcal mol^{-1}; $\Delta H^{\ddagger} = 11.4$ kcal mol^{-1}; $\Delta S^{\ddagger} = 6.7$ eu.

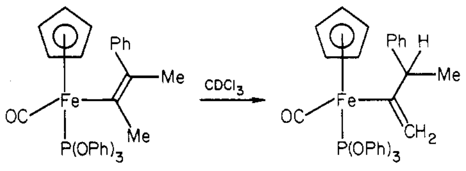
Only the molecules formed in addition reactions of $[CpFeCO[P(OPh)_3](\eta^2\text{-}MeC{\equiv}CMe)]BF_4$ (**1a**–**7a**) show this dynamic behavior. All of the L = PPh_3 and other L = $P(OPh)_3$ complexes (this includes $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(H)Me]$ and $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(CO_2Et){=}C(H)Me]$[9] not reported here) do not show dynamic behavior at any temperature studied. These results are best explained on steric grounds. For molecules **1a**–**7a**, the steric requirements of the methyl groups trans to one another must be fairly similar in rotamers A and B. This allows for the significant population of both rotamers. For all other cases, one rotamer must be substantially more stable. The barrier to rotation for **1a**–**7a** reflects mainly steric interactions. The Fe–C(alkenyl) bond length in all three molecules studied crystallographically is 2.03 Å, the distance expected for an Fe–C(sp^2) single bond in these molecules.[11] Thus no major contribution to the barrier from Fe–C(alkenyl) multiple bonding is expected.

Assignment of Stereochemistry. Trans addition of the nucleophiles reported above has been assigned based on the following considerations. The structure of **9a** has been established crystallographically. This also defines the structure of its cis–trans isomer **2a**. Thus nucleophiles derived from the cuprate reagents add trans. The complex **2a** shows two rotamers at low temperature as do all of the products in Scheme I, L = $P(OPh)_3$. The complex **9a** and all complexes that do not have trans methyl groups do not show rotamers. Thus it is felt that the observation of two rotamers at low temperature indicates a molecule with trans methyl groups and thus defines the stereochemistry of all of the products in Scheme I, L = $P(OPh)_3$. By analogy, the same stereochemistry is assigned to the L = PPh_3 cases.

In our earlier communication,[10] ^1H nuclear Overhauser effect (NOE) enhancement experiments were used to establish stereochemistry of these alkenyl complexes. We no longer feel that these are definitive experiments and are particularly meaningless for cases like $CpFeCO(L)[\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)CN]$ where the stereochemistry can only be assigned by the *absence* of an observed NOE enhancement.

Our initial experiments were with $CpFeCO(PPh_3)[\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)Ph]$. In this case, we have observed with some samples an enhancement in the integrated intensities of both methyl groups vs. an added standard upon irradiation of the phenyl region. For other samples, no NOE is observed. All of the samples were carefully prepared with the exclusion of oxygen. It is possible that in the cases where no NOE is observed that slight (not visually observable) decomposition of the complex occurs. This decomposition could release paramagnetic iron into the solution, and this would quench the NOE enhancement. In any case, we feel that these experiments, particularly for cases where the assignment is made on the absence of an observed enhancement, are not generally definitive for the assignment of stereochemistry of iron alkenyl complexes.

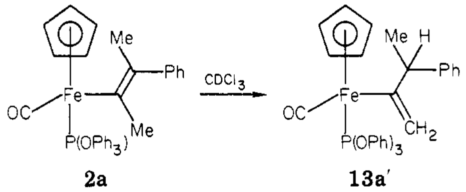
Isomerization Reactions. In certain cases, these internal alkenyl derivatives will undergo isomerization reactions. The most interesting case is shown in eq 10. This reaction takes place slowly at room temperature (followed in sealed, carefully degassed NMR tubes) and does not go to completion. About a 2:1 mixture of **9a**/**13a** results after 24 h. Even though **13a** has only been observed by ^1H and ^{13}C NMR as a mixture with **9a**, there is little doubt about the assignment of structure. In the ^1H NMR, one observes resonances at δ 5.34 and 5.15, typical of a $C{=}CH_2$ group in these molecules (we have made many of these from nucleophilic addition reactions with $[CpFeCO[P(OPh)_3](\eta^2\text{-}CH_2{=}C{=}CH_2)]^+$),[9b] a multiplet at δ 3.8 for the CH and a doublet at δ 1.5 for the Me group. The ^{13}C NMR spectrum is more definitive and was completely assigned by using the INEPT[15] pulsing sequences (see Experimental Section). Most definitive was the assignment of the vinyl carbon atom resonances. The α-vinyl resonance is at δ 166.1 with $J_{C-P} = 43$ Hz, and the β-vinyl resonance is at δ 125.1 with $J_{C-P} = 3$ Hz. These chemical shift values and coupling constants are very characteristic for this group. Also, the INEPT sequence showed that the vinyl α-carbon atom had no directly bound H atoms and the β-carbon atom had two directly bonded H atoms.



(10)

9a **13a**

The molecule **13a** has two chiral centers and thus exists as two diastereomers. In general for these types of iron molecules, one can clearly observe a different NMR spectrum for each diastereomer. In reaction 10, the ^1H and $^{13}C\{^1H\}$ spectra show only a single set of resonances, indicating that a *single* diastereomer forms in the reaction. This result is verified by reaction 11. This slow reaction yields a new set of resonances very similar to those observed in reaction 10, but the resonances show different chemical shift values. Thus reactions 10 and 11 yield the same structural isomers but each yields a specific diastereomer.



(11)

2a **13a′**

Two other facts about these reactions are of interest. First, if one does not remove the O_2 carefully from the $CDCl_3$ solvent in reactions 10 and 11, resonances for all four complexes are observed. Second, neither reaction 10 nor 11 takes place in other solvents such as C_6D_6, acetone-d_6, CD_3CN, or CH_2Cl_2. As observed in $CDCl_3$, **9a** or **2a** in oxygenated CH_2Cl_2 rearranges to yield all four isomers.

Two other compounds also undergo isomerization reactions. The trimethyl complexes **1a** and **1b** both readily isomerize when purified by chromatography on alumina as shown in eq 12. Complex **1b** is particularly unstable

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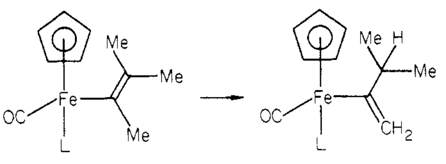
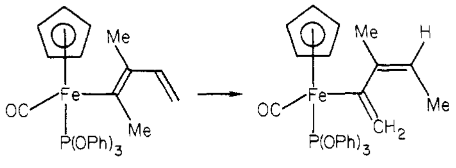
[15] Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

with some isomerization noted when the complex is run through a short plug of alumina.



1 14 (12)

Complex **3a** also undergoes an isomerization reaction, but in this case the product is the one expected for a 1–5 hydrogen shift as shown in eq 13. The stereochemistry of the trisubstituted double bond in **15a** has not been determined but is shown as the more reasonable *Z* isomer. This rearrangement takes place when **3a** is purified (**10a** and a high boiling hydrocarbon are present after the addition reaction and need to be separated) on an alumina column. Ratios of **3a**/**15a** varying from 2.6 to 2.1/1 have been observed depending on the time the compound stays on the column. We have never had a sample of **3a** that was not contaminated by small amounts of either **10a** or **15a**. Reaction 13 also takes place very slowly in $CDCl_3$, but substantial line broadening, indicating sample degradation, is also noted. Addition of oxygen accelerates the reaction. No isomerization takes place in degassed benzene-d_6 or CH_2Cl_2 over 200 h.



3a 15a (13)

We do not yet have meaningful mechanistic information on these reactions. Purification of $CDCl_3$ by a number of methods had no effect on reactions 10 and 11 nor did the addition of a radical scavanger. Addition of radical initiators to benzene-d_6 solutions of **9a** did not cause reaction 10 to take place. We have shown that the *Z* isomer **9a** isomerizes rapidly to the *E* isomer **2a** in CH_2Cl_2 in the presence of catalytic amounts of $AgBF_4$ with no **13** observed. This presumably explains the effect of O_2 in causing this same reaction in that both reagents could generate $[CpFeCO[P(OPh)_3][\eta^1\text{-}C(Me){=}C(Ph)Me]]^+$ which then undergoes a rapid *Z*–*E* isomerization reaction. Further mechanistic work on these reactions is planned.

Experimental Section

General Procedure. All operations on complexes in solution were carried out under an atmosphere of nitrogen using solvents that were purified and degassed before use. Chromatography columns were 2.5 cm in diameter. The $AgBF_4$ (Ozark-Mahoning) was stored and weighed out in a drybox. Proton NMR spectra were recorded at 60 or 90 MHz and chemical shifts are reported as δ vs. Me_4Si. Carbon-13 spectra were recorded with proton decoupling at 20 MHz by using either $CDCl_3$ (δ 76.9), CD_2Cl_2 (δ 53.8), or CH_2Cl_2 (δ 54.0) as the solvent and internal standard and are also reported as δ vs. Me_4Si. All resonances are singlets unless otherwise indicated. Alkyllithium reagents were purchased from Aldrich (vinyllithium from Organometallics) and CuCN from Fisher. $CpFeCO[P(OPh)_3]I$ was prepared by the method of Brown et al.[16] and $CpFeCO(PPh_3)I$ by the method of Treichel et al.[17] using the modification listed below to convert the $[CpFe(CO)_2(PPh_3)]I$ byproduct to the desired material. We have previously reported the preparations of $CpFeCO(PPh_3)[\eta^1\text{-}C(CO_2Et){=}CMe_2]$[12] and the *Z* and *E* isomers of $CpFeCO[P(OPh)_3][\eta^1\text{-}C(Me){=}C(Ph)Me]$.[11] Elemental analyses were performed by Robertson Laboratory. Simulated spectra for **7a** were calculated by using the DNMR-3 computer program and were matched visually with the experimental spectra. The activation parameters were calculated from a standard Eyring plot. ΔG^* is estimated to be accurate to ±0.5 kcal mol^{-1}.

$CpFeCO[P(OPh)_3][\eta^1\text{-}C(Me){=}CMe_2]$ (1a). A mixture of $CpFeCO[P(OPh)_3]I$ (1.64 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0 mmol) was stirred in CH_2Cl_2 (25 mL) at room temperature, and after 10 min MeC≡CMe (0.20 g, 0.30 mL, 3.7 mmol) was added. This solution was stirred for 30 min and then filtered through Celite. The filtrate was collected and the solvent evaporated affording a reddish brown fluffy solid. This solid was dissolved in THF (40 mL) *prechilled to -78 °C* and mixed with a cold THF solution of $Me_2Cu(CN)Li_2$ (made by addition of MeLi (4.0 mL of a 1.4 M solution, 5.6 mmol) to CuCN (0.25 g, 2.8 mmol) in THF (20 mL) previously cooled to -60 °C). This mixture was stirred cold for 30 min and allowed to warm to ambient temperature. The solvent was then evaporated to yield a dark green oil. This oil was redissolved in CH_2Cl_2 (20 mL) and filtered through a short plug of alumina, followed by elution with CH_2Cl_2 (40 mL). Evaporation of the CH_2Cl_2 afforded an orange oil (1.14 g, 85% based on $CpFeCO[P(OPh)_3]I$): ^1H NMR (δ in C_6D_6) 7.0 (15, m, $P(OPh)_3$), 4.17 (5, s, Cp), 2.28, 2.10, 1.94 (3, 3, 3; br s, s, s; Me's); IR spectrum (cm^{-1} in hexane) ν(CO) 1932. Anal. Calcd for $C_{29}H_{29}FeO_4P$: C, 65.92; H, 5.53. Found: C, 65.65; H, 5.38.

$CpFeCO(PPh_3)[\eta^1\text{-}C(Me){=}CMe_2]$ (1b). $CpFeCO(PPh_3)I$ (1.50 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0 mmol) were stirred at room temperature in CH_2Cl_2 (30 mL) for 1 min after which the mixture was cooled to 0 °C, MeC≡CMe (0.30 mL, 3.7 mmol) was added, and the mixture was allowed to stir for 10 min. The mixture was filtered through Celite affording a purple filtrate which, upon solvent evaporation, yielded a purple oil. This oil was dissolved in prechilled (-78 °C) THF (50 mL), and a cold (-60 °C) THF (20 mL) solution of $Me_2Cu(CN)Li_2$ (prepared as in **1a**) was added via cannula. The reaction mixture was stirred cold (-78 °C) for 50 min and allowed to warm to room temperature and the THF evaporated. The resulting green oil was dissolved in CH_2Cl_2 (20 mL) and filtered through a short plug of Celite (6 cm), eluting with CH_2Cl_2 (40 mL). A red filtrate was collected and the solvent evaporated. Monitoring the resultant solid by ^1H NMR shows only the desired complex **1b** but IR shows some impurity is present. The solid was redissolved in CH_2Cl_2 (20 mL) and filtered through a plug of alumina (5 cm), eluting with CH_2Cl_2 (40 mL). A red filtrate was collected and the solvent evaporated. An ^1H NMR spectrum of this red solid shows it to be the desired compound **1b** and an isomer which is clearly $CpFeCO(PPh_3)(\eta^1\text{-}C(CHMe_2){=}CH_2)$ (**14b**) in about even amounts. These cannot be separated, and, in fact, column chromatography on alumina leads to ca. a 1:2.5 mixture of **1b**/**14b**. The yield of the mixture after the short alumina plug is 1.1 g (81%): ^1H NMR spectrum of **1b** (δ in $CDCl_3$) 7.3 (15, m, PPh_3), 4.44 (5, d, *J* = 1 Hz, Cp), 2.07, 1.77, 1.67 (3, 3, 3; br s, s, s; Me's); ^1H NMR spectrum of **14b** (δ in $CDCl_3$) 7.3 (15, m, PPh_3), 5.47, 4.60 (1, 1; s, s; $=CH_2$), 4.45 (5, d, *J* = 1 Hz, Cp), 2.2 (1, m (br), $CHMe_2$), 1.04, 0.96 (3, 3; d, d, *J* = 7 Hz, $CHMe_2$); IR spectrum of mixture (cm^{-1} in CH_2Cl_2) ν(CO) 1908. Anal. Calcd for $C_{29}H_{29}FeOP$: C, 72.51; H, 6.09. Found: C, 72.76; H, 5.91.

$CpFeCO(PPh_3)[\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)Ph]$ (2b). $[CpFeCO(PPh_3)(\eta^2\text{-}MeC{\equiv}CMe)]BF_4$ was prepared in the same manner and amount as in **1b**. This solid was stirred in THF (35 mL, prechilled to -78 °C), and $LiCuPh_2$ (prepared by addition of PhLi (3.7 mL, 1.5 M, 5.6 mmol) to CuI (0.53 g, 2.8 mmol) in THF at -10°C) was added by a cannula. The reaction mixture was allowed to warm to ambient temperature and the solvent removed by evaporation. The solid was redissolved in CH_2Cl_2 (10 mL) and placed on an alumina column (10 cm). The column was eluted with a CH_2Cl_2/pentane solution (1/1, v/v) producing a single red band that was collected and the solvent evaporated to yield a red solid (1.32 g, 87%): ^1H NMR (δ in CS_2) 7.25, 6.75 (20, m, PPh_3, Ph), 4.30 (5, s, Cp), 2.20, 1.78 (3, 3; s, s; Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1919; ^{13}C NMR (δ in $CDCl_3$) 223.2 (d, *J* = 36.8 Hz, CO), 148.8, 140.3, 128.8, 124.1 (Ph), 141.9 (d, *J* = 20.2 Hz, Fe–C), 135.7 (d, *J* = 41.9 Hz, P-bound Ph), 133.5 (d, *J* = 9.9 Hz,

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[16] Brown, D. A.; Lyons, H. J.; Manning, A. R.; Rowley, J. M. *Inorg. Chim. Acta* **1969**, *3*, 346.

[17] Treichel, P. M.; Shubkin, R. L.; Barnett, K. W.; Reichard, D. *Inorg. Chem.* **1966**, 1177.

ortho Ph), 129.3 (para Ph), 128.3 (d, J = 10.3 Hz, meta Ph), 84.6 (Cp), 37.4, 29.7 (d, s; J = 8.5 Hz; Me's). Anal. Calcd for $C_{34}H_{31}FeOP$: C, 75.28; H, 5.76. Found: C, 75.12; H, 6.01.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)CH=CH$_2$] (3a). [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF_4 was prepared in the same amount as outlined in the preparation of **1a**. Prechilled THF (50 mL, −78 °C) was added followed by $(CH_2{=}CH)_2Cu(CN)Li_2$ (prepared by addition of vinyllithium (3.7 mL of a 1.5 M solution, 5.6 mmol) to CuCN (0.25 g, 2.8 mmol) in THF (20 mL) at −35 °C), also cooled to −78 °C. After 5 min the solution was allowed to warm to ambient temperature and the solvent was evaporated to yield a dark green oil. This oil was redissolved in 10 mL of benzene and placed on an alumina column (20 cm). The column was first eluted with 50 mL of pentane to remove the high boiling hydrocarbon introduced by the vinyllithium. Subsequent elution with a benzene/pentane mixture (1/1, v/v) produced two yellow bands that were collected and the solvent was evaporated. The second fraction is CpFeCO[P(OPh)$_3$](η^1-CH=CH$_2$) (10) (18% yield). The first fraction, a yellow oil, is CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)CH=CH$_2$] contaminated with CpFeCO[P(OPh)$_3$][η^1-C(=CH$_2$)C(Me)=C(H)Me] (**15a**) (1.08 g, 71% yield): ^{1}H NMR (δ in $CDCl_3$) 7.3 (15, m, P(OPh)$_3$), 4.83, 4.63, 4.50 (3, m, CH=CH$_2$), 4.29 (5, s, Cp), 2.31, 2.07 (3, 3; s (br), s; Me's); IR spectrum of mixture (cm^{-1} in CH_2Cl_2) ν(CO) 1940; ^{13}C NMR (δ CD_2Cl_2) 219.7 (d, J = 47.3 Hz, CO), 154.3 (d, J = 33.6 Hz, FeC=), 152.1, 129.9, 125.2, 122.2 (d, d, d, d; J = 9.8, 1.1, 1.1, 4.0 Hz; P(OPh)$_3$), 140.4 (HC=), 134.9 (d, J = 3.6 Hz, =*C*(Me)), 104.2 (=CH$_2$), 84.9 (d, J = 1.7 Hz, Cp) 34.7, 24.0 (d, s; J = 5.6 Hz, Me's); ^{1}H NMR of **15a** (δ in $CDCl_3$) 7.10 (15, m, P(OPh)$_3$), 5.65, 5.03 (2, m, =CH$_2$), 5.03 (1, m, =CMe*H*), 4.25 (5, s, Cp), 1.75 (3, s, CMe), 1.53 (3, d, J = 6 Hz, C*Me*H). Anal. Calcd for $C_{30}H_{29}FeO_4P$: C, 66.68; H, 5.41. Found: C, 66.91; H, 5.42.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)C≡CMe] (4a). [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF_4 was prepared as above by using CpFeCO[P(OPh)$_3$]I (1.64 g, 2.8 mmol), $AgBF_4$ (0.58 g, 3.0 mmol), and MeC≡CMe (0.30 mL, 3.8 mmol). This solid was stirred in cold (−78 °C) THF (35 mL), and $(MeC{\equiv}C)_2Cu(CN)Li_2$ (prepared by addition of cold (−8 °C) THF to a mixture of propynyllithium (0.26 g, 5.6 mmol) and CuCN (0.25 g, 2.8 mmol)) was added at −78 °C via cannula. This mixture was stirred cold for 30 min and allowed to warm to ambient temperature. A filtration was preformed by using Celite, and the solvent was evaporated. The oil was redissolved in 10 mL of benzene and placed on a 20-cm alumina column. Elution of the column with a hexane/benzene solution (1/1, v/v) yielded three bands. The third, yellow-brown band is CpFeCO[P(OPh)$_3$](η^1-C≡CMe) (0.13 g, 9%). The second, brown fraction is CpFeCO[P(OPh)$_3$]CN (0.08 g, 6%). The first, yellow-brown fraction is CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)C≡CMe] (0.96 g, 62%): ^{1}H NMR (δ in C_6D_6) 7.1 (15, m, P(OPh)$_3$), 4.10 (5, s, Cp), 2.83, 2.43 (3, 3; s, s; vinyl Me's), 1.93 (3, s, ≡CMe); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1942; ^{13}C NMR (δ in CD_2Cl_2) 219.4 (d, J = 49.9 Hz, CO), 158.1 (d, J = 35.3 Hz, FeC=), 151.9, 129.8, 125.2, 122.4 (d, d, d, d; J = 10.0, 0.8, 1.0, 4.2 Hz; P(OPh)$_3$), 122.3 (d, J = 5.0 Hz, =*C*(Me)), 84.5 (d, J = 1.3 Hz, Cp), 83.2, 83.2 (d, s, J = 4.6 Hz, alkynyl carbons), 37.87, 27.33 (d, s; J = 6.6 Hz, vinyl Me's), 4.39 (≡C*Me*). Anal. Calcd for $C_{37}H_{29}FeO_4P$: C, 67.41; H, 5.29. Found: C, 67.24; H, 5.20.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)CH(CO$_2$Et)$_2$] (5a). A −78 °C THF solution of [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)BF_4 was prepared as in **1a**, and Na[CH(CO$_2$Et)$_2$] (0.50 g, 2.8 mmol) was added as a solid. This mixture was allowed to warm to ambient temperature and the solvent evaporated. This oil was redissolved in CH_2Cl_2 (10 mL) and placed on an alumina column (20 cm). The column was eluted with a CH_2Cl_2/hexane (2/1) mixture yielding a single yellow-brown band which was collected and the solvent evaporated (1.50 g, 80%): ^{1}H NMR (δ in $CDCl_3$) 7.2 (15, m, P(OPh)$_3$), 4.90 (1, s, CH), 4.30 (5, s, Cp), 4.19, 4.17 (2, 2; q, q; J = 7.0 Hz; OCH$_2$), 2.20, 2.05 (3, 3; br s, s; vinyl Me's), 1.26, 1.23 (3, 3; t, t; J = 7.0 Hz; CH$_2$*CH$_3$*); IR spectrum (cm^{-1} in THF) ν(CO) 1937 (FeCO), 1740 (ester); ^{13}C NMR (δ in $CDCl_3$) 218.7 (d, J = 51.0 Hz, CO), 169.7 (CO$_2$), 151.2, 129.2, 124.6, 121.5 (d, s, s, d; J = 9.7, 3.8 Hz; P(OPh)$_3$), 143.9 (d, J = 32.5 Hz, FeC=), 127.3 (=*C*(Me)), 84.2 (Cp), 60.5 (OCH$_2$), 55.3 (d, J = 2.4 Hz, CH), 33.7, 24.1 (vinyl Me's), 14.0 (CH$_2$*CH$_3$*). Anal. Calcd for $C_{35}H_{37}FeO_8P$: C, 62.51; H, 5.55. Found: C, 62.43; H, 5.80.

CpFeCO(PPh$_3$)[η^1-(*E*)-C(Me)=C(Me)CH(CO$_2$Et)$_2$] (5b). This complex was prepared as with 1b using Na[CH(CO$_2$Et)$_2$] in THF and purified on an alumina column eluting with hexane/toluene (1/1). A red fraction was collected, reduced to 10 mL, and diluted with pentane (20 mL). Cooling at −20 °C for 5 days yielded red crystals: mp 165–166.5 °C (1.7 g, 86%); ^{1}H NMR (δ in $CDCl_3$) 7.35 (15, m, PPh$_3$), 5.54 (1, m, CH), 4.35 (5, d, J = 0.8 Hz, Cp), 4.10 (4, m, CH$_2$), 2.05, 1.65 (3, 3; m, s; vinyl Me's), 1.30 (6, t, J = 7.0 Hz, CH$_2$*CH$_3$*); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1915 (FeCO), 1727 (ester); ^{13}C NMR (δ in $CDCl_3$) 222.6 (d, J = 36.6 Hz, CO), 170.3, 169.7 (CO$_2$R), 148.1 (d, J = 20.0 Hz, FeC=), 135.5 (d, J = 37.8 Hz, P-bound Ph), 133.0 (d, J = 9.9 Hz, ortho-Ph), 129.5 (para-Ph), 128.0 (d, J = 9.4 Hz, meta-Ph), 126.7 (=*C*(Me)), 60.7, 60.5 (CH$_2$O), 55.1 (CH), 34.7, 24.1 (d, s; J = 8.3 Hz, vinyl Me's), 14.3 (CH$_2$*Me*). Anal. Calcd for $C_{35}H_{37}FeO_5P$: C, 67.31; H, 5.97. Found: C, 67.33; H, 5.08.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)CN] (6a). [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF_4 was prepared as in **1a**. The solid was stirred in cold (−78 °C) methanol, and KCN (0.18 g, 2.8 mmol) was added as a solid. The reaction mixture was stirred for 30 min at −78 °C and then allowed to warm to ambient temperature and the solvent evaporated. This solid was extracted with CH_2Cl_2 (10 mL) and placed on a 10-cm alumina column. The column was eluted with benzene to yield first a yellow band and second an orange band. The bands were collected, and the solvent was evaporated. The first band is the desired product (0.54 g, 36%). This complex is also prepared in 48% yield by using [Et$_4$N]CN in CH_2Cl_2: ^{1}H NMR (δ in $CDCl_3$) 7.2 (15, m, P(OPh)$_3$), 4.27 (s, 5, Cp), 2.43, 2.07 (3, 3; s, s; Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(C≡N) 2180, ν(CO) 1950; ^{13}C NMR (δ in $CDCl_3$) 218.1 (d, J = 47.6 Hz, CO), 187.0 (d, J = 35.9 Hz, FeC=), 151.0, 129.5, 125.0, 121.2 (d, s, s, d; J = 9.7, 3.0 Hz; P(OPh)$_3$), 83.9 (s, Cp), 38.9, 23.6 (d, s; J = 2.5 Hz, Me's), the =C and CN resonances were not located. Anal. Calcd for $C_{29}H_{26}FeO_4P$: C, 64.58; H, 4.86. Found: C, 64.59; H, 4.65. The second band is CpFeCO[P(OPh)$_3$]CN (0.59 g, 43%). This compound can be prepared in 90% yield by the addtion of Et$_4$NCN to a CH_2Cl_2 mixture of CpFeCO[P(OPh)$_3$]I and $AgBF_4$: ^{1}H NMR (δ in $CDCl_3$) 7.25 (15, m, P(OPh)$_3$), 4.15 (5, d, J = 1.5 Hz, Cp); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CN) 2155, ν(CO) 1980.

CpFeCO(PPh$_3$)[η^1-(*E*)-C(Me)=C(Me)CN] (6b). This complex was prepared in CH_2Cl_2 as with 1b using Et$_4$NCN (87%): ^{1}H NMR (δ in $CDCl_3$) 7.2 (15 m, PPh$_3$), 4.40 (5, d, J = 0.8 Hz, Cp), 2.20 (6, Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CN) 2183, ν(CO) 1928; ^{13}C NMR (δ in CH_2Cl_2) 222.3 (d, J = 35.5 Hz, CO), 194.1 (d, J = 20.5 Hz, FeC=), 136.0 (d, J = 41.1 Hz, P-bound Ph), 133.3 (d, J = 9.6 Hz, ortho-Ph), 130.3 (para-Ph), 128.6 (d, J = 9.2 Hz, meta-Ph), 110.6 (CN), 39.6, 24.1 (d, s; J = 6.2 Hz, Me's). The =C(CN)Me carbon resonance was not located and is believed buried under the PPh$_3$ resonances.

CpFeCO[P(OPh)$_3$][η^1-(*E*)-C(Me)=C(Me)SPh] (7a). [CpFeCO[P(OPh)$_3$](η^2-MeC≡CMe)]BF_4 was prepared as in **1a**, and NaSPh (0.60 g, 5.6 mmol) was added as a solid to this CH_2Cl_2 solution. The mixture was stirred at room temperature for 2 h after which the solvent was evaporated affording a brown oil. This oil was redissolved in ca. 10 mL of CH_2Cl_2 and filtered thru a 5-cm plug of alumina, eluting with ca. 60 mL of CH_2Cl_2. The amber filtrate was collected and the solvent evaporated, yielding an orange-amber oil (2.79 g, 80%). The compound was crystallized from hot-cold hexane affording orange crystals (2.04 g 59%): mp 114–115 °C; ^{1}H NMR (δ in $CDCl_3$) 7.2 (20, m, P(OPh)$_3$, SPh), 4.37 (5, s, Cp), 2.5, 2.28 (3, 3; br s, s; Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1942; ^{13}C NMR (δ in $CDCl_3$) 218.8 (d, J = 50.4 Hz, CO), 157.8 (d, J = 32.0 Hz, FeC=), 151.3, 129.4, 124.7, 121.5 (d, s, s, d; J = 9.7, 3.8 Hz; P(OPh)$_3$), 140.3, 128.3, 126.5, 123.7 (S*Ph*), 127.7 (=CSPh), 84.0 (Cp), 37.32, 29.21 (d, s; J = 2.2 Hz, Me's). Anal. Calcd for $C_{34}H_{31}FeO_4PS$: C, 65.60; H, 5.02. Found: C, 65.90; H, 5.11.

CpFeCO(PPh$_3$)[η^1-(*E*)-C(Me)=C(Me)SPh] (7b). This complex was prepared in CH_2Cl_2 as with **7a**. It was crystallized from CH_2Cl_2/hexane (1/3, 40 mL): mp 127–129 °C (86%); ^{1}H NMR (δ in $CDCl_3$) 7.3 (20, m, PPh$_3$, Ph), 4.39 (5, d, J = 1.2 Hz, Cp), 2.40, 2.07 (3, 3; s, s; Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1913.

CpFeCO[P(OPh)$_3$][η^1-C(CO$_2$Me)=CMe$_2$] (8a). A mixture of CpFeCO[P(OPh)$_3$]I (1.64 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0

mmol) was stirred in CH_2Cl_2 (35 mL), and after 10 min $MeC\equiv CCO_2Me$ (0.29 g, 0.30 mL, 2.9 mmol) was added. The solution was stirred for 15 min and filtered by using Celite, and the solvent was evaporated to yield $CpFeCO[P(OPh)_3](\eta^2\text{-}MeC\equiv CCO_2Me)]BF_4$ as a red fluffy solid (1.72 g, 95%): ^1H NMR (δ in $CDCl_3$) 7.3 (15, m, $P(OPh)_3$), 5.18 (5, s, Cp), 3.90 (3, s, OMe), 2.71 (3, s (br), alkyne Me); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 2015. This solid was dissolved in THF (40 mL) prechilled to −78 °C, and $LiCuMe_2$ (prepared by addition of MeLi (4.0 mL, 1.6 M, 5.6 mmol) to CuI (0.53 g, 2.8 mmol) in THF at 0 °C) was added at −78 °C via cannula. The reaction mixture was allowed to warm to ambient temperature and the solvent removed by evaporation. The oil was redissolved in a CH_2Cl_2/pentane (10 mL) solution and placed on a 20-cm alumina column. The column was eluted with a CH_2Cl_2/pentane solution (1/1, v/v) producing two yellow bands that were collected and the solvent evaporated. The first band, a yellow oil, is $CpFeCO[P(OPh)_3][\eta^1\text{-}C(CO_2Me){=}CMe_2]$ (1.25 g, 77%): ^1H NMR (δ in $CDCl_3$) 7.30 (15, m, $P(OPh)_3$), 4.42 (5, s, Cp), 3.53 (3, s, OMe), 1.93, 1.76 (3, 3; s, s; vinyl Me's); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1940; ^{13}C NMR (δ in $CDCl_3$) 218.6 (d, J = 47.8 Hz, CO), 178.6 (*C*(O)OMe), 151.5, 129.3, 124.5, 121.6 (d, s, s, d; J = 11.1, 3.6 Hz, $P(OPh)_3$), 137.7 (d, J = 3.7 Hz, $={C}Me_2$), 131.5 (d, J = 32.5 Hz, FeC=), 83.9 (Cp), 49.9 (OMe), 26.6, 24.9 (s, d; J = 2.4 Hz; vinyl Me's). Anal. Calcd for $C_{30}H_{29}FeO_6P$: C, 62.95, H, 5.11. Found: C, 63.21; H, 5.27. The second band is $CpFeCO[P(OPh)_3][\eta^1\text{-}(Z)\text{-}C(Me){=}C(CO_2Me)Me]$ (0.24 g, 16%): ^1H NMR (δ in $CDCl_3$) 7.3 (15, m, $P(OPh)_3$), 4.39 (5, s, Cp), 3.60 (3, s, OMe), 2.30, 1.88 (3, 3; s, s; vinyl Me's). When this complex is heated at 80 °C for 20 min in toluene-d_8, a *Z–E* isomerization of the vinyl group is observed to yield $CpFeCO[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(Me)CO_2Me]$: ^1H NMR (δ in toluene-d_8) 7.1 (15, m, $P(OPh)_3$), 4.22 (5, s, Cp), 3.20 (3, s, OMe), 2.60, 1.80 (3, 3; s, s; vinyl Me's).

$CpFeCO(PPh_3)[\eta^1\text{-}(Z)\text{-}C(Me){=}C(Ph)Me]$ (9b). A 250-mL round-bottom flask was charged with $CpFeCO(PPh_3)I$ (1.5 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0 mmol). CH_2Cl_2 (30 mL) was syringed into the flask followed by $PhC\equiv CMe$ (0.33 mL, 3.0 mmol). The mixture was stirred for 10 min at 0 °C and filtered through Celite. A purple filtrate was collected which, upon solvent evaporation, afforded a purple oil. This oil was dissolved in the THF (60 mL) prechilled to −78 °C and mixed with a cold THF solution of $Me_2Cu(CN)Li_2$ (prepared as in **1a**). The mixture was stirred cold for 20 min and allowed to warm to ambient temperature. THF evaporation yielded a dark green oil. This oil was redissolved in CH_2Cl_2 (20 mL) and filtered through a short plug of alumina. The red filtrate was collected and the solvent evaporated affording a red solid. This solid was chromatographed on a 20 × 2.5 cm alumina column using benzene/hexane (1/1). A red band emerged followed by a faint yellow and green band. The red compound was collected. The other compounds remained on the top of the column. Evaporation of the solvent afforded a red solid (1.10 g, 73%): ^1H NMR (δ in $CDCl_3$) 7.3 (20, m, PPh_3, Ph), 4.40 (5, s, Cp), 1.97, 1.83 (3, 3; s, s; Me's); IR spectrum (cm^{-1} in hexane) ν(CO) 1930. Anal. Calcd for $C_{34}H_{31}FeOP$: C, 75.28; H, 5.76. Found: C, 75.43; H, 5.67.

$CpFeCO[P(OPh)_3](\eta^1\text{-}CH{=}CH_2)$ (10). $CpFeCO[P(OPh)_3]I$ (1.64 g, 2.8 mmol) and $AgBF_4$ (0.58 g, 3.0 mmol) were stirred at room temperature in THF (40 mL) for 30 min. The solution was filtered through Celite and cooled to −78 °C. $(CH_2{=}CH)_2Cu(CN)Li_2$ (prepared as in **3a** and cooled to −78 °C) was added via cannula. The solution was allowed to warm to ambient temperature and filtered through a Celite/alumina plug and the solvent evaporated to leave a yellow-green oil. The oil was redissolved in 7 mL of benzene and placed on an alumina column. This was first eluted with 50 mL of pentane (to remove the high boiling hydrocarbon introduced from the $(CH_2{=}CH)Li$) and then eluted with a benzene/pentane solution (1/1, v/v) to produce a single yellow band that was collected and the solvent evaporated to yield a yellow solid (0.90 g, 66%): ^1H NMR (δ in $CDCl_3$) 7.25 (15, m, $P(OPh)_3$), 6.0, 5.6, 5.4 (3, m, vinyl H's), 4.00 (s, Cp); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1955; ^{13}C NMR (δ in CD_2Cl_2) 219.6 (d, J = 45.8 Hz, CO), 152.3, 130.0, 125.1, 122.0 (d, d, d, d; J = 7.3, 1.2, 1.2, 4.3 Hz; $P(OPh)_3$), 147.0 (d, J = 45.2 Hz, FeC=), 120.5 (d, J = 4.9 Hz, $=CH_2$), 84.0 (d, J = 1.8 Hz, Cp). Anal. Calcd for $C_{26}H_{23}FeO_4P$: C, 64.22; H, 4.77. Found: C, 64.40; H, 4.90.

$CpFeCO[P(OPh)_3](\eta^1\text{-}C\equiv CMe)$ (11). $CpFeCO[P(OPh)_3]I$ (1.64 g, 2.8 mmmol) and $AgBF_4$ (0.58 g, 3.0 mmol) were stirred in THF for 30 min and filtered through Celite. The solution was cooled to −78 °C, and $(MeC\equiv C)_2Cu(CN)Li_2$ (prepared as in 4a; 2.8 mmol) was added cold (−78 °C) via cannula. The solution was stirred at 0 °C for 1 h and then filtered through an alumina plug and the solvent evaporated. The solid was dissolved in 10 mL of benzene and placed on a 20-cm alumina column. The column was eluted with a benzene/pentane solution (1/1.33, v/v) to yield first a brown band followed by a yellow band. The bands were collected, the solvent was evaporated, and the compounds were weighed. The first band is $CpFeCO[P(OPh)_3]CN$ (0.20 g, 15%). The second band is $CpFeCO[P(OPh)_3](\eta^1\text{-}C\equiv CMe)$ (0.50 g, 36%): ^1H NMR (δ in $CDCl_3$) 7.30 (15, m, $P(OPh)_3$), 4.15 (5, s, Cp), 1.97 (d, J = 1.5 Hz, Me); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1975; ^{13}C NMR (δ in CD_2Cl_2) 217.7 (d, J = 43.9 Hz, CO), 152.2, 129.9, 125.3, 122.1 (d, d, d, d; J = 7.3, 1.2, 1.6, 4.3 Hz; $P(OPh)_3$), 110.1 (d, J = 5.6 Hz, $\equiv$*C*Me), 83.0 (d, J = 1.3 Hz, Cp), 75.7 (d, J = 63.4 Hz, FeC≡), 19.8 (Me). Anal. Calcd for $C_{27}H_{23}FeO_4P$: C, 65.08; H, 4.65. Found: C, 64.44; H, 4.51.

$CpFeCO(PPh_3)I$ from $[CpFe(CO)_2PPh_3]I$. To a slurry of $[CpFe(CO)_2PPh_3]I$ (22.64 g, 40 mmol) in CH_2Cl_2 (110 mL) was added Me_3NO (3.0 g, 40 mmol) slowly as a solid. The reaction proceeded with vigorous evolution of gas. After being stirred for 45 min at room temperature, the mixture was filtered through a glass frit. The green solid was collected as well as a green filtrate which, upon solvent evaporation, afforded a green powder. The solids were examined independently and found to be identical (combined yield 20.95 g, 93%): ^1H NMR (δ in $CDCl_3$) 7.4 (15, m, PPh_3), 4.48 (5, d, J = 3 Hz, Cp); IR spectrum (cm^{-1} in CH_2Cl_2) ν(CO) 1951.

Spectral Properties of 13a and 13a′. **13a**: ^1H NMR (δ in $CDCl_3$) 7.15 (20, m, $P(OPh)_3$, Ph), 5.34, 5.15 (1, 1; br s, $=CH_2$), 4.13 (5, s, Cp), 3.80 (1, m, CH), 1.50 (3, d, J = 7 Hz, Me); ^{13}C NMR (δ in $CDCl_3$) 219.8 (d, J = 48.8 Hz, CO), 166.1 (d, J = 42.9 Hz, FeC=) 151.6, 129.4, 124.6, 121.5 (d, s, s, d; J = 10.0, 3.9 Hz; $P(OPh)_3$), 147.7, 128.4, 127.6 (Ph), 125.1 (d, J = 3 Hz, $=CH_2$), 83.5 (d, J = 1.8 Hz, Cp), 57.6 (d, J = 2.4 Hz, CH), 22.4 (Me). **13a′**: ^1H NMR (δ in $CDCl_3$) 7.10 (20, m, $P(OPh)_3$, Ph), 5.95, 5.28 (1, 1; br s, $=CH_2$), 3.88 (5, s, Cp), 3.41 (1, m, CH), 1.28 (3, d, J = 7 Hz, Me).

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Registry No. **1a**, 87556-38-5; **1b**, 74718-69-7; **2b**, 74718-70-0; **3a**, 87556-39-6; **4a**, 87556-40-9; **5a**, 87556-41-0; **5b**, 87556-42-1; **6a**, 87566-98-1; **6b**, 74718-73-3; **7a**, 87556-43-2; **7b**, 74718-76-6; **8a**, 87556-44-3; **9b**, 87585-21-5; **10**, 79292-34-5; **11**, 87556-45-4; **13a**, 87556-46-5; **13a′**, 87585-22-6; $CpFe(CO)[P(OPh)_3]I$, 31988-05-3; $[CpFe(CO)[P(OPh)_3](MeC\equiv CMe)]BF_4$, 87556-47-6; $Me_2Cu(CN)Li_2$, 80473-70-7; $CpFe(CO)(PPh_3)I$, 12099-18-2; $[CpFe(CO)(PPh_3)(MeC\equiv CMe)]BF_4$, 70568-99-9; $CpFe(CO)(PPh_3)(\eta^1\text{-}C(CHMe_2){=}CH_2$, 87556-48-7; $LiCuPh_2$, 23402-69-9; $(CH_2{=}CH)_2Cu(CN)Li_2$, 80473-65-0; $CpFe(CO)[P(OPh_3)][\eta^1\text{-}C({=}CH_2)C(Me){=}C(H)Me]$, 87556-49-8; $(MeC\equiv C)_2Cu(CN)Li_2$, 87556-50-1; $CpFe(CO)[P(OPh_3)]CN$, 32730-94-2; $NaCH(CO_2Et)_2$, 996-82-7; KCN, 151-50-8; Et_4NCN, 13435-20-6; NaSPh, 930-69-8; $CpFe(CO)[P(OPh)_3](\eta^2\text{-}MeC\equiv CCO_2Me)]BF_4$, 87556-51-2; $LiCuMe_2$, 15681-48-8; $CpFe(CO)[P(OPh)_3][\eta^1\text{-}(Z)\text{-}C(Me){=}C(CO_2Me)Me]$, 87556-52-3; $CpFe(CO)[P(OPh)_3][\eta^1\text{-}(E)\text{-}C(Me){=}C(CO_2Me)Me]$, 87585-23-7; $[CpFe(CO)_2PPh_3]I$, 12100-40-2.