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The Wittig reaction in the generation of organometallic compounds containing alkenes as side groups

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Abstract

The Wittig reaction has been identified as a viable route to transition metal monomers. It has been used to synthesize $\{\eta^5\text{-}C_5[C(CH_3)=CHR]\}Mn(CO)_3$ [R = –H (68% yield), $-CH_3$ (60%), $-CH_2CH_3$ (51%), $-CH_2CH_2CH_3$ (40%), $-C_6H_5$ (46%)] from acetylcymantrene and the appropriate phosphorane at room temperature. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CHR]\}(\eta^5\text{-}C_5H_5)Fe$ [R = –H (81%), $-CH_3$ (77%), $-CH_2CH_3$ (36%), $-CH_2CH_2CH_3$ (27%) have been prepared from acetylferrocene and phosphorane at room temperature. $[\eta^5\text{-}C_5(CH=CRR')H_4](\eta^5\text{-}C_5H_5)Fe$ [R, R' = –H,H (79%); $-CH_3$,H (69%); $-CH_2CH_3$,H (48%); $-CH_2CH_2CH_3$,H (49%); $-C_6H_5$,H (80%); $-C(CH_3)_2$H,H (73%); $-CH_3$,CH_3 (67%)] have been produced from formylferrocene and phosphorane in refluxing benzene. *E*/*Z* isomeric ratios were identified for alkenylcymantrenes and are consistent with past Wittig studies. The aldol reaction has been identified as a side route in the Wittig reactions of acetylferrocene and phosphoranes. Carbomethoxyphosphoranes did not produce alkenes at room temperature with nonpolar solvents.

Introduction

There has been growing interest in the incorporation of organometallic molecules into polymers [1] since vinylferrocene was first polymerized [2]. These molecules provide polymeric materials with increased fire resistance and electrical activity [3]. One focus in our laboratory is to synthesize novel organometallic polymeric compounds and examine their properties [4].

As part of our ongoing efforts to prepare organometallic polymers, vinylcymantrene [5] was prepared by reduction/dehydration of acetylcymantrene in an overall yield of about 70% (see Scheme 1). We investigated the use of the Wittig reaction as a more time efficient alternative to these two steps. Table 1 illustrates the past utility of the Wittig approach in the conversion of metal carbonyl complexes to a molecule with an alkene unit [6].

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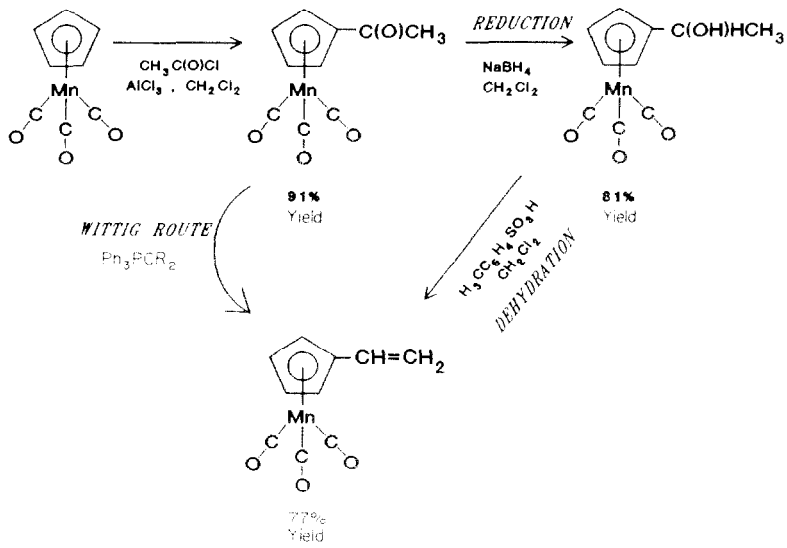

Scheme 1. Synthesis of vinylcymantrene using literature methods. The overall yield for the reduction/dehydration steps is approximately 70%. Yields noted are those obtained by the authors.

We report here on the syntheses of cymantrenylalkenes using Wittig reactions (in place of the reduction and dehydration steps) and a systematic extension of the Wittig studies of ferrocene complexes.

Experimental

General laboratory materials and techniques

Petroleum ether and C_5H_{12} (Fisher Scientific) were used as received. C_6H_6 (Fisher) was dried by azeotropic distillation and stored over molecular sieves (4–8 mesh, 4 Å). CH_2Cl_2, CH_3Li, C_6H_5Li (2.0 *M*), $[C_6H_5CH_2P(C_6H_5)_3]Br$, $[n\text{-}C_3H_7P(C_6H_5)_3]Br$, $[CH_3P(C_6H_5)_3]Br$, $(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4[C(O)H]\}Fe$, $(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4[C(O)CH_3]\}Fe$, silica gel (Grade 62, 60–200 mesh, 140 Å), $CDCl_3$, NaH, and neutral Al_2O_3 (standard grade, 150 mesh, 58 Å) were used as received (Aldrich). $[CH_3CH_2P(C_6H_5)_3]Br$, $[CH_3OC(O)CH_2P(C_6H_5)_3]Br$, $[n\text{-}C_4H_9P(C_6H_5)_3]Br$, $\{[H(CH_3)_2C]CH_2P(C_6H_5)_3\}Br$, $[(CH_3)_2CHP(C_6H_5)_3]I$, were used as received (Lancaster Chemical Company). THF (Fisher) was dried over sodium/benzophenone and distilled prior to use.

$[CH_3P(C_6H_5)_3]I$ [17], $\{\eta^5\text{-}C_5H_4[C(O)CH_3]\}Mn(CO)_3$ [6] (purified by chromatography on silica gel with hexane/CH_2Cl_2 eluant), 1,3-diferrocenylbut-2-en-1-one [18], were prepared according to literature methods.

All Wittig reactions were performed under dinitrogen in a Kewaunee Scientific Dry Box or by Schlenk techniques. These manipulations were performed at room temperature (22–27°C) unless otherwise stated. Dinitrogen for Schlenk manipulations was dried by passage through a column of KOH pellets (46 cm × 50 cm). Reactions were monitored and purities were assessed using thin layer chromatography (TLC). Silica gel plates (Kodak) and standard spotting and developing techniques were used for the TLC.

^{1}H NMR spectra were recorded on a 60 MHz Varian EM360A spectrometer at 40°C. ^{13}C NMR spectra were recorded on a Bruker WM250 spectrometer at 21°C. All samples were dissolved in $CDCl_3$ and the chemical shifts were reported in ppm from TMS as an internal standard. IR spectra were recorded on a Perkin–Elmer 783 spectrometer. Elemental analyses were performed by Desert Analytics, Tucson, Arizona or Oneida Research Services, Whithall, New York.

Reaction conditions for acetylcymantrene

Method A. The phosphonium salt (4.06 mmol), C_6H_6 (100 mL) and C_6H_5Li (4.06 mmol) were stirred for the times listed in Table 2. $\{\eta^5$-$C_5H_4[C(O)CH_3]\}$-$Mn(CO)_3$ (4.06 mmol) was added and stirred for the times noted. The reaction mixture was filtered and the filtrate concentrated to 20 mL under reduced pressure. The concentrate was chromatographed on a silica gel column (28 cm × 2 cm) using petroleum ether or hexanes as eluant. The single yellow band from the silica column was further chromatographed on a neutral alumina column with petroleum ether. The second yellow band containing the product was collected. The solvent was removed at reduced pressure to produce the organometallic alkene as a mixture of *E*/*Z* isomers. A sample pure enough for elemental analysis was obtained by a vacuum distillation.

Method B. This method is the same as Method A except that after the acetylcymantrene was added, the reaction mixture was refluxed for the times noted in Table 2.

Method C. C_6H_5Li (4.57 mmol) was added to a solution of $[C_2H_5P(C_6H_5)_3]Br$ (1.66 g, 4.47 mmol) in THF (50 ml, 0.6% H_2O by assay) and stirred while the reaction vessel was cooled with a dry ice/acetone bath. The reaction was allowed to warm to 25°C. $\{\eta^5$-$C_5H_4[C(O)CH_3]\}Mn(CO)_3$ (1.0 g, 4.06 mmol) in THF (35 mL) was added to the ylide with cooling over a 10 min period. The reaction was stirred for 8 h. TLC on silica gel indicated that alkene formation had occurred almost instantly upon addition of the ketone. After stirring, the reaction mixture was concentrated to an oil under reduced pressure at 40°C. The oil was chromatographed on silica gel (30.5 cm × 2 cm) with hexane/CH_2Cl_2 (3:1). The first yellow band was collected and the solvent removed under vacuum to produce 0.80 g of $\{\eta^5$-$C_5H_4[C(CH_3)=CH(CH_3)]\}Mn(CO)_3$. A small amount of phosphine oxide was present in the sample and was removed by neutral alumina chromatography.

Reaction conditions for acetylferrocene

Method D. The phosphonium salt (4.82 mmol) was stirred with C_6H_5Li (4.60 mmol) in benzene (100 mL) for 2 h. The solution was brought to reflux after acetylferrocene was added. The mixture was refluxed for 1 h. After cooling to 25°C, an equal volume of petroleum ether was added and the mixture was filtered. Basic alumina (20 mL) was added to the filtrate and the solvent was removed under vacuum. The resultant powder was chromatographed on a basic alumina column (30.5 cm × 2.5 cm) with $(CH_3CH_2)_2O$/petroleum ether (1:1). The large yellow band which followed the solvent front was collected and evaporated under reduced pressure to produce the alkene (yields are noted in Table 3).

Method E. Method E is similar to Method D except that after the acetylferrocene was added, the reaction was stirred at room temperature (times shown in Table 3). The reaction mixture was chromatographed on basic alumina with

Table 1

Organometallic alkenes from Wittig reactions

Carbonyl	R [a]	Yield (%)	Ref.
$\{\eta^5\text{-}C_5H_4[C(O)H]\}(\eta^5\text{-}C_5H_5)Fe$	CH_2 [b]	81	7
	CH_2 [c]	87	8
	$CH(CH_3)$ [b]	50	7
	$CH(CH_3)$ [c]	75	8
	$C(CH_3)_2$ [b]	70	7
	$CH(Ph)$ [b,d]	70	7
	$CH(Ph)$ [c]	75	8
	$CH(Ph)$ [e]	45	9
	$CH[C(O)OC_2H_5]$ [f]	68	7
	$CH[C(O)OC_2H_5]$ [g]	82	10
	CPh_2 [c]	80	8
	$CH[(4)\text{-}C_6H_4CH_3]$ [e]	53	9
	$CH[(9)\text{-anthracenyl}]$ [e]	23	9
	$CH(CH{=}CHPh)$ [e]	35	9
	$CH[(4)\text{-}C_6H_4CH{=}CHPh]$ [e]	33	9
	$CH[(4)\text{-}C_6H_4CH{=}CH\text{-}[(\eta^5\text{-}C_5H_4)(C_5H_5)Fe]]$ [e]	31	9
	$CH_2CH{=}CH_2$ [h]	12	11
$\{\eta^5\text{-}C_5H_4[C(O)CH_3]\}(\eta^5\text{-}C_5H_5)Fe$	CH_2 [b]	82	7
	CH_2 [c]	83	8
	$CHCH_3$ [b]	63	7
	$C(CH_3)_2$ [b]	85	7
$\{\eta^5\text{-}C_5H_4[C(O)(n)\text{-}C_4H_9)]\}\text{-}(\eta^5\text{-}C_5H_5)Fe$	$CH(Ph)$ [c]	75	8
$\{\eta^5\text{-}C_5H_4[C(O)Ph]\}(\eta^5\text{-}C_5H_5)Fe$	CH_2 [c]	64	8
$\{\eta^6\text{-}C_6H_5[C(O)H]\}Cr(CO)_3$	$CHPh$ [i]	63	12
	$CH[(4)\text{-}C_6H_4(Ph)]$ [i]	78	12
	$CH[(4)\text{-}C_6H_4((4)\text{-}C_6H_4Ph)]$ [i]	70	12
	$CH(naphthalenyl)$ [i]	75	12
	$CH[(4)\text{-}C_6H_4CN]$ [i]	79	12
	$CH[(4)\text{-}C_6H_4(CH{=}CHPh)]$ [i]	78	12
	$CH[(4)\text{-}C_6H_4C{\equiv}CPh]$ [i]	52	12
	$\text{-}CH[(4)\text{-}C_6H_4(CH)]\text{-}$ [j,k]	45	12
	$\text{-}CH[(4)\text{-}C_6H_4\text{-}[(4)\text{-}C_6H_4(CH)]\text{-}$ [j,l]	68	12
$\{\eta^5\text{-}C_5H_4[C(O)H]\}W(CH_3)(CO)_5$	CH_2 [k]	80	13
$\{\eta^5\text{-}C_5H_4[C(O)H]\}Co(CO)_2$	CH_2 [l]	30	14, 15
$\{\eta^5\text{-}C_5H_4[C(O)CH_3]\}Co(CO)_2$	CH_2 [l]	30	14, 15
$\{\eta^5\text{-}C_5H_4[C(O)]\}(\eta^5\text{-}C_5H_5)Fe$	$[\text{-}CH(\eta^5\text{-}C_5H_4)](\eta^5\text{-}C_5H_5)Fe$ [m]	26	16
$C_6H_4C(O)H$	$[\text{-}CH(\eta^5\text{-}C_5H_4)](\eta^5\text{-}C_5H_5)Fe$ [m]	48 [n]	16
$(C_6H_4)_2CO$	$[\text{-}CH(\eta^5\text{-}C_5H_4)](\eta^5\text{-}C_5H_5)Fe$ [m]	67 [o]	16
$HC(O)C{\equiv}CH$	$[\text{-}CH(\eta^5\text{-}C_5H_4)](\eta^5\text{-}C_5H_5)Fe$ [m]	71 [p]	16

[a] Ylide is $(C_6H_5)_3PR$. [b] Solvent is dimethylsulfoxide; base is dimethylsulfinyl anion; reaction time = 15 min (25°C). [c] Solvent is diethylether; base is n-butyllithium; reaction time = 1 h (reflux). [d] Ph, phenyl. [e] Solvent is anhydrous ethanol; base is $LiOC_2H_5$. [f] Solvent is ethylacetate; reaction time = 96 h (25°C). [g] Solvent is C_6H_6. [h] Solvent is ether; base is n-butyllithium; reaction time = 24 h (25°C). [i] Solvent is ethanol; base is 0.2 *N* $LiOC_2H_5$. [j] Reaction with the chromium aldehyde performed with the diylide shown. [k] Phase transfer system of C_6H_6 and 5 *N* NaOH(aqueous). $\{\eta^5\text{-}C_5H_4[C(O)R]\}M(CH_3)(CO)_5$ (M = W or Mo; R = H or CH_3) are also reported to yield alkene [14] but no yields are given. [l] Solvent is ether (25°C). [m] Solvent is ether (10 h at room temperature) and then THF (2 h at reflux); base is PhLi. [n] Solvent is ether/C_6H_6 (48 h at room temperature, 3 h at reflux); base is PhLi. [o] Solvent is ether/C_6H_6 (2 h at room temperature, 3 h at reflux); base is PhLi.

Table 2

Results for Wittig reactions with acetylcymantrene

Phosphonium salt	Ylide time [a]	Reaction time [b]	Yield [c]	Method [d]
$[Ph_3PCH_3]Br$ [e]	4	12 (25°C)	70	A
$[Ph_3PCH_3]Br$	3	1 (reflux)	20	B [f]
$[Ph_3PCH_3]I$	2	1 (25°C)	0	A [f]
$[Ph_3PCH_2CH_3]Br$	4	12 (25°C)	61	A
$[Ph_3PCH_2CH_3]Br$	0.25	8 [g]	79	C
$[Ph_3PCH_2CH_2CH_3]Br$	4	12 (25°C)	56	A
$[Ph_3P(CH_2)_3CH_3]Br$	4	12 (25°C)	47	A
$[Ph_3PCH(CH_3)_2]I$	4	12 (25°C)	0	A
$[Ph_3PCH_2(C(CH_3)_2H)]Br$	4	12 (25°C)	0	A
$[Ph_3PCH_2(C(CH_3)_2H)]Br$	4	4 [h] (reflux)	0	B
$[Ph_3PCH_2[C(O)OCH_3]]Br$	4	12 (25°C)	0	A
$[Ph_3PCH_2Ph]Br$	4	12 (25°C)	46	A

[a] Ylide time = time of reaction between salt and base in hours. [b] Reaction time = time of reaction between ylide and ketone in hours. Temperature noted in parentheses. [c] Percentage yields presented are the highest obtained. [d] Method letter refers to Experimental section. [e] Ph, phenyl. [f] The reaction was followed throughout using TLC. High yields are obtained early in the reaction but drop off rapidly. [g] The reaction was initially at dry-ice/acetone bath temperatures and was allowed to slowly warm to room temperature. [h] One reaction time was 12 h and one was 2 h. No yield in either case.

$(C_2H_5)_2O$/petroleum ether (3:1). This afforded compounds which were phosphine oxide free. Yields are noted in Table 3.

Reaction conditions for formylferrocene

Method F. The phosphonium salt (5.4 mmol) and phenyllithium (2.7 mL, 2 *M*, 5.4 mmol) were stirred in THF (60 mL) for 1 h. Formylferrocene (1.00 g, 4.69

Table 3

Results for Wittig reactions with acetylferrocene

Phosphonium salt [a]	Reaction time [b]	Yield [c]	Method [d]
$[Ph_3PCH_3]I$	1 (reflux)	66	D [e]
$[Ph_3PCH_3]Br$	1 (25°C)	81	E
$[Ph_3PCH_3]Br$	20 min (25°C)	66	E
$[Ph_3PCH_3]Br$	40 min (25°C)	61	E
$[Ph_3PCH_2CH_3]Br$	1 (reflux)	69	D
$[Ph_3PCH_2CH_3]Br$	1 (25°C)	77	E
$[Ph_3P(CH_2)_2CH_3]Br$	1 (reflux)	42	D
$[Ph_3P(CH_2)_2CH_3]Br$	1 (25°C)	36	E
$[Ph_3P(CH_2)_3CH_3]Br$	1 (reflux)	37	D
$[Ph_3P(CH_2)_3CH_3]Br$	1 (25°C)	27	E
$[Ph_3PCH_2Ph]Br$	1 (reflux)	0	D
$[Ph_3PCH_2C(O)CH_3]Br$	1 (reflux)	0	D
$[Ph_3PCH_2(C(CH_3)_2H)]$	1 (reflux)	0	D
$[Ph_3PCH_2(C(CH_3)_2H]$	–	0	F
$[Ph_3PC(CH_3)_2H]$	–	0	F

[a] Ph, phenyl. [b] Reaction time = time of reaction between ylide and ketone in hours unless otherwise noted. Temperature noted in parentheses. [c] Percentage yields presented are highest obtained. [d] Method letter refers to Experimental section. [e] Small amount of phosphine oxide present.

Table 4

Results for Wittig reactions with formylferrocene

Phosphonium salt [a]	Yield [b]
$[Ph_3PCH_3]Br$	89
$[Ph_3PCH_2CH_3]Br$	78
$[Ph_3P(CH_2)_2CH_3]Br$	49
$[Ph_3P(CH_2)_3CH_3]Br$	52
$[Ph_3PCH_2Ph]Br$	80
$[Ph_3PCH_2C(O)OCH_3]Br$	0
$[Ph_3PCH_2C(CH_3)H]Br$	73
$[Ph_3PCH(CH_3)_2]Br$	67

[a] Ph, phenyl. [b] Method F was used in all cases. Percentage yields presented are the highest obtained.

mmol) in THF (20 mL) was added dropwise over 20 min and the reaction was stirred for an additional hour. Petroleum ether (30 mL) was added to precipitate some of the byproducts. After filtering, the solvent was removed under reduced pressure. The crude alkene was chromatographed on basic alumina using petroleum ether/diethyl ether (2:1). The first yellow band was collected. The solvent was removed at reduced pressure and the pure product obtained was dried on a vacuum line. Yields are shown in Table 4.

Analytical data

All $^1H/^{13}C$ NMR and elemental analyses data are shown in Table 5. NMR assignments were made on the basis of past studies [19] using the numbering scheme shown in Fig. 1.

Discussion

Examination of the yields of the reactions between the organometallic complexes and the ylides (see Tables 2–4) indicate that increasing the steric bulk of the ylide carbon by increasing the length of the substituent alkyl chain causes a decrease in the yield of alkene obtained. This, in addition to the fact that alkenes were produced from the formyl complex (see Table 4) but not from the acetylcomplex (see Table 3) in reactions with disubstituted or sterically demanding ylides, supports the influence of steric bulk in Wittig reactions [20].

TLC analyses of the reaction mixtures indicates that maximum yields were obtained shortly after mixing the reactants. The procedures used here, however, do not provide organometallic acrylates from carbomethoxyl ylides as has been found in the past [7,10]. It is unclear how the more polar solvents function in those Wittig schemes.

The use of iodide phosphonium salts with acetylcymantrene yielded alkenes which rapidly decomposed to paramagnetic materials. This decomposition was not observed with the bromide salts. In addition, a red aldol byproduct was also observed to form in the case when acetylferrocene (but not formyl ferrocene cymantrene) was the target carbonyl. The quantity of this product, identified by comparison of its properties to an authentic sample produced under standard aldol conditions [18], was highest when the ylide was added rapidly to the acetylferrocene.

Table 5

^1H, ^{13}C, IR and elemental analyses data [a]

1. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CH_2]\}Mn(CO)_3$

   ^1H NMR: 5.10 (m, $J < 1$ Hz, 1H, =C–H); 4.82 (m, 2H, =C–H, H^2 and H^5 of C_5H_4); 4.59 (t, 2H, H^3 and H^4 of C_5H_4); 1.90 (m, $J < 1$ Hz, 3H, =C–CH_3)

   ^{13}C NMR: 225.0 (CO); 135.2, 110.0 (C^6, C^8); 102.6 (C^1); 82.5, 81.2 (C^{2-5}); 21.0 (CH_3)

   Anal. Found: C, 53.95; H, 3.73. Calc.: C, 54.12; H, 3.72%). IR: 2018, 1925 (CO), 1632 (C=C)

2. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CH(CH_3)]\}Mn(CO)_3$

   ^1H NMR: 5.45, 5.15 (q for each isomer, $J = 7$ Hz for each, 1H for each, =C–H); 4.90 (m, 2H, $H^{2,5}$ of C_5H_4); 4.32 (q, 2H, $H^{3,4}$ of C_5H_4); 1.50–1.85 (m, 6H, =C(C_5H_4)CH_3 and =CHCH_3)

   ^{13}C NMR: 225.0 (CO); 127.1, 127.0, 125.0, 122.9 (C^6, C^8); 103.0, 107 (C^1); 83.5, 81.9, 81.0, 79.5 (C^{2-5}); 24.5, 15.3, 14.8, 13.9 (alkane)

   Anal. Found: C, 56.12; H, 4.31. Calc.: C, 56.05; H, 4.31%. IR: 2018, 1925 (CO); 1650 (C=C)

3. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CH(CH_2CH_3)]\}Mn(CO)_3$

   ^1H NMR: 5.73, 5.39 (t for each isomer, $J = 6$–7 Hz for each, 1H, =C–H); 4.82 (m, 2H, $H^{2,5}$ of C_5H_4); 4.65 (m, 2H, $H^{3,4}$ of C_5H_4); 2.20 (m, $J = 6$–7 Hz, 2H, =CHCH_2); 1.89, 1.79 (s for each isomer, 3H, =C(C_5H_4)CH_3; 1.01 (t, $J = 6$–7 Hz, 3H, –CH_2CH_3)

   ^{13}C NMR: 225.0 (CO); 133.9, 130.3, 126.0, 125.5 (C^6, C^8); 108.0, 103.4 (C^1); 83.0, 81.5, 81.0, 79.1 (C^{2-5}); 25.0, 23.0, 21.5, 15.0, 14.5, 14.0 (alkane)

   Anal. Found: C, 57.56; H, 4.73. Calc.: 57.37; H, 4.81%. IR: 2018, 1925 (CO); 1655 (C=C)

4. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CH(CH_2CH_2CH_3)]\}Mn(CO)_3$

   ^1H NMR: 5.85, 5.51 (t for each isomer, $J = 6$–7 Hz for each, 1H, =C–H); 4.94 (m, 2H, $H^{2,5}$ of C_5H_4); 4.69 (m, 2H, $H^{3,4}$ of C_5H_4); 2.19 (q, $J = 6$–7 Hz, 2H, =C–CH_2–); 1.95, 1.80 (s and m respectively for the isomers, $J < 1$ Hz, 3H, =C(C_5H_4)CH_3); 1.15–1.75 (m, $J = 6$–7 Hz, 2H, –$CH_2CH_2CH_3$); 0.89 (t, $J = 6$–7 Hz, 3H, –CH_2CH_3)

   ^{13}C NMR: 225.0 (CO); 132.1, 128.9, 126.5, 125.4 (C^6, C^8); 107.9, 103.2 (C^1); 83.5, 81.9, 81.1, 79.9 (C^{2-5}), 31.9, 31.0, 25.0, 23.0, 22.8, 15.2, 13.9 (alkane)

   Anal. Found: C, 58.48; H, 5.39. Calc.: C, 58.75; H, 5.28. IR: 2018, 1925 (CO)

5. $\{\eta^5\text{-}C_5H_4[C(CH_3)=CH(C_6H_5)]\}Mn(CO)_3$

   ^1H NMR (*E* isomer): 7.20 (bs, 5H, C_6H_5); 6.75 (s, 1H, =C(C_6H_5)*H*); 4.92 (bs, 2H, $H^{2,5}$ of C_5H_4); 4.65 (bs, 2H, $H^{3,4}$ of C_5H_4); 1.99 (s, 3H, =C(C_5H_4)CH_3)

   ^1H NMR (*Z* isomer): 7.15 (m, 5H, C_6H_5); 6.48 (d, $J = 1$ Hz, 1H, =C(C_6H_5)*H*); 4.55 (m, 4H, C_5H_4); 2.08 (d, $J = 1$ Hz, 3H, =C(C_5H_4)CH_3)

   ^{13}C NMR: 225.0 (CO); 137.8, 136.9, 129.9, 128.3, 128.0, 127.8, 127.5, 126.7 (C^6, C^8, C_6H_5); 106.8, 101.5 (C^1); 84.5, 82.0, 81.0, 79.9 (C^{2-5}); 6.5, 25.0 (C^7)

   Anal. Found: C, 64.10; H, 4.15. Calc.: C, 63.76; H, 4.06%. IR: 2018, 1925 (CO); 1600 (C=C)

6. $(\eta^5\text{-}C_5H_5)[\eta^5\text{-}C_5H_4(CH=CH_2)]Fe$

   ^1H NMR: 6.7–4.7 (vinyl pattern, 3H); 4.30 (bs, 2H, $H^{2,5}$ of C_5H_4); 4.20 (bs, 2H, $H^{3,4}$ of C_5H_4); 4.10 (s, 5H, C_5H_5)

   ^{13}C NMR: 134.9 (=*C*C_5H_4); 111.1 (=CH_2); 83.6 (C^1); 69.1 (C_5H_5); 68.8, 66.8 (C^{2-5} of C_5H_4)

   IR: 1635 (C=C)

7. $(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4[CH=CH(CH_3)]\}Fe$

   ^1H NMR: 5.0–6.4 (m, 2H, –*H*C=C*H*–); 4.0–4.4 (bs, 9H, C_5H_5 and C_5H_4); 1.77 (m, 3H, =C–CH_3)

   ^{13}C NMR: 127.9, 127.0 (=*C*C_5H_4); 123.7, 123.0 (=*C*(CH_3)H); 69.0 (C_5H_5); 68.2, 68.1, 66.1 (C^{2-5} of C_5H_4); 18.5, 14.9 (=*C*CH_3).

   IR: 1640 (C=C).

Table 5 (continued)

8. (η^5-C_5H_5)(η^5-C_5H_4[CH=CH(CH_2CH_3)])Fe

^{1}H NMR: 5.10–6.15 (m, 2H, –C*H*=C*H*–); 4.30 (m, 2H, $H^{2,5}$ of C_5H_4); 4.20 (m, 2H, $H^{3,4}$ of C_5H_4); 4.08 (s, 5H, C_5H_5); 1.90–2.50 (m, 2H, =C–CH_2–); 0.9–1.35 (m, 3H, –CH_2CH_3)

^{13}C NMR: 131.6, 130.1 (–*C*C_5H_4); 125.6, 125.3 (=*C*(CH)H); 69.1 (C_5H_5); 68.3, 68.2, 66.1 (C^{2-5} of C_5H_5); 29.5, 26.0, 22.3, 14.4, 14.0 (=C*C*H_2*C*H_3)

IR: 1640 (C=C)

9. (η^5-C_5H_5)(η^5-C_5H_4[CH=CH($CH_2CH_2CH_3$)])Fe

^{1}H NMR: 5.15–6.35 (m, 2H, –*H*C=C*H*–); 4.30 (m, 2H, $H^{2,5}$ of C_5H_4); 4.20 (m, 2H, $H^{3,4}$ of C_5H_4); 4.10 (s, 5H, C_5H_5); 1.80–2.50 (m, 2H, =CCH_2–); 1.75–1.10 (m, 2H, =C–CH_2–CH_2); 0.80–1.10 (m, 3H, –CH_3)

^{13}C NMR: 129.7, 128.1, 126.7, 125.6 (–*C*H=*C*H–); 69.1 (C_5H_5); 68.5, 68.2, 66.1 (C^{2-5} of C_5H_4); 35.0, 31.2, 29.8, 23.1, 22.8, 14.2, 13.8 (=C*C*H_2*C*H_2*C*H_3)

Anal. Found: C, 71.16; H, 7.31. Calc.: C, 70.89; H, 7.14%. IR: 1640 (C=C)

10. (η^5-C_5H_5)(η^5-C_5H_4[CH=CH(C(CH_3)$_2$H)])Fe

^{1}H NMR: 4.9–6.10 (m, 2H, –*H*C=C*H*–); 4.25 (m, 2H, $H^{2,5}$ of C_5H_4); 4.15 (m, 2H, $H^{3,4}$ of C_5H_4); 4.05 (s, 5H, C_5H_5); 2.4–3.10 (m, 1H, –C(CH_3)*H*); 1.00 (d, J = 8 Hz, 6H, –C(CH_3)H))

^{13}C NMR: 137.3, 128.9, 127.0, 123.3 (–*C*H=*C*H–); 82.3, 69.1, 68.5, 68.2, 66.4 (C_5H_5, C_5H_4); 31.5, 29.8, 27.9, 23.0, 22.4 (*C*H(*C*H_3)$_2$)

Anal. Found: C, 70.71; H, 7.41%. Calc.: C, 70.89; H, 7.14%. IR: 1640 (C=C)

11. (η^5-C_5H_5)(η^5-C_5H_4[CH=C(C_6H_5)H])Fe

^{1}H NMR: 7.29 (bs, 5H, Ph); 6.35, 6.75 (d for each, J = 2 Hz, 2H total, –*H*C=C*H*–); 4.45, 4.25, 4.15, 4.05 (m, m, s, s, respectively, C_5H_5 and C_5H_4)

^{13}C NMR: 138.4, 138.1, 129.0, 128.7, 128.4, 128.2, 127.3, 127.1, 126.9, 126.8, 126.3, 125.9 (C_6H_5, –*C*H=*C*H–); 83.4, 81.8, 69.7, 69.4, 69.3, 68.7, 67.1 (C_5H_5, C_5H_4)

IR: 1600, 1635 (C=C)

12. (η^5-C_5H_5)(η^5-C_5H_4[C(CH_3)=CH_2])Fe

^{1}H NMR: 5.00, 4.70 (bs, 2H, =CH_2); 4.25 (t, 2H, $H^{2,5}$ of C_5H_4); 4.05 (t, 2H, $H^{3,4}$, of C_5H_4); 3.95 (s, 5H, C_5H_5); 2.00 (bs, 3H, CH_3)

^{13}C NMR: 141.1, 108.7 (*C*H_2=*C*C_5H_4); 86.7, 69.9, 68.8, 66.0 (C_5H_5, C_5H_4); 21.2 (CH_3)

Anal. Found: C, 69.3; H, 6.52. Calc.: C, 69.06; H, 6.24%. IR: 1620 (C=C)

13. (η^5-C_5H_5)(η^5-C_5H_4[C(CH_3)=C(CH_3)H])Fe

^{1}H NMR: 5.03–5.89 (m, 1H, J = 6 Hz, =CH); 4.29 (m, 2H, $H^{2,5}$ of C_5H_4); 4.15 (m, 2H, $H^{3,4}$ of C_5H_4 obscured by 4.05 resonance); 4.05 (s, 5H, C_5H_5); 2.02 (t, 3H, J < 2 Hz, *Z*-isomer, C(CH_3)=C); 1.90 (bs, 3H, *E*-isomer, C (CH_3)=C); 1.68 (t, 3H, J = 6 Hz, some additional splitting of less than 2 Hz observed but unmeasurable, =CHCH_3)

^{13}C NMR: 128.9, 127.2, 121.0, 118.0 (C_5H_4*C*=*C*); 90.1, 86.2, 69.1, 68.5, 67.5, 65.1 (C_5H_5, C_5H_4); 30.0, 24.8, 15.1, 14.1 (CH_3); impurity at 132 ppm

Anal. Found: C, 70.58; H, 6.81. Calc.: C, 70.02; H, 6.72%. IR: 1630 (C=C)

14. (η^5-C_5H_5)(η^5-C_5H_4[C(CH_3)=C(CH_2CH_3)H])Fe

^{1}H NMR: 5.09–5.90 (m, 1H, J = 7 Hz, smaller splitting of less than 2 Hz observed, =CH); 4.30 (t, 2H, $H^{2,5}$ of C_5H_4); 4.15 (t, 2H, $H^{3,4}$ of C_5H_4); 4.09 (s, 5H, C_5H_5); 2.10 (m, 2H, J = 7 Hz, CH_2); 1.95 (s, 3H, =CCH_3); 0.99 (q, 3H, J = Hz, CH_2CH_3); isomers not identified from spectra

^{13}C NMR: 130.8, 130.5, 129.5, 128.8, 127.3, 126.1 (–*C*=*C*–); 90.0, 86.1 (C^{1}); 68.9, 68.2, 67.5, 65 (C_5H_5, C^{2-5} of C_5H_4); 24.8, 22.9, 21.5, 15.2, 14.8, 14.1 (alkanes)

Anal. Found: C, 71.35; H, 7.25%. Calc.: C, 70.89; H, 7.14%. IR: 1630 (C=C)

Table 5 (continued)

15. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4[C(CH_3)=C(CH_2CH_2CH_3)H])Fe$

^1H NMR: 4.92–5.70 (m, 1H, $J = 7$ Hz, smaller splitting of less than 2 Hz present, =CH); 4.19 (t, 2H, $H^{2,5}$ of C_5H_4); 4.04 (m, 2H, $H^{3,4}$ of C_5H_4); 3.99 (s, 5H, C_5H_5); 2.00 (m, 2H, $=CCH_2-$); 1.89 (s, 3H, $=CCH_3$); 1.05–1.65 (m, 2H, $J = 7$ Hz, $-CH_2CH_2CH_3$); 0.95 (t, 3H, $J = 7$ Hz, CH_2CH_3)

^{13}C NMR: 131.5, 130.9, 128.0, 124.5 ($-CH=CH-$); 90.0, 86.1 (C^1); 69.0, 68.2, 67.1, 65.1 (C_5H_5, C^{2-5} of C_5H_4); 31.5, 30.8, 29.9, 24.7, 23.8, 23.0, 15.6, 14.1, 13.9 (alkanes)

Anal. Found: C, 72.28; H, 7.94. Calc.: C, 71.66; H, 7.52%. IR: 1630 (C=C)

16. $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4[CH=C(CH_3)_2])Fe$

^1H NMR: 5.75–6.30 (bs, 1H, C=CH); 4.23, 4.15 (m, 4H, C_5H_4); 4.09 (s, C_5H_5, 5H), 1.78 (s, 6H, CH_3)

^{13}C NMR: 132.5 (C^8); 121.5 (C^6); 84.0 (C^1); 68.9 (C_5H_5); 68.5, 66.8 (C^{2-5} of C_5H_4); 27.0, 19.8 (CH_3)

17. $[(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)Fe]C(O)CH=CH_3](\eta^5\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Fe]$ (aldol product)

^1H NMR: 6.75 (bs, 1H, =CH); 4.85, 4.65, 4.51 (m, 8H, C_5H_4); 4.25, 4.21 (s, 10H, C_5H_5); 2.60 (d, 3H, $J < 2$ Hz, $-CH_3$)

^{13}C NMR: 117.9 ($-C=C-$); 86.3, 82.8 (C^1); 72.3, 71.9, 69.8, 69.1, 68.8, 68.7, 67.2 (C^{2-5} of the C_5H_4 and C_5H_5); 27.0, 18.0 (CH_3)

[a] NMR shifts are given in ppm relative to internal TMS. Infrared shifts are given in cm^{-1}. In some cases C=C stretching frequencies were not observed. Infrared data are provided for verification of the identity of the compounds. Elemental analysis is provided for new compounds only.

The E/Z isomer ratios of the alkene products were determined for the cymantrenylalkenes by examining the relative intensities of the alkene ^1H NMR resonances. In agreement with past studies [21], the ratio of E to Z alkenes was about 3:1 for the unstable ylides (alkyltriphenylphosphoranes) and 1:2 for the moderately stable ylide (benzyltriphenylphosphorane). Substitution of THF for benzene and lower reaction temperatures caused a reversal of the E to Z ratio when ethyltriphenylphosphorane and acetylcymantrene were reacted.

At the onset of this work, determination of the usefulness of substituting the Wittig process for the reduction/dehydration steps in the formation of cymantrenylalkenes was a major goal. The two-step process nets about a 70% yield

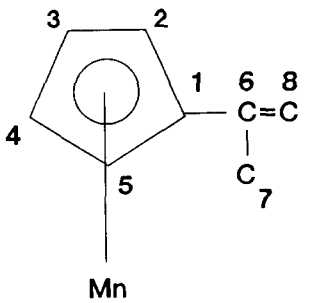

Fig. 1. Numbering scheme for ^{13}C NMR assignments. Designations for the cyclopentadienyl protons correlate with those of the carbons.

of vinylcymantrene. The Wittig route yields 70% of 2-cymantrenylpropene. While the Wittig route provides virtually no improvement in yields and may be somewhat more costly, it is much more efficient in terms of laboratory time.

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