geneous catalytic reduction processes.[7,8] The insight gained by this study is as follows: *If* the hydride-interacting cation could be rendered both less mobile and less attractive electrostatically, then we might expect partial labilization or weakening of the transition metal–hydride bond that might favor processes such as CO insertion or hydride transfer to an adjacent CO ligand site. Whereas such a situation is difficult to achieve in homogeneous systems,[34] the ready availability of rigid basic sites to hold the promoter cation in metal oxide, alumina, or silica supported catalysts would seem to be conducive to CO/H^- activation of precisely this type.

(34) Powell, J.; Gregg, M.; Kuksis, A.; Meindl, P. *J. Am. Chem. Soc.* **1983**, *105*, 1064.

Acknowledgment. This work was supported by the National Science Foundation, CHE-8304162.

Registry No. $PPN^+HCr(CO)_5^-$, 78362-94-4; $Na^+HCr(CO)_5^-$, 83399-32-0; $Li^+HCr(CO)_5^-$, 89676-23-3; $PPN^+HW(CO)_5^-$, 78709-76-9; $Na^+HW(CO)_5^-$, 89676-24-4; $Li^+HW(CO)_5^-$, 89676-25-5; $PPN^+ClW(CO)_5^-$, 39048-34-5; $Na^+ClW(CO)_5^-$, 89676-26-6; $Li^+ClW(CO)_5^-$, 89676-27-7; $PPN^+HCr(CO)_4P(OMe)_3^-$, 89676-28-8; $Na^+HCr(CO)_4P(OMe)_3^-$, 89676-29-9; $PPN^+HW(CO)_4P(OMe)_3^-$, 82963-28-8; $Na^+HW(CO)_4P(OMe)_3^-$, 89676-30-2; $Li^+HW(CO)_4P(OMe)_3^-$, 89676-31-3; $PPN^+HW(CO)_4PMe_3^-$, 82963-32-4; $Na^+HW(CO)_4PMe_3^-$, 89676-32-4; $Li^+HW(CO)_4PMe_3^-$, 89676-33-5; $PPN^+HW(CO)_4P(Ph)_3^-$, 82963-30-2; $Na^+HW(CO)_4P(Ph)_3^-$, 89676-34-6; $Li^+HW(CO)_4P(Ph)_3^-$, 89676-35-7; $PPN^+ClW(CO)_5P(OMe)_3^-$, 89676-36-8; $Na^+ClW(CO)_5P(OMe)_3^-$, 89676-37-9; $Li^+ClW(CO)_5P(OMe)_3^-$, 89676-38-0.

Preparation of Alkenyliron Complexes from the Addition of Anionic Nucleophiles to Cationic Vinylidene Complexes

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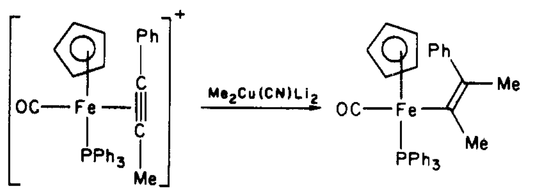
The reaction of $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$ with $R_2Cu(CN)Li_2$ (R = Ph, $CH{=}CH_2$) reagents leads to addition at the vinylidene α-carbon atom to produce $CpFeCO(PPh_3)[\eta^1\text{-}C(R){=}CMe_2]$ complexes. For R = $CH{=}CH_2$, this η^1-allyl complex smoothly converts into $CpFe(PPh_3)(\eta^3\text{-}CH_2CHC{=}CMe_2)$, a complex with an unusual η^3-allyl ligand. Addition of $[SPh]^-$ to the vinylidene complex yields $CpFeCO(PPh_3)[C(SPh){=}Me_2]$. The unsymmetrical vinylidene complex $[CpFeCO(PPh_3)\{C{=}C(Ph)Me\}][OSO_2CF_3]$ was prepared and reacts with $Me_2Cu(CN)Li_2$ to produce a 93:7 ratio of the *Z*:*E* isomers of $CpFeCO(PPh_3)[\eta^1\text{-}C(Me){=}C(Ph)Me]$.

Introduction

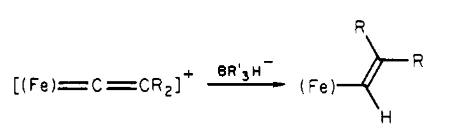
We have recently been able to demonstrate that a variety of anionic nucleophiles will add to alkynes η^2-coordinated to cationic iron species to yield η^1-alkenyl complexes.[1] As shown with a specific example in eq 1, the



(1)

nucleophiles add trans[2] (with the exception of hydride[3]) and for the cases tested, to date, the reaction is regioselective.[1] Because many types of nucleophiles are successful in the reaction, one has considerable control of the β-alkenyl substituent trans to the metal. The other two substituents are controlled by the choice of alkyne. Control of the alkenyl substituents is important because we are developing a variety of reactions that specifically cleave the iron leading to tetrasubstituted olefins.[4]

Another route to these alkenyl complexes would be the addition of anionic nucleophiles to cationic vinylidene complexes that are isomeric to the η^2-alkyne complexes used in eq 1. Two known examples[5] using hydride as the nucleophile are shown in eq 2. A number of examples using neutral nucleophiles such as PPh_3, pyridine, ROH, RSH, and R_2NH have also been reported.[5a,6]



(2)

(Fe) = $CpFeCO(PPh_3)$, R = H, (Fe) = CpFe(dppe), R = Me

If the reaction of anionic nucleophiles with vinylidene cations were as general as that shown in eq 1, one would gain additional control of the alkenyl substituents. In these vinylidene addition reactions, the nucleophile becomes a substituent at the α-alkenyl carbon atom. In the chemistry shown in eq 1, it becomes a β-alkenyl substituent. Also, a number of attractive routes to these vinylidene starting materials are available (eq 3[5a] and 4[7]), giving one control

(1) (a) Reger, D. L.; McElligott, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 5923. (b) Reger, D. L.; Belmore, K. A.; Mintz, E.; McElligott, P. J. *Organometallics* **1984**, *3*, 134.
(2) Reger, D. L.; Belmore, K. A.; Mintz, E.; Charles, N. G.; Griffith, E. A. H.; Amma, E. L. *Organometallics* **1983**, *2*, 101.
(3) Reger, D. L.; Belmore, K. A.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1983**, *105*, 5710.
(4) Reger, D. L.; Mintz, E., unpublished results.

(5) (a) Boland-Lussier, B. E.; Churchill, M. R.; Hughes, R. P.; Rheingold, A. L. *Organometallics* **1982**, *1*, 628. (b) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 2455.
(6) (a) Boland-Lussier, B. E.; Hughes, R. P. *Organometallics* **1982**, *1*, 635. (b) Kolobova, N. Y.; Skripkin, V. V.; Alexandrov, G. G.; Struchkov, Y. T. *J. Organomet. Chem.* **1979**, *169*, 293.
(7) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 7763.

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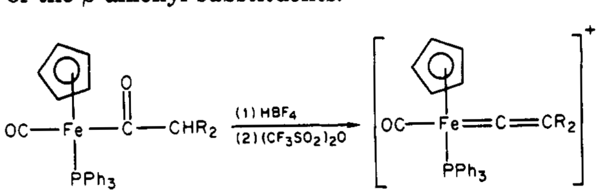
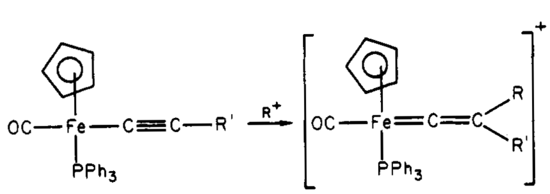
of the β-alkenyl substituents.



(3)



(4)

Reported here are the results of an investigation designed to test this potential alternate route to alkenyliron complexes. It is shown that carbon-based nucleophiles, delivered from $R_2Cu(CN)Li_2$ reagents, and $[SPh]^-$ add readily to these iron–vinylidene complexes. Also, we show using an unsymmetrical vinylidene complex that the reaction is nearly stereoselective yielding the more sterically hindered alkenyl isomer. Finally, the synthesis of an unusual η^3-allyl complex is reported.

Experimental Section

General Procedure. All operations were carried out under an atmosphere of nitrogen either by using standard Schlenk techniques or by using a Vacuum Atmospheres HE-43 drybox. All solvents were purified, dried, and degassed prior to use. Alkyllithium reagents were purchased from Aldrich (vinyllithium from Organometallics) and CuCN from Fisher. $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$[5a] and $CpFeCO(PPh_3)I$[1b] were obtained from established procedures. Elemental analysis were performed by Robertson Laboratory. Decomposition points were determined in sealed capillary tubes and are uncorrected. ^1H NMR spectra were recorded on a Varian EM390 or a Brüker WH400 spectrometer and are reported in δ vs. Me_4Si. ^{13}C spectra were recorded on either an IBM NR80 or a Varian CFT20 spectrometer in either C_6D_6 (128.0 ppm) or $CDCl_3$ (77.0 ppm) as both solvent and internal standard and are reported in ppm vs. Me_4Si. Infrared spectra were obtained on a Beckman 4210 spectrophotometer.

$CpFeCO(PPh_3)[\eta^1\text{-}C(Ph){=}CMe_2]$ (1). A slurry of $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$ (1.0 g, 1.8 mmol) in THF (30 mL) at −78 °C was treated with $Ph_2Cu(CN)Li_2$ (prepared from 0.16 g, 1.8 mmol, of CuCN and 1.5 mL of 2.4 M phenyllithium in 10 mL of THF at −78 °C) which was added by cannula. The mixture was allowed to warm with stirring to ambient temperature. After 30 min, the blood-red solution was evaporated to dryness and the resulting oil extracted with CH_2Cl_2 (50 mL) and filtered through a plug of alumina. The volume was reduced to ca. 15 mL and an equal volume of hexane added. The solution was cooled to 0 °C for 24 h. Deep purple crystals were collected, and the filtrate was halved and recooled to yield a second crop. A third crop was obtained by further reducing the solvent: total yield 0.44 g, 45%; decomp pt 168–171 °C; ^1H NMR ($CDCl_3$) δ 7.15 (m, 20, PPh_3, Ph), 4.39 (br s, 5, Cp), 1.97, 1.38 (br s, br s; 3, 3; Me's); IR (cm^{-1}, toluene) ν(CO) 1910. Anal. Calcd for $C_{34}H_{31}OPFe$: C, 75.28; H, 5.76. Found: C, 75.15; H, 5.88.

$CpFeCO(PPh_3)[\eta^1\text{-}C(CHCH_2){=}CMe_2]$ (2). A THF (30-mL) slurry of $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$ (1.94 g, 3.5 mmol) at −78 °C was treated with $(CH_2{=}CH)_2Cu(CN)Li_2$ (prepared from 0.31 g, 3.5 mmol, of CuCN and 4.1 mL of 1.7 M vinyllithium at −35 °C) which was added by cannula at −78 °C. The resulting solution was allowed to warm with stirring to ambient temperature. After the mixture was stirred for 30 min, the solvent was removed under vacuum and the resulting oil was extracted with 40 mL of benzene and filtered through a plug of alumina. The benzene was evaporated under vacuum to yield a red oil. The red oil was taken up in ca. 20 mL of pentane and cooled to −30 °C for 24 h to yield bright red crystals: yield 0.94 g, 54%; ^1H NMR ($CDCl_3$) δ 7.37 (m, 15, Ph), 5.78 (m, 1, CH), 4.32 (d, J = 1.5 Hz, Cp), 4.12, 3.96 (s, m; 1, 1; CH_2), 2.10, 1.87 (br s, br s; 3, 3; Me's); $^{13}C\{^1H\}$ NMR (C_6D_6) 216.1 (d, J = 41.2 Hz, CO), 152.7 (d, J = 20.9 Hz, FeC), 137.4 (d, J = 38.6 Hz, PC), 133.6 (d, J = 9.3 Hz, ortho-Ph), 128.2 (d, J = 9.6 Hz, meta-Ph), 129.7 (s, para-Ph), 103.7 (s, CH_2), 85.7 (s, Cp), 28.9, 25.0 ppm (s, s; Me's) (CH and CMe_2 carbon resonances were not identified); IR (cm^{-1}, toluene) ν(CO) 1910. Anal. Calcd for $C_{30}H_{29}OPFe$: C, 73.18; H, 5.94. Found: C, 73.04; H, 6.29.

$CpFeCO(PPh_3)[\eta^1\text{-}C(SPh){=}CMe_2]$ (4). A round-bottomed flask containing $[CpFeCO(PPh_3)(C{=}CMe_2)]BF_4$ (1.0 g, 1.8 mmol) and sodium thiophenol (0.24 g, 1.8 mmol) was cooled to −78 °C. Precooled THF (50 mL) was added, and the mixture stirred while being warmed to ambient temperature. After 2 h, the THF was evaporated under vacuum and the resulting oil extracted with 30 mL of benzene and filtered through a Celite plug. The solution was reduced to 5 mL and chromatographed on an alumina column eluting with benzene/hexane (50:50). Only one band was observed and collected. The solution was evaporated to dryness and redissolved in 30 mL of hexane. This solution was cooled to −30 °C for 48 h. Brown needles were collected: yield 0.62 g, 61%; decomp pt 133–136 °C. Anal. Calcd for $C_{34}H_{31}OPSFe$: C, 71.08; H, 5.44. Found: C, 70.61; H, 5.25. In the 0.12 m samples used for collecting the NMR data, two isomers are observed in a 2/1 ratio: ^1H NMR ($CDCl_3$) δ 7.18 (m, 20, SPh, PPh_3), 4.37 (d, 5, J = 1.5 Hz, Cp), 2.29, 2.20, 2.16, 1.86 (s, s, s, s; 1, 2, 1, 2; Me's); $^{13}C\{^1H\}$ NMR of the major isomer ($CDCl_3$) 222.9 (d, J = 36.9 Hz, CO), 152.5 (s, $={CMe_2}$), 142.0, 128.7, 124.9, 122.7 (s, s, s, s; SPh), 136.5 (d, J = 40.0 Hz, PC), 133.5 (d, J = 9.4 Hz, ortho-Ph), 129.4 (d, J = 2.0 Hz, para-Ph), 127.8 (d, J = 9.2 Hz, meta-Ph), 84.2 (d, J = 1.1 Hz, Cp), 29.1, 25.6 ppm (s, s; Me's); the following resonances could be identified for the minor isomer 133.4 (d, J = 9.6 Hz, ortho-Ph), 129.9 (d, J = 2.4 Hz, para-Ph), 128.2 (d, J = 9.6 Hz, meta-Ph), 84.5 (Cp), 28.0, 24.1 ppm (s, s; Me's); IR (cm^{-1}, toluene) ν(CO) 1910.

$CpFeCO(PPh_3)(\eta^1\text{-}C{\equiv}CPh)$. A flask containing $CpFeCO(PPh_3)I$ (1.0 g, 1.8 mmol) and $AgBF_4$ (0.36 g, 1.8 mmol) was cooled in an ice bath. To these two solids were simultaneously added phenylacetylene (0.20 mL, 1.8 mmol) and CH_2Cl_2 (30 mL). The reaction mixture was stirred for 45 min while the color changed from deep green to brown. Filtration through an alumina plug yielded a brown-orange solution. The solvent was evaporated under vacuum to give 0.63 g (68%) of an orange solid. This solid was used without further purification. The ^1H NMR spectrum (($CDCl_3$) δ 7.26 (m, 20, PPh_3, Ph), 4.4 (s, 5, Cp)) matched that reported in the literature for this complex when prepared by a different route.[8]

$[CpFeCO(PPh_3)\{C{=}C(Ph)Me\}]OSO_2CF_3$ (5). To a stirred solution of $CpFeCO(PPh_3)(\eta^1\text{-}C{\equiv}CPh)$ (0.61 g, 1.2 mmol) in benzene (30 mL) was slowly added dropwise 0.14 mL of freshly distilled $CH_3OSO_2CF_3$ (0.20 g, 1.2 mmol). The resulting solution was allowed to stir for 5 h or until the color of the solution changed from orange to blue-black. The dark blue solid was collected by filtration and washed with 10 mL of benzene and 10 mL of pentane and dried under vacuum (0.52 g, 65%). This unstable solid was used immediately in the reaction outlined below: ^1H NMR ($CDCl_3$) δ 7.30 (m, 20, Ph, PPh_3), 5.44 (s, 5, Cp), 1.80 (s, 3, CH_3).

$CpFeCO(PPh_3)[\eta^1\text{-}C(Me){=}C(Me)Ph]$ (6 and 7). To a stirred mixture of $[CpFeCO(PPh_3)\{C{=}C(Ph)Me\}]OSO_2CF_3$ (0.50 g, 0.74 mmol) in THF (30 mL) at −78 °C was added $Me_2Cu(CN)Li_2$ (prepared by adding 1.1 mL of 1.4 M methyllithium to 0.066 g, 0.74 mmol, of CuCN in 10 mL of THF at −78 °C) with a cannula. After being warmed to ambient temperature and stirred for 30 min, the reaction mixture was evaporated to dryness. The resulting black oil was extracted with 30 mL of CH_2Cl_2 and filtered through an alumina plug. The resulting red solution was evaporated to dryness to yield a red oil (0.4 g, 100%). The ^1H NMR spectrum ($CDCl_3$) showed that both the *Z* isomer 6 (93%) and the *E* isomer 7 (7%)[1] were formed in the reaction. These products were identified by comparison of their NMR spectra with those of authentic samples.[1b]

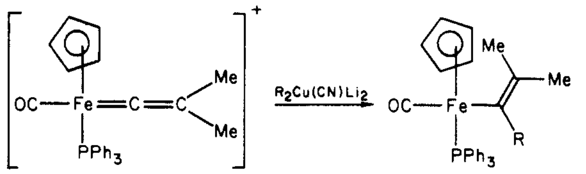
$CpFe(PPh_3)(\eta^3\text{-}CH_2CHC{=}C(Me)_2)$ (3). $CpFeCO(PPh_3)[\eta^1\text{-}C(CHCH_2){=}CMe_2]$ (0.50 g, 1.0 mmol) was dissolved in 15 mL of CH_2Cl_2. The red solution was heated at reflux for 2.5 h. The CH_2Cl_2 was evaporated to yield a red-yellow oil. The

(8) Green, M. L. H.; Mole, T. *J. Organomet. Chem.* **1968**, *12*, 404.

oil was extracted with 15 mL of pentane, filtered, and evaporated to dryness to yield a spectroscopically pure oil (0.41 g, 87%). Attempts to crystallize this oil from a variety of solvent mixtures were not successful and chromatography on alumina caused decomposition of the complex: ^1H NMR (C_6D_6, 400 MHz) δ 7.36 (m, 15, PPh_3), 4.15 (s, 5, Cp), 3.46 (m, 1, CH), 2.46 (d, 1, J = 7.3 Hz, CH_2-syn), 2.11, 2.03 (s, d, 3, 3; J = 1.0 Hz, Me's), 1.15 (d, 1, J = 11.0 Hz, CH_2-anti); ^{13}C NMR (C_6D_6) 156.7 (s, $C{=}CMe_2$), 138.1 (d, J = 12.3 Hz, PC), 134.1 (d, J = 19.8 Hz, ortho-Ph), 128.8 (s, para-Ph), 128.8 (d, J = 6.7 Hz, meta-Ph), 121.5 (s, CMe_2), 80.1 (s, Cp), 47.2 (s, CH), 34.7 (s, CH_2), 27.3, 24.1 ppm (s, s; CH_3's).

Results and Discussion

Carbon-based nucleophiles add readily to the iron-vinylidene complex as shown in eq 5. The PPh_3-substi-



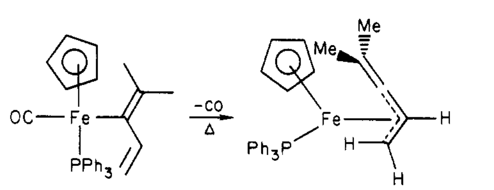
(5)

R = Ph (1), CH=CH$_2$ (2)

tuted dimethylvinylidene starting material was chosen for this survey because it is readily prepared and stable.[5a] The $R_2Cu(CN)Li_2$ reagents lead to high yield reactions from which the products are readily isolated. We have previously shown the utility of these reagents in similar reactions with η^2-alkyne complexes.[1b]

Complex 1 was of interest because it represents the third possible isomer that we have isolated with these alkenyl substituents. The other two are prepared as shown in eq 1 and in a similar reaction with MeC≡CMe as the alkyne and $Ph_2Cu(CN)Li_2$ as the nucleophilic reagent.[1b] This nicely demonstrates the flexibility that these various routes to iron–alkenyl complexes offer.

The η^1-allyl derivative converts in refluxing CH_2Cl_2 to an η^3-allyl complex as shown in eq 6. The ^1H NMR

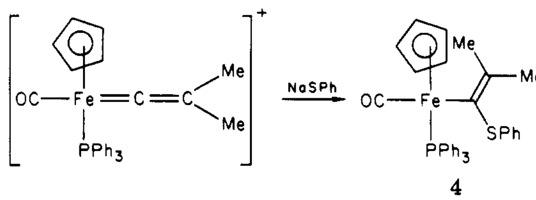


(6)

3

spectrum of 3 shows the expected resonances with appropriate coupling constants (see Experimental Section)[9] for this unusual η^3-allyl ligand.[10] In the ^{13}C NMR spectrum, in addition to the expected resonances for the Cp, PPh_3, and $C{=}CMe_2$ groups, resonances at 47.2 and 34.7 ppm are observed. Although these resonances appear at higher field than expected,[11] their assignment as arising from the allylic carbon atoms was verified by an INEPT[12] series of spectra that show that the 47.2 ppm resonance arises from a carbon atom bonded to a single H atom and the 34.7 ppm resonance from a CH_2 group.

A sulfide nucleophile also adds smoothly as shown in eq 7. In both the ^1H and ^{13}C NMR spectra, two isomers of

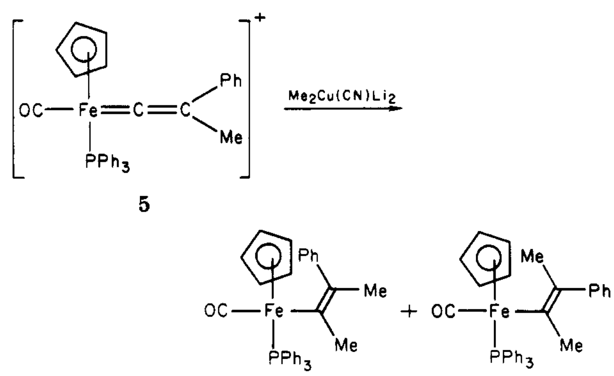


(7)

4

this molecule are observed. For example, in both types of spectra run on 0.12 m samples in $CDCl_3$, two pairs of resonances in a ratio of ca. 2/1 are observed in the region expected for the CH_3 group resonances. With ^1H NMR spectroscopy, it was observed that in less concentrated samples the amount of the lower concentration isomer increases such that in a 0.03 m solution the ratio is about even. Similar data are observed in benzene-d_6 where in concentrated solutions the ratio of isomers is ca. 2/1 and in the most dilute sample run (0.02 m) the ratio changes to 1/1.4. Note that in the benzene-d_6 spectra a separate Cp resonance is observed for each isomer that shows phosphorous coupling (1.5 Hz). This, combined with the fact that free PPh_3 is not observed in the ^{13}C spectrum, rules out phosphite dissociation (and possible S-coordination) as an explanation for the observation of two concentration dependent isomers. Heating these samples above 35 °C leads to irreversible line broadening in the ^1H spectra due to sample decomposition. Further studies are necessary to definitively establish an explanation for these observations.

In order to determine the stereospecificity of this reaction type, the unsymmetrical vinylidene complex 5 was prepared by the reaction of $CpFeCO(PPh_3)(\eta^1\text{-}C{\equiv}CPh)$ and CF_3SO_3Me. Addition of the methyl cuprate reagent as shown in eq 8 yields 6 and 7. This particular reaction



5

(8)

6 (93%) 7 (7%)

was chosen because these two products had been previously prepared as outlined above[1b] (for 6, see eq 1) and their stereochemistry determined.[2] This is important because it is difficult to determine the stereochemistry of these alkenyliron complexes. As shown in the equation, the reaction yields mainly the less stable Z isomer.[1b] Presumably the specificity arises from the addition reaction taking place preferentially away from the bulky phenylvinylidene substituent. A similar reaction of $[CpFe(CO)_2\{C{=}C(Ph)H\}]^+$ with PPh_3 yields a cationic alkenyl product with the Ph group cis to iron (as determined crystallographically).[6b]

Conclusion

The addition of anionic nucleophiles to $[CpFeCO(PPh_3)(C{=}CR_2)]^+$ complexes proceeds in good yield to form alkenyliron species. As one can vary both the nucleophile and the vinylidene substituents, this represents a flexible route to these alkenyliron species. This complements the alternate route of adding nucleophiles to

(9) (a) Fish, R. W.; Giering, W. P.; Marten, D.; Rosenblum, M. *J. Organomet. Chem.* **1976**, *105*, 101. (b) Faller, J. W.; Johnson, B. V.; Dryja, T. P. *Ibid.* **1974**, *65*, 395.

(10) A few examples of this type of η^3-allyl ligand have been previously reported: Bauch, T. E.; Giering, W. P. *J. Organomet. Chem.* **1978**, *144*, 335 and references therein.

(11) Chisholm, M. H.; Godleski, S. In "Progress in Inorganic Chemistry"; Lippard, S. J., Ed.; Wiley: New York, 1976; Vol 20, pp 366–370.

(12) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760.

analogous η^2-alkyne complexes.[1b]

Acknowledgment is made to the National Science Foundation for its support of this research through Grant CHE 8019513.

Registry No. 1, 89637-02-5; 2, 89637-03-6; 3, 89637-04-7; 4, 89655-90-3; 5, 89637-06-9; 6, 87585-21-5; 7, 74718-70-0; [CpFeCO(PPh$_3$)(C=CMe$_2$)]BF$_4$, 80642-54-2; Ph$_2$Cu(CN)Li$_2$, 80473-66-1; (CH$_2$=CH)$_2$Cu(CN)Li$_2$, 80473-65-0; CpFeCO(PPh$_3$)I, 12099-18-2; CpFeCO(PPh$_3$)(η^1-C≡CPh), 12313-22-3.

Reactions of Benzylrhenium Complexes (η^5-C_5H_5)Re(NO)(L)(CH_2Ar) with $Ph_3C^+PF_6^-$. Analysis of the Re–C_α Rotamers Involved in α-Hydride Abstraction

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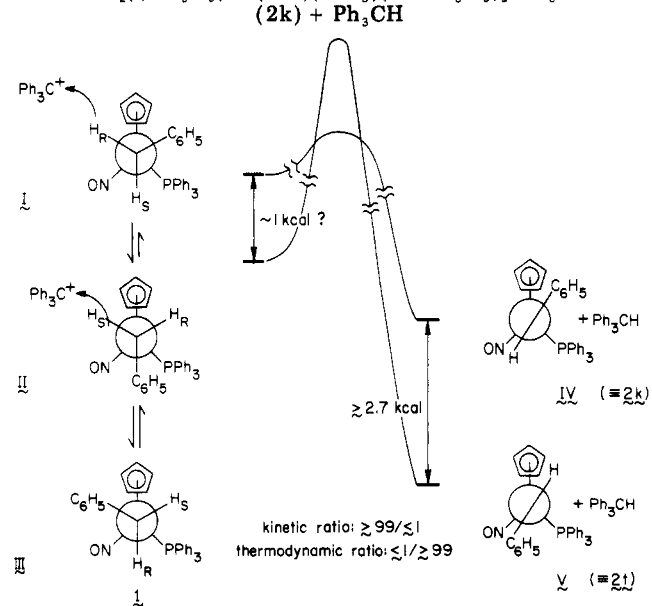
Sequential reaction of [(η^5-C_5H_5)Re(NO)(PMe_3)(CO)]$^+BF_4^-$ (4) with CH_3ONa, C_6H_5MgBr, and then BH_3·THF gives (η^5-C_5H_5)Re(NO)(PMe_3)($CH_2C_6H_5$) (7, 15%). Reaction of [(η^5-C_5H_5)Re(NO)(PPh_3)(=CH_2)]$^+PF_6^-$ with o-$CH_3C_6H_4MgBr$ and mesitylmagnesium bromide gives (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2-(2-$C_6H_4CH_3$)) (8, 52%) and (η^5-C_5H_5)Re(NO)(PPh_3)(CH_2(2,4,6-$C_6H_2(CH_3)_3$)) (9, 78%), respectively. Reactions of $Ph_3C^+PF_6^-$ with 7, 8, and 9 are examined and compared to that of $Ph_3C^+PF_6^-$ with (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (1). With 1, the *pro-R* H_α is abstracted to give *sc*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**2k**). In contrast, 9 undergoes exclusively *pro-S* H_α abstraction to give *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CH(2,4,6-$C_6H_2(CH_3)_3$))]$^+PF_6^-$ (**12t**). With 8, both the *pro-R* and *pro-S* H_α are abstracted to give approximately equal amounts of *sc*- and *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CH(2-$C_6H_4CH_3$))]$^+PF_6^-$ (**11k** and **11t**). With 7, the *pro-S* H_α is abstracted to give *ac*-[(η^5-C_5H_5)Re(NO)(PMe_3)(=CHC_6H_5)]$^+PF_6^-$ (**13t**). These data are discussed within the context of the Curtin–Hammett principle. Photolysis of **12t** and **13t** at −78 °C gives ca. 50:50 mixtures of **t**/**k** (*ac*/*sc*) Re=C isomers, but in the dark at 25 °C ≳99:≲1 equilibrium mixtures are reestablished. For **12k** → **12t**, $\Delta H^\ddagger = 18.8 \pm 0.3$ kcal/mol and $\Delta S^\ddagger = 0.5 \pm 1.1$ eu. Reaction of **13t** with Li(C_2H_5)$_3$BD gives a (77 ± 1):(23 ± 1) mixture of (η^5-C_5H_5)Re(NO)(PMe_3)($CHDC_6H_5$) diastereomers.

Introduction

We recently reported a detailed study of the reaction of benzyl complex (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (1) with $Ph_3C^+PF_6^-$.[3] Hydride abstraction occurred at −78 °C to give benzylidene *sc*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**2k**).[4] Subsequently, **2k** isomerized to a new Re=C geometric isomer, *ac*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (**2t**), with $t_{1/2}$ of 443 min at 4 °C and 17 min at 29.5 °C. The structures of **2k** and **2t** are represented in Scheme I in Newman projection form (IV, V).

Nucleophiles (Nu) were found to attack C_α of the benzylidene ligand of **2k** and **2t** either stereospecifically or with high stereoselectivity to give adducts (η^5-C_5H_5)Re(NO)(PPh_3)(CH(Nu)C_6H_5). X-ray crystallography established that attack occurred preferentially from a direction anti to the bulky PPh_3 ligand. Studies with deuterium-labeled substrates (*SS,RR*)- and (*SR,RS*)-(η^5-C_5H_5)Re(NO)(PPh_3)($CHDC_6H_5$)[4b] then demonstrated that $Ph_3C^+PF_6^-$

Scheme I. Qualitative Energy–Reaction Coordinate Diagram for the Reaction (η^5-C_5H_5)Re(NO)(PPh_3)($CH_2C_6H_5$) (1) + $Ph_3C^+PF_6^-$ → *sc*-[(η^5-C_5H_5)Re(NO)(PPh_3)(=CHC_6H_5)]$^+PF_6^-$ (2k) + Ph_3CH



abstracts essentially only the *pro-R* α-hydride of 1 and that abstraction occurs from a direction anti to the PPh_3. This direction allows overlap of the rhenium d orbital HOMO, the plane of which contains the Re–PPh_3 bond and is perpendicular to the Re–NO bond,[3] with the developing

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(3) Kiel, W. A.; Lin, G.-Y.; Constable, A. G.; McCormick, F. B.; Strouse, C. E.; Eisenstein, O.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4865.
(4) (a) The designations **k** ("kinetic") and **t** ("thermodynamic") will be used to indicate synclinal (*sc*) and anticlinal (*ac*) isomers, respectively (see Scheme I). The latter nomenclature is defined in *Pure Appl. Chem.* **1976**, *45*, 11. See section E-5.6, p 24. (b) In complexes with more than one chiral center, the rhenium configuration is specified first.

