A CONVENIENT STEREOSELECTIVE SYNTHESIS OF CATIONIC (η³-ALLYL)IRON TETRACARBONYL COMPLEXES

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Summary

Allylic alcohols have been found to react with $Fe_2(CO)_9$ in ether to afford, after addition of HBF_4/acetic anhydride, the corresponding $(\eta^3\text{-allyl})Fe(CO)_4^+$-$BF_4^-$ species (I) in moderate to good yields. The geometry of the starting alcohol is retained in the product complex; thus *E*-crotyl and -cinnamyl alcohols led to *anti*-substituted complexes, whereas the corresponding *Z*-alcohols produced *syn*-complexes.

Since the cationic iron allyl complexes I were first reported by Pettit and Emerson [1] *, there has been considerable interest in the chemistry of these species, particularly with respect to their stoichiometry and mechanism of *syn/anti* interconversion [1,2a,2c]. The most important preparative routes to these complexes proceed 1) from dienes via protonation of the corresponding iron

$$\text{(1)}$$

$$\text{(I)}$$

$$\text{(2)}$$

$$\text{(I)}$$

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* Originally formulated as $[(\eta^3\text{-allyl})Fe(CO)_3]^+BF_4^-$: the corresponding tricarbonyl cations are formed via eq. 2 in the absence of CO [2a].

tricarbonyl (or tetracarbonyl) complexes (eq. 1) [1,2a,b,d,e], or 2) from allyl halides via halide abstraction from the derived allyliron tricarbonyl halide compounds (eq. 2) [2a,d].

Prompted by an early preliminary report by Whitesides and coworkers [2d] on the reactions of several nucleophiles with I and our own interest in the potential synthetic utility of metal-complexed carbenium ions [3a—d], we have begun to examine in greater detail the reactivity of these cationic complexes as electrophilic allyl equivalents. It became apparent to us immediately that the known preparative routes to I were unacceptable if the complexes were to be used as practical synthetic intermediates. Both of the aforementioned methods (eq. 1, 2) suffer from modest to poor yields, less than optimum availability of organic starting materials, ineconomy in the case of method 2 (requiring stoichiometric quantities of silver salts), and the inapplicability of route 1 for the preparation of the parent allyl complex.

Simple olefins or allylic alcohols would be preferrable as starting materials for I due to their more general availability both commercially and synthetically. The prospects for employing the latter at first, however, did not appear promising in view of the known iron carbonyl-promoted isomerization of allylic alcohols to carbonyl compounds [1,4]. We hoped, however, that appropriate hydroxyl protection or, beter yet, utilization of very mild reaction conditions might permit in situ generation of the intermediate $(\eta^2\text{-allyl-X})\text{Fe(CO)}_4$ species which upon protonation would yield the desired $(\eta^3\text{-allyl})\text{Fe(CO)}_4{}^+$ salts (eq. 3).
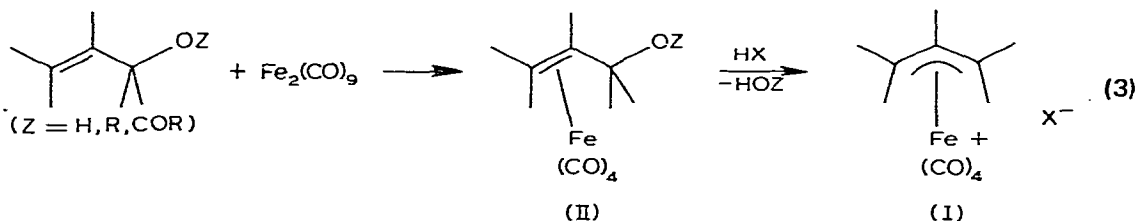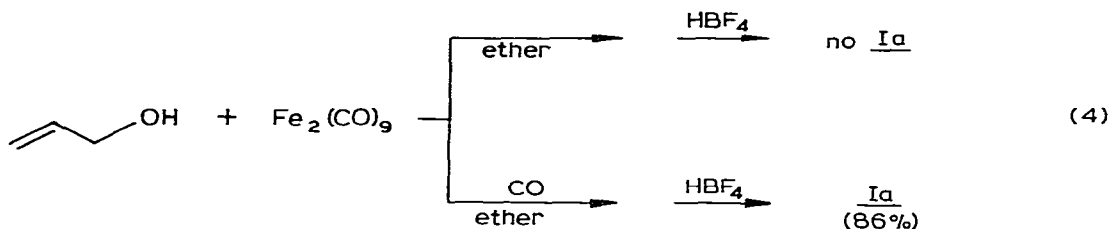

Results and discussion

Adopting the more conservative approach initially, the reaction between allyl acetate and $\text{Fe}_2(\text{CO})_9$ was examined. Stirring a 1/1 mixture of these components in ether under an atmosphere of CO led to gradual disappearance of insoluble $\text{Fe}_2(\text{CO})_9$ over 9 hours. Withdrawal of an aliquot followed by solvent evaporation left a yellow oil whose IR and NMR spectra were consistent with the formulation $(\eta^2\text{-allyl acetate})\text{Fe(CO)}_4$ (II, Z = OCOCH$_3$). Addition of excess HBF$_4$/acetic anhydride to the reaction mixture immediately precipitated pale yellow $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_4{}^+\text{BF}_4{}^-$ (62% yield after nitromethane/ether reprecipitation). Omission of carbon monoxide prior to protonation led to I in reduced yield (41%) possibly a result of some prior conversion of intermediate η^2-complex to $(\eta^3\text{-C}_3\text{H}_5)\text{Fe(CO)}_3(\text{OCOCH}_3)$ requiring CO dissociation.

Encouraged by this preliminary success, we turned our attention to the synthetically more attractive direct allyl alcohol/$\text{Fe}_2(\text{CO})_9$ route. The beneficial effect of added CO was even more marked here: in its absence the reaction

mixture prior to protonation was dark green indicating substantial $Fe_3(CO)_{12}$ formation and none of the desired I was obtained after protonation. Under an atmosphere of CO, however, allyl alcohol and $Fe_2(CO)_9$ formed a light, orange-yellow solution after stirring in ether for 8—10 hours which, upon addition of HBF_4/acetic anhydride, immediately precipitated $(\eta^3\text{-}C_3H_5)Fe(CO)_4^+BF_4^-$ in 86% yield.

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\begin{array}{c}
\text{ether} \xrightarrow{\ HBF_4\ } \text{no } \underline{Ia} \\[2em]
\text{CO} \xrightarrow{\ HBF_4\ } \underset{(86\%)}{\underline{Ia}}
\end{array}
\tag{4}
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We believe that added CO blocks the allyl alcohol—propanol isomerization reaction by suppressing hydride transfer to iron which presumably requires prior CO dissociation (eq. 5) [4].
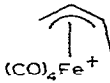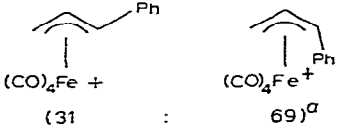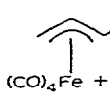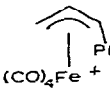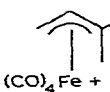
$$\tag{5}$$
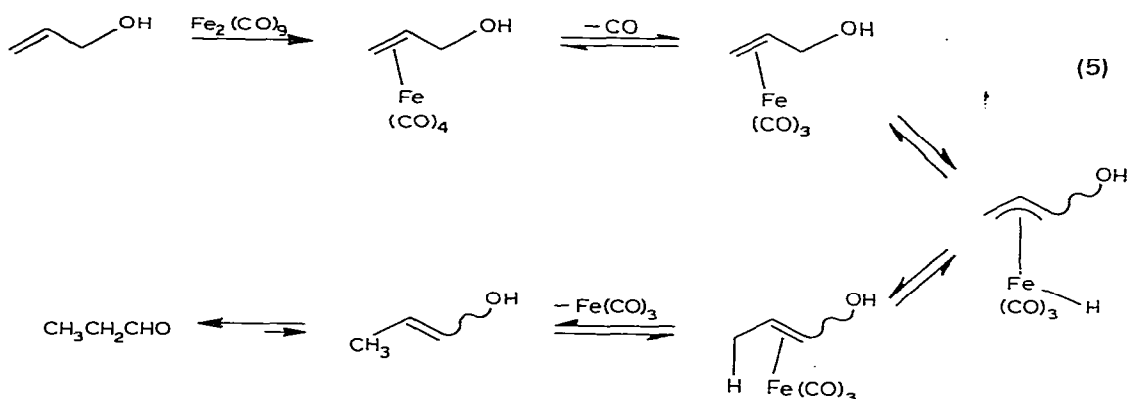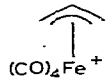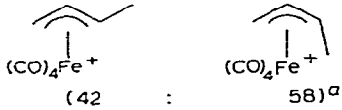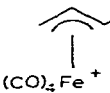
The generality of this new preparative route is clearly demonstrated by the entries in Table 1. Besides the moderate to good yields obtained, we point out the following additional features of the reactions: 1) starting with geometrically defined allylic alcohols complexation proceeds stereospecifically with retention of olefin geometry (e.g. entries 3, 4, 6, 7) and 2) modest *anti*-stereoselectivity is observed with 1-substituted alcohol substrates (entries 2, 5). Stereochemical assignments were unambiguously made on the basis of the well known shielding of *anti*-protons of the coordinated allyl unit [5] and characteristic coupling constants: $J_{H-H}(anti) = 12$—14 Hz, $J_{H-H}(syn) = 6$—8 Hz, $J_{H-H}(gem) = 1$—3 Hz (see Experimental section).

The mild reaction conditions apparently suppress both olefin and allyl isomerization *. This feature should prove very useful in future studies since many isomerically pure allylic alcohols are naturally occurring (terpenes) or available specifically from propargyl alcohols via catalytic hydrogenation over Lindlar

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* *Anti/syn* conversion in $(\eta^3\text{-crotyl})Fe(CO)_4^+$ occurs only after several minutes at $60°C$ in TFA [6].

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Entry	Alcohol	Product	Yield (%)
1	$CH_2{=}CHCH_2OH$	 $(CO)_4Fe^+$	86
2	$CH_2{=}CHCH(CH_3)OH$	 $(CO)_4Fe^+$ $(42$: $58)^a$ $(CO)_4Fe^+$	74
3	trans-$CH_3CH{=}CHCH_2OH$	 $(CO)_4Fe^+$	56
4	cis-$CH_3CH{=}CHCH_2OH$	 $(CO)_4Fe^+$	47
5	$CH_2{=}CHCH(Ph)OH$	 Ph $(CO)_4Fe+$ $(31$: $69)^a$ $(CO)_4Fe^+$ Ph	65
6	trans-$PhCH{=}CHCH_2OH$	 Ph $(CO)_4Fe+$	56
7	cis-$PhCH{=}CHCH_2OH$	 Ph $(CO)_4Fe+$	47
8	$CH_2{=}CHC(CH_3)_2OH$	 $(CO)_4Fe+$	64

^{a} Determined by ^1H NMR.

catalysts ($\rightarrow Z$-allylic alcohols) or reduction with $LiAlH_4$ [7] ($\rightarrow E$-alcohols). While the stereoselectivity from alcohols substituted on the hydroxyl-bearing carbon is low (entries 2, 5), the *anti*-preference is nonetheless interesting since it is contrathermodynamic. We suspect that the allyl stereochemistry is established in the rate-determining olefin complexation step since protonation at $-60°C$ of the crotyl alcohol/$Fe(CO)_4$ intermediate complex failed to change the *syn/anti* ratio. Until additional experiments are conducted, it would be premature to propose a detailed mechanism to explain the unexpected stereoselectivity but hydroxyl-assisted olefin complexation, well-documented in arene/

Cr(CO)$_6$ [8] and alkene/Ag$^+$ chemistry [9], may be involved.

In summary, we find the preparation of (η^3-allyl)Fe(CO)$_4$$^+$ complexes from allyl alcohols to be a convenient, efficient, economical and stereospecific method. Potential entry to these species from simple olefins and their applications in organic synthesis are under examination.

Experimental

^{1}H NMR spectra were obtained on Hitachi Perkin-Elmer R-24 (60 MHz) or Varian FT-80A (80 MHz) spectrometers. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (δ_{TMS} = 0.00). Infrared spectra were obtained on Perkin-Elmer 137 or 599B spectrometers.

Diiron enneacarbonyl was obtained from Pressure Chemical Co. and was purifed by shaking with 35% (v/v) aq. HCl, then filtered, and washed with 100 ml water; it was then shaken with 100 ml water, and 50 ml each of 95% ethanol and ether and dried in vacuo.

cis-Crotyl alcohol [10]

2-Butyn-1-ol was partially hydrogenated in ethyl acetate with 5% palladium on barium sulfate (2 wt.% of acetylenic alcohol) poisoned with quinoline (2 wt.% of acetylenic alcohol). The catalyst was removed by filtration through Celite and cis-crotyl alcohol was obtained by distillation; b.p. 65—66°C at 60 mmHg. (lit. [11] 65—66°C/60 mm).

cis-Cinnamyl alcohol

Prepared according to the procedure described for cis-crotyl alcohol. Kugelrohr distillation at 65—75°C/0.3 mmHg gave a 90/10 mixture of cis-cinnamyl alcohol/3-phenyl propanol.

Preparation of [(η^3-allyl)Fe(CO)$_4$]BF$_4$ (I) from allyl acetate

A solution of allyl acetate (1.00 g, 10 mmol) in 100 ml anhydrous ethyl ether was added to freshly washed Fe$_2$(CO)$_9$ (3.64 g, 10 mmol) under a carbon monoxide atmosphere. The reaction mixture was stirred at room temperature under a slow flow of carbon monoxide gas until the Fe$_2$(CO)$_9$ disappeared (9 h). HBF$_4$ (20 mmol) in acetic acid/acetic anhydride (prepared from 3.59 g 49% aq. HBF$_4$ and 25 ml acetic anhydride at 0°C) was added to the yellow-olive green solution and a faintly yellow solid immediately precipitated. The reaction mixture was stirred an additional 15 minutes and then filtered under nitrogen. The crude solid was dissolved in a minimal volume of nitromethane and the filtered solution was added dropwise to 450 ml of cold anhydrous ether to reprecipitate the iron salt. Filtration and drying in vacuo afforded I as an off-white solid (62%); IR: Fe—CO: 2160, 2100, 2090 cm^{-1}; ^{1}H NMR (CH$_3$CO$_2$D), δ 2.35 (dd, J = 12 Hz, 1.5 Hz, 2 H), 4.24 (dd, J = 6 Hz, J = 2 Hz, 2 H), 5.86 (m, 1 H). Compound I had identical spectroscopic properties to an authentic sample prepared according to ref. 5.

(η^2-Allyl acetate)Fe(CO)$_4$. The procedure follows the above described method for the preparation of [(η^3-allyl)Fe(CO)$_4$]BF$_4$ from allyl acetate up to the protonation step. Following the disappearance of Fe$_2$(CO)$_9$ the greenish yellow

reaction mixture was concentrated in vacuo to afford a yellow-brown oil: IR (petroleum ether) 2075, 1976 cm^{-1} (FeC≡O), 1742 cm^{-1} (C=O), ^{1}H NMR (CS$_2$): δ 1.96 (s, 3 H), 2.45 (d, J = 12 Hz, 1 H), 2.62 (d, J = 9 Hz, 1 H), 3.40 (m, 1 H), 4.13 (m, 2 H).

General procedure for the preparation of [(η^3-allyl)Fe(CO)$_4$]BF$_4$ complexes from allyl alcohols

A solution of the allylic alcohol (10 mmol) in 100 ml anhydrous ether was added to freshly washed Fe$_2$(CO)$_9$ (3.64 g, 10 mmol) under a carbon monoxide atmosphere. The mixture was stirred at room temperature under a slow flow of carbon monoxide gas until the Fe$_2$(CO)$_9$ disappeared (~8—10 h). To the yellow-orange solution was added HBF$_4$ (20 mol) in acetic acid/acetic anhydride (prepared from 3.59 g 49% aq HBF$_4$ in 25 ml acetic anhydride at 0°C). The iron salt immediately precipitated. The reaction mixture was stirred an additional 15 minutes and then filtered under nitrogen. The products produced in this manner are spectroscopically pure (IR, NMR). With the exception of the (η^3-cinnamyl)Fe(CO)$_4$$^+$ complexes, all are known compounds and exhibited identical ^{1}H NMR spectra to those reported (see below). Attempts to obtain analytically pure samples of the cinnamyl derivatives by recrystallization were only marginally successful due to their lesser solution stability. Results of typical analyses are given below.

syn-[(η^3-1-methyallyl)Fe(CO)$_4$]BF$_4$. IR (CH$_3$NO$_2$): 2155, 2100, 2095, 2085 cm^{-1}; ^{1}H NMR (TFA-d): δ 2.15 (d, J = 6 Hz, 3 H), 2.95 (dd, J = 3 Hz, J = 12 Hz, 1 H), 4.01 (dd, J = 3 Hz, J = 7 Hz, 1 H), 4.60 (m, 1 H), 5.65 (m, 1 H); lit. [6] (TFA-d): δ 2.16 (d, 3 H), 2.98 (dd, 1 H), 4.09 (dd, 1 H), 4.55 (m, 1 H), 5.84 (m, 1 H).

anti-[(η^3-1-methylallyl)Fe(CO)$_4$]BF$_4$. IR (CH$_3$NO$_2$): 2155, 2095—2085 cm^{-1}; ^{1}H NMR (TFA-d): δ 1.70 (d, J = 6 Hz, 3 H), 3.63 (dd, J = 3 Hz, J = 12 Hz, 1 H), 4.45 (dd, J = 2 Hz, J = 6 Hz, 1 H) 5.55 (m, 2 H); lit. [2b] IR: 2145, 2100, 2088, 2080 cm^{-1}; ^{1}H NMR: δ 1.72 (d, 3 H); 3.72 (dd, 1 H), 4.57 (dd, 1 H), 5.67 (m, 2 H).

syn-[(η^3-1-phenylallyl)Fe(CO)$_4$]BF$_4$. IR (CH$_3$NO$_2$): 2150, 2110, 2085 cm^{-1}; ^{1}H NMR: δ 3.22 (dd, J = 2 Hz, J = 13 Hz, 1 H), 4.21 (dd, J = 2 Hz, J = 6 Hz, 1 H), 5.45 (d, J = 12 Hz, 1 H), 6.61 (m, 1 H), 7.60 (m, 5 H); Anal. Found: C, 41.03; H, 2.67. C$_{13}$H$_9$BF$_4$FeO$_4$ calcd.: C, 41.98; H, 2.42%.

anti-[(η^3-1-phenylallyl)Fe(CO)$_4$]BF$_4$. IR (CH$_3$NO$_2$): 2150, 2115, 2095, 2065 cm^{-1}; ^{1}H NMR (TFA-d): δ 4.31 (dd, J = 1.5 Hz, J = 14 Hz, 1 H), 4.73 (dd, J = 1.5 Hz, J = 6 Hz, 1 H), 5.58 (m, 1 H), 6.92 (d, J = 8 Hz, 1 H), 7.45 (s, 5 H), Anal. Found: C, 40.46; H, 2.75. C$_{13}$H$_9$BF$_4$FeO$_4$ calcd.: C, 41.98; H, 2.42%.

[(η^3-1,1-dimethylallyl)Fe(CO)$_4$]BF$_4$. IR (CH$_3$NO$_2$): 2145, 2100, 2085, 2050 cm^{-1}; ^{1}H NMR (TFA-d): δ 1.87 (s, 3 H), 2.30 (s, 3 H), 3.28 (dd, J = 1.5 Hz, J = 13 Hz, 1 H), 4.20 (dd, J = 2.5 Hz, J = 6 Hz, 1 H), 5.55 (dd, J = 6 Hz, J = 13 Hz, 1 H); lit. [2b,2e] (TFA-d) δ 1.90 (s, 3 H), 2.35 (s, 3 H), 3.35 (dd, 1 H), 4.30 (dd, 1 H), 5.70 (dd, 1 H).

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