Preparation and Utilisation of Organometallic Ylids containing the Tricarbonyliron Unit

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The reaction of tertiary phosphines, PR_3, with six- and seven-membered ring dienyl complexes of $Fe(CO)_3$ produces the corresponding phosphoniodiene salts. These salts undergo deprotonation on treatment with either $LiBu^n$ or NaH and undergo a subsequent reaction with aldehydes (R'CHO) to yield the appropriate olefinic complexes. With $[Fe(CO)_3(\eta\text{-}C_5H_5)][BPh_4]$, reaction with PR_3 produces simple substitution complexes of the type $[Fe(CO)_2(\eta\text{-}C_5H_5)(PR_3)][BPh_4]$. Treatment of $[Fe(CO)_3(C_8H_7CH_2OH)]$ with HPF_6 produces a salt of unknown structure which reacts with PPh_3 to produce tricarbonyl(triphenylphosphoniomethylcyclo-octatetraene)iron hexafluorophosphate. Reaction of this salt with $LiBu^n$ and HCHO yields tricarbonyl(vinylcyclo-octatetraene)iron.

THE reaction of aldehydes and ketones with phosphonium salts to produce olefins was developed in 1953 by Wittig and Geissler.[1] Since then the Wittig reaction has been widely used as a convenient high-yield synthesis of olefins, especially in the field of natural products.[2]

Recently, much interest has been centred on the use of organometallic species in the synthesis of organic compounds not readily available otherwise. We now report that treatment of carbonium ions co-ordinated to tricarbonyliron moieties with tertiary phosphines gives phosphonium salts,[3] which with strong bases such as $LiBu^n$ and sodium hydride are converted to unstable ylids. These ylids react with aldehydes but not ketones to produce the expected olefins in high yield.

RESULTS

1. *Cyclo-octatetraene Derivatives.*—Monosubstituted cyclo-octatetraene derivatives have been prepared by co-condensation of acetylene with a substituted acetylene using nickel acetylacetonate as a catalyst.[4,5] Recently, Harman and Streitweiser[6] have utilised the readily available bromo-cyclo-octatetraene to prepare a number of previously inaccessible monosubstituted cyclo-octatetraene derivatives. On complexation with tricarbonyliron, cyclo-octatetraene was shown[7] to have properties significantly different from the unco-ordinated molecule. For example, the species undergoes Vilsmeir formylation to produce tricarbonyl(formyl-cyclo-octatetraene)iron in good yield. Reduction of this compound with $Na[BH_4]$ gives tricarbonyl(hydroxymethyl-cyclo-octatetraene)iron, which on treatment with hexafluorophosphoric acid gives yellow crystals of hexafluorophosphate salt. Elemental analyses of this product corresponded to a carbonium ion formed by hydroxide loss from the alcohol. However, the precise structure of the salt remains unknown.

Triphenylphosphine reacts instantaneously with this salt in dichloromethane at room temperature to produce the red solid phosphonium salt $[Fe(CO)_3(C_8H_7CH_2PPh_3)][PF_6]$ (1) in almost quantitative yield. Addition of a solution of $LiBu^n$ to an ether suspension of this phosphonium salt at −78 °C under nitrogen gives rise to a deep red unstable solution. When formaldehyde is bubbled through this solution at room temperature, triphenylphosphine oxide is precipitated and $[Fe(CO)_3(C_8H_7CH{=}CH_2)]$ (2) can be isolated from the solution in 82% yield. This compound can also be prepared by the reaction of $[Fe(CO)_3(C_8H_7CHO)]$ with $CH_2{=}PPh_3$ and by dehydration of tricarbonyl(hydroxyethyl-cyclo-octatetraene)iron on silica gel.

Similarly, treatment of the deep red ether solution [presumably tricarbonyl(triphenylphosphoranylmethylenecyclo-octatetraene)iron] with benzaldehyde gives both *cis*- and *trans*-$[Fe(CO)_3(C_8H_7CH{=}CHPh)]$ (3a) and (3b). This reaction proceeds in higher yield in dichloromethane using sodium hydride as base. Separation of the *cis* and *trans* isomers was achieved by chromatography and a *cis* : *trans* ratio of 65 : 35 was found. In contrast, neither benzophenone nor cyclohexanone reacts with $[Fe(CO)_3(C_8H_7CH{=}PPh_3)]$ to produce the expected olefins.

Removal of the $Fe(CO)_3$ fragment from complex (1) was achieved by reaction with carbon monoxide (80 atm,† 80 °C, 20 h), in acetone solution. The pale yellow, crystalline complex (1) reacted rapidly at −20 °C with $LiBu^n$ in ether to give a deep red solution of the ylid $C_8H_7\bar{C}H{-}\overset{+}{P}Ph_3$. This solution reacted with benzophenone over 24 h at room temperature to give a 70% yield of 1-cyclo-octatetraenyl-2,2-diphenylethylene, $C_8H_7CH{=}CPh_2$, as a yellow oil. Similarly, treatment of an ether solution of the ylid with cyclohexanone gave after 30 min at room temperature a yellow solution from which (cyclohexylmethyl)cyclo-octatetraene, $C_8H_7CH_2C_6H_{11}$, was isolated in 30% yield.

Interestingly, when $C_8H_7\bar{C}H{-}\overset{+}{P}Ph_3$ was produced in dichloromethane solution using sodium hydride as base, no reaction was observed with either cyclohexanone or benzophenone even after refluxing for prolonged periods. However, benzaldehyde did react with the ylid in this solvent quite readily at room temperature to give a 90% yield of 1-cyclo-octatetraenyl-2-phenylethylene. The *cis* and *trans* isomers were separated chromatographically and the *cis* : *trans* ratio was virtually the same as that formed when the tricarbonyliron analogue was similarly treated.

2. *Five-, Six-, and Seven-membered Ring Diene Complexes.*—Previously, six- and seven-membered diene ring compounds containing exocyclic double bonds were prepared by dehydration of the product, obtained from the Reformatsky reaction on cyclohexadienone- and cycloheptadienone-tricarbonyl iron.[8]

Treatment of tricarbonyl(cycloheptadienyl)iron tetrafluoroborate with a variety of tertiary phosphines gives the

† Throughout this paper: 1 atm = 101 325 N m^{-2}.

Hydrogen-1 n.m.r. spectra of the new compounds [a]

	Compound	Peak position (τ)	Multiplicity	Protons
(1)	$[Fe(CO)_3(C_8H_7CH_2PPh_3)][PF_6]$	2.30	m	15
		4.70—5.20	m	7
		5.97	d, J(H–P) 14 Hz	2
	$[C_8H_7CH_2PPh_3][PF_6]$	2.30	m	15
		4.10—4.90	m	7
		6.08	d, J(H–P) 14 Hz	2
(2)	$[Fe(CO)_3(C_8H_7CH{=}CH_2)]$	3.82	1, M part of ABM system J(H–H) 10 and 16 Hz	1
		4.30—5.05	m	9
(3a)	*cis*-$[Fe(CO)_3(C_8H_7CH{=}CHPh)]$	2.78	s	5
		3.55	d, J(H–H) 12 Hz	1
		4.25	m	4
		4.98	t, J(H–H) 10 Hz	2
		5.30	d, J(H–H) 10 Hz	2
(3b)	*trans*-$[Fe(CO)_3(C_8H_7CH{=}CHPh)]$	2.70	m	5
		3.18	d, J(H–H) 16 Hz	1
		3.45	d, J(H–H) 16 Hz	1
		4.68	m	7
	cis-$C_8H_7CH{=}CHPh$	2.74	m	5
		3.59	d, J(H–H) 12 Hz	1
		3.93	d, J(H–H) 12 Hz	1
		4.15	m	7
	trans-$C_8H_7CH{=}CHPh$	2.72	m	5
		3.20	d, J(H–H) 17 Hz	1
		3.61	d, J(H–H) 17 Hz	1
		4.12	m	7
	$C_8H_7CH_2C_6H_{11}$	4.20	s	7
		4.40	s	1
		7.59	m	2
		7.90	m	2
		8.45	m	6
	$C_8H_7CH{=}CPh_2$	2.80	s	10
		3.43	s	1
		4.0—5.0	s	7
(4)	$[Fe(CO)_3(C_7H_9PMe_2Ph)][BF_4]$ [b]	2.09	m	5
		4.46	m	2
		6.55—7.20	m	3
		7.62	d, J(H–P) 14 Hz	6
		7.40—8.20	m	4
(5)	$[Fe(CO)_3(C_8H_7PMe_2Ph)][BF_4]$ [b]	2.10	m	5
		4.30	m	1
		4.60	m	1
		6.73	m	3
		7.74	d, J(H–P) 15 Hz	6
		7.60—8.30	m	2
(6)	$[Fe(CO)_3(C_7H_8{=}CHPh)]$ [c]	2.68	m	5
		3.54	s	1,3
		3.80	s	2,3
		4.56	m	2
		6.02	m	1
		6.72	m	1
		7.45—8.15	m	4
(7a)	$[Fe(CO)_3\{C_7H_8{=}CPhCr(CO)_3\}]$ [d]	4.01	s	1
		4.70	m	7
		6.25	m	1
		6.75	m	1
		7.45—8.60	m	4
(7b)	$[Fe(CO)_3\{C_7H_8{=}CPhCr(CO)_3\}]$ [e]	4.25	s	1
		4.57	m	7
		6.18	m	1
		6.67	m	1
		7.50—8.50	m	4
(8)	$[Fe(CO)_3(C_8H_8{=}CHPh)]$ [e]	2.89	m	5
		3.80	s	4,5
		4.18	s	1,5
		4.40—4.90	m	2
		5.80	d, J(H–H) 6 Hz	1,5
		6.19	d, J(H–H) 6 Hz	4,5
		6.60—6.90	m	1
		7.20—7.70	m	2
(9a)	$[Fe(CO)_3\{C_8H_8{=}CPhCr(CO)_3\}]$ [f]	4.65	m	8
		5.95	m	1
		6.56	m	1
		7.51	m	2

TABLE (*continued*)

Compound	Peak position (τ)	Multiplicity	Protons
(9b) $[Fe(CO)_3\{C_6H_6{=}CHPhCr(CO)_3\}]$ [g]	4.25	s	1
	4.70	m	7
	6.27	m	1
	6.66	m	1
	7.48	m	2
(10) $[Fe(CO)(C_5H_5)(PMe_2Ph)_2][BF_4]$ [h]	2.50—3.20	m	30
	5.65	t, J(H–P) 0.9 Hz	5
	8.65	m	12

[a] In $CDCl_3$ at 29.5 °C, unless otherwise stated. [b] In $[^2H_6]$acetone. [c] Mixture of isomers. [d] Isomer with m.p. 158—160 °C. [e] Isomer with m.p. 138—140 °C. [f] Isomer with m.p. 160—163 °C. [g] Isomer with m.p. 152—155 °C. [h] In CD_2Cl_2.

corresponding tricarbonyl(cyclohexadienyl)iron phosphonium salts.[3] Those used were triphenyl-, dibenzylphenyl-, dimethylphenyl-, and dimentholylphenyl-phosphine. Various attempts have been made to induce these phosphonium salts to undergo proton abstraction and subsequent Wittig reaction with a range of bases and aldehydes. Although proton abstraction occurred readily with sodium hydride in dichloromethane, the resulting ylids are, in general, extremely unstable and undergo decomposition in the presence of aldehydes or ketones rather than the Wittig reaction.

However, $[Fe(CO)_3(C_7H_9PMe_2Ph)][BF_4]$ (4) reacted with NaH and benzaldehyde in dichloromethane to give an 80% yield of $[Fe(CO)_3(C_7H_8{=}CHPh)]$ (6) as an inseparable mixture of geometric isomers in a ratio of about 1 : 2.

A parallel reaction occurred on treatment of the same phosphonium salt with (benzaldehyde)tricarbonylchromium and sodium hydride in dichloromethane under the same conditions. A 95% yield of $[Fe(CO)_3\{C_7H_8{=}CPhCr(CO)_3\}]$ (7) was obtained which could be separated into two geometric isomers in a ratio of about 2 : 3, although the exact identity of the isomers could not be established. Attempts to extend this reaction to ketones under the same conditions were not successful due to the extremely unstable nature of the ylid.

In contrast to its tricarbonyliron analogue, the salt dicarbonyl(dimethylphenylphosphine)(1-dimethylphenylphosphoniocyclohepta-2,4-diene)iron hexafluorophosphate did not undergo proton abstraction on treatment with sodium hydride in dichloromethane.

Treatment of a dichloromethane suspension of $[Fe(CO)_3(C_6H_7)][BF_4]$ with PMe_2Ph at room temperature gave an almost quantitative yield of $[Fe(CO)_3(C_6H_7PMe_2Ph)][BF_4]$ (5). Reaction of this salt with NaH and benzaldehyde in CH_2Cl_2 at low temperatures rapidly gave a 90% yield of $[Fe(CO)_3(C_6H_6{=}CHPh)]$ (8) as an inseparable mixture of geometric isomers in a ratio of 4 : 1. In a similar reaction (1-benzylidenecyclohepta-2,4-diene)tricarbonyliron was also prepared. The isomers of this species could be separated chromatographically in a ratio of 2 : 1, although a complete identification of the isomers was not possible. Again, however, attempts to extend the scope of this reaction by using ketones were precluded by the instability of the ylid.

Treatment of (8) (as a 4 : 1 mixture of isomers) with HPF_6 in ether gave a yellow precipitate of $[Fe(CO)_3(C_6H_7CH_2C_6H_5)][PF_6]$ in 90% yield. Dissolution of this salt in dimethyl sulphoxide (dmso) regenerated the original diene although the isomer ratio had changed from 4 : 1 to 3 : 2.

In contrast, the reaction of $[Fe(CO)_3(\eta\text{-}C_5H_5)][BPh_4]$ with excess PMe_2Ph in CH_2Cl_2 resulted in nucleophilic attack on the metal and formation of $[Fe(CO)(\eta\text{-}C_5H_5)(PMe_2Ph)_2][BPh_4]$ in 75% yield.

DISCUSSION

The use of the Wittig reaction in organometallic chemistry is not new, having been used successfully in preparing new derivatives of (benzene)dicarbonylchromium [9] and ferrocene,[10] among others. However, phosphonium ylids containing co-ordinated tricarbonyliron moieties are novel and the ease of formation of phosphonium salts by treatment of tricarbonyliron-stabilised carbonium ions with tertiary phosphines is in contrast to the severe conditions generally required in their synthesis.[11,12]

In contrast to the relatively stable ylids formed by proton abstraction from the phosphoniomethylcyclooctatetraene salts or their tricarbonyliron co-ordinated compounds, ylids formed on treatment of tricarbonyl(phosphoniocyclohexadiene)iron and tricarbonyl(phosphoniocycloheptadiene)iron salts with strong bases were so extremely unstable that the possibility of isolation was severely limited, but not necessarily their usefulness in solution. Under carefully controlled conditions the ylids from complexes (4) and (5) reacted with both benzaldehyde and (benzaldehyde)tricarbonylchromium to give high yields of the expected olefins.

Attempts to obtain the iron-free six- and seven-membered ring phosphonium salts by treatment of the tricarbonyliron compounds at high temperatures with high pressures of carbon monoxide were unsuccessful, thus precluding a comparison of their reactivities with their co-ordinated analogues.

Our efforts to prepare tricarbonyliron co-ordinated derivatives of the well known ylids, cyclopentadienylidenetriorganophosphorane,[12] failed. Treatment of $[Fe(CO)_3(\eta\text{-}C_5H_5)][BPh_4]$ with excess phosphine resulted in attack at the metal with expulsion of carbon monoxide rather than attack on the five-membered ring. This probably is a result of increased metal-to-ring back bonding in the five-membered ring compounds over the six- and seven-membered ring systems. This is also indicated by the increased carbonyl stretching frequencies in the five-membered ring compound.

EXPERIMENTAL

Tricarbonyl(cyclo-octatetraene)iron [13] and its derivatives [7] were prepared by published procedures, as were $[Fe(CO)_3(C_6H_7)][BF_4]$,[14] $[Fe(CO)_3(C_7H_9)][BF_4]$,[15] and $[Cr(CO)_3(C_6H_5CHO)]$.[16] Other chemicals were obtained from commercial sources. N.m.r. spectra were obtained either on a Varian

Associates 4A 100-MHz machine or a Perkin-Elmer R 12B 60-MHz machine, while a Perkin-Elmer 257 spectrometer was used to obtain i.r. spectra. Elemental analyses were carried out by the Microanalytical Department of the University of Cambridge.

Tricarbonyl(triphenylphosphoniomethylcyclo-octatetraene)-iron Hexafluorophosphate (1).—A portion of the yellow salt (1 mmol) obtained by protonation with HPF_6 of $[Fe(CO)_3(C_8H_7CH_2OH)]$ was suspended in CH_2Cl_2 (15 cm^3) at room temperature. A slight molar excess of PPh_3 was added with stirring. After 10 min, the red solution was filtered and a red oil was precipitated by the addition of pentane. The red oil was washed repeatedly with pentane and then subjected to reduced pressure on a vacuum line, whereupon it solidified (m.p. 80—82 °C). Yield, 96% (Found: C, 55.1; H, 4.0; P, 9.3. Calc. for $C_{30}H_{24}F_6FeO_2P_2$: C, 54.3; H, 3.6; P, 9.3%). I.r. ($CHCl_3$): 2 059, 2 000, and 1 989 cm^{-1}.

Triphenylphosphoniomethylcyclo-octatetraene Hexafluorophosphate.—Compound (1) (5 mmol) was dissolved in acetone (50 cm^3) and placed in a 100-cm^3 capacity autoclave. The solution was then heated to 80 °C under carbon monoxide (80 atm) for 20 h. After cooling and venting the excess gas, the almost colourless acetone solution was evaporated and the residue extracted with chloroform. After the addition of pentane, the off-white precipitate was recrystallised from methanol to give the *product* as pale yellow crystals (m.p. 193—195 °C). Yield, 85% (Found: C, 61.8; H, 4.7. Calc. for $C_{27}H_{24}F_6P_2$: C, 61.8; H, 4.6%).

Tricarbonyl(vinylcyclo-octatetraene)iron (2).—Compound (1) (1 mmol) was suspended in dry ether (40 cm^3) under nitrogen at −78 °C. A slight molar excess of 2.5 mol dm^{-3} LiBu in hexane was added and the mixture stirred at −78 °C for 1 h, during which time the phosphonium salt dissolved to give a deep red solution. After warming to room temperature, formaldehyde (generated externally by gentle heating of paraformaldehyde) was bubbled through the solution for 5 min. After filtration and evaporation of the ether solution, the residue was chromatographed on silica gel using pentane as eluant to give the *product* as a red oil. Yield, 82% [Found: *M* (mass spectrometry) 270; Calc. for $C_{13}H_{10}FeO_3$: *M* 270]. I.r. (pentane): 2 054, 1 997, and 1 981 cm^{-1}.

cis- *and* trans-*Tricarbonyl(styrylcyclo-octatetraene)iron* (3a) *and* (3b).—Compound (1) (1 mmol) was dissolved in dry CH_2Cl_2 (20 cm^3) under nitrogen. Sodium hydride (2 mmol) and benzaldehyde (2 mmol) were then added and the mixture was stirred at room temperature for 2 h. The mixture was then hydrolysed to destroy excess NaH and the organic layer was separated and dried ($Mg[SO_4]$). After evaporation of the dichloromethane, the residue was chromatographed in small quantities on thick-layer silica plates using pentane as eluant. Two bands separated. The first band gave *cis*-$[Fe(CO)_3(C_8H_7CH{=}CHPh)]$ (3a) as red crystals (m.p. 68—70 °C). Yield, 43% [Found: *M* (mass spectrometry) 346; C, 66.2; H, 4.2. Calc. for $C_{19}H_{14}FeO_3$: *M* 346; C, 65.9; H, 4.0%]. I.r. (CCl_4): 2 049, 1 990, and 1 973 cm^{-1}. The second band gave deep red crystals (m.p. 87—89 °C) of *trans*-$[Fe(CO)_3(C_8H_7CH{=}CHPh)]$ (3b). Yield, 23%. [Found: *M* (mass spectrometry) 346; C, 65.2; H, 4.1. Calc. for $C_{19}H_{14}FeO_3$: *M* 346; C, 65.9; H, 4.0%]. I.r. (CCl_4): 2 049, 1 991, and 1 973 cm^{-1}.

(Cyclohexylmethyl)cyclo-octatetraene.—Compound (1) (1 mmol) was suspended in dry ether (20 cm^3) at −20 °C under nitrogen. A slight molar excess of 2.5 mmol dm^{-3} LiBu^t in hexane was added and the mixture stirred for 20 min at −20 °C, during which time the salt dissolved giving a deep red solution. After warming to room temperature, a two-fold excess of cyclohexanone was added and the solution stirred for 30 min at this temperature, during which time the deep red colour of the ylid was discharged leaving a yellow solution containing suspended PPh_3O. After filtration, the other solution was evaporated and the residue chromatographed on silica gel. A yellow band was eluted with pentane, which on evaporation gave the *product* as a yellow oil. Yield, 30% [Found: *M* (mass spectrometry) 198. Calc. for $C_{15}H_{18}$: *M* 198].

(2,2-Diphenylethenyl)cyclo-octatetraene.—Compound (1) (1 mmol) was suspended in dry ether (20 cm^3) at −20 °C under nitrogen. A slight molar excess of 2.5 LiBu^t in hexane was added and the mixture stirred for 20 min at −20 °C. After warming to room temperature, a two-fold excess of benzophenone was added and the solution stirred at room temperature for 24 h. After filtration, the ether solution was evaporated and the residue chromatographed on silica gel, eluting with pentane. A yellow band gave the *product* as a yellow oil. Yield, 70% [Found: *M* (mass spectrometry) 282. Calc. for $C_{22}H_{18}$: *M* 282].

cis- *and* trans-*Styrylcyclo-octatetraene.*—These were prepared and isolated in an exactly analogous manner to their tricarbonyliron co-ordinated derivatives. The *cis* isomer was a yellow oil isolated in 58% yield [Found: *M* (mass spectrometry) 206. Calc. for $C_{16}H_{14}$: *M* 206]. The *trans* compound was a yellow solid (m.p. 43—45 °C) isolated in 32% yield (Found: *M* 206; C, 93.0; H, 6.9. Calc. for $C_{16}H_{14}$: *M* 206; C, 93.2; H, 6.8%).

Tricarbonyl(1-dimethylphenylphosphoniocyclohepta-2,4-diene)iron Tetrafluoroborate (4).—Tricarbonyl(cycloheptadienyl)iron tetrafluoroborate (1 mmol) was suspended in CH_2Cl_2 (20 cm^3) and treated at room temperature with a slight molar excess of PMe_2Ph with stirring. Immediate dissolution was observed. After filtration and washing repeatedly with ether, the *product* was dried under vacuum to give a pale yellow solid (m.p. 134—136 °C). Yield, 95% (Found: C, 47.2; H, 4.2. Calc. for $C_{18}H_{20}BF_4FeO_3P$: C, 46.2; H, 4.3%). I.r. (CH_2Cl_2); 2 055, 1 985br cm^{-1}.

Tricarbonyl(1-dimethylphenylphosphoniocyclohexa-2,4-diene)iron Tetrafluoroborate (5).—This was prepared and isolated in an analogous manner to the above seven-membered ring compound, as a pale yellow solid (m.p. 157—160 °C). Yield, 95% (Found: C, 46.5; H, 4.0. Calc. for $C_{17}H_{18}BF_4FeO_3P$: C, 46.3; H, 4.1%). I.r. ($CHCl_3$): 2 060, 1 989br cm^{-1}.

(1-Benzylidenecyclohepta-2,4-diene)tricarbonyliron (6).—Compound (4) (1 mmol) was dissolved in dry CH_2Cl_2 (20 cm^3) under nitrogen and the solution was cooled to −78 °C. Sodium hydride (2 mmol) and benzaldehyde (2 mmol) were then added and the cooling bath was removed. A rapid reaction occurred at about −20 °C. After hydrolysis, the organic layer was separated, dried ($Mg[SO_4]$), and evaporated. Chromatography of the residue on silica gel and elution with pentane gave the *product* as a yellow oil. Hydrogen-1 n.m.r. showed the isolated *product* to be a mixture of isomers in a ratio of 1 : 2. However, attempted chromatographic separation failed. Yield, 80% [Found: *M* (mass spectrometry) 322; C, 63.9; H, 4.6. Calc. for $C_{17}H_{14}FeO_3$: *M* 322; C, 63.3; H, 4.4%]. I.r. ($CHCl_3$): 2 042, 1 967, and 1 958 cm^{-1}.

Tricarbonyl[1-(tricarbonylchromiobenzylidene)cyclohepta-2,4-diene]iron (7).—This was prepared in an analogous manner

to compound (6), using $[Cr(CO)_3(C_6H_5CHO)]$ instead of benzaldehyde. Chromatography in small quantities on thick-layer silica plates, eluting with a benzene–pentane mixture, gave two bands. The first band gave orange crystals of one isomer of the *product* (m.p. 138—140 °C). Yield, 57% [Found: *M* (mass spectrometry) 458; C, 53.1, H, 3.5. Calc. for $C_{20}H_{14}CrFeO_6$: *M* 458; C, 52.3; H, 3.0%]. I.r. ($CHCl_3$): 2 045, 1 980, 1 966, and 1 890br cm^{-1}. The second band gave orange crystals of the other isomer of the *product* (m.p. 158—160 °C). Yield, 38% [Found: *M* (mass spectrometry) 458; C, 53.1; H, 3.4. Calc. for $C_{20}H_{14}FeCrO_6$: *M* 458; C, 52.3; H, 3.0%]. I.r. ($CHCl_3$): 2 045, 1 980, 1 966, and 1 890br cm^{-1}.

(*1-Benzylidenecyclohexa-2,4-diene*)*tricarbonyliron* (8).—Compound (5) (1 mmol) was dissolved in dry CH_2Cl_2 (20 cm^3) under nitrogen and the solution was cooled to −78 °C. Then sodium hydride (2 mmol) and benzaldehyde (2 mmol) were added and the mixture allowed to warm slowly to room temperature. A rapid reaction occurred at about −20 °C. After hydrolysis, the organic layer was separated, dried ($Mg[SO_4]$), and evaporated. The residue was chromatographed on silica gel, eluting with pentane. A yellow band gave a yellow solid (m.p. 77—84 °C) which was shown by ^1H n.m.r. to be a 4 : 1 mixture of isomers. Total yield, 90% [Found: *M* (mass spectrometry) 308; C, 64.7; H, 4.5. Calc. for $C_{16}H_{12}Fe_3O$: *M* 308; C, 62.0; H, 3.9%]. I.r. (CCl_4): 2 047, 1 984, and 1 971 cm^{-1}.

Tricarbonyl[*1-(tricarbonylchromiobenzylidene)cyclohexa-2,4-diene*]*iron* (9a) *and* (9b).—This was prepared in an entirely analogous manner to the previous compound, except that $[Cr(CO)_3(C_6H_5CHO)]$ was used instead of benzaldehyde. Chromatography, in small quantities, on thick-layer silica plates, eluting with a benzene–pentane mixture gave two isomers of the *product*. The first was an orange solid (m.p. 152—155 °C). Yield, 63% [Found: *M* (mass spectrometry) 444; C, 51.5; H, 3.0. Calc. for $C_{19}H_{12}CrFeO_6$: *M* 444; C, 51.4; H, 2.7%]. I.r. (CCl_4): 2 050, 1 983, 1 971, and 1 903 cm^{-1}. The second isomer was isolated as orange crystals (m.p. 160—163 °C). Yield, 26% [Found: *M* (mass spectrometry) 444; C, 51.6; H, 2.7. Calc. for $C_{19}H_{12}CrFeO_6$: *M* 444; C, 51.4; H, 2.7%]. I.r. (CCl_4): 2 050, 1 982, 1 970, and 1 904 cm^{-1}.

Carbonyl(*cyclopentadienyl*)*bis*(*dimethylphenylphosphine*)*iron*(II) *Tetraphenylborate* (10).—Tricarbonyl(cyclopentadienyl)iron tetraphenylborate (1 mmol) and PMe_2Ph (3 mmol) were refluxed together in CH_2Cl_2 (25 cm^3) for 39 min. After removal of the solvent, the residue was chromatographed on silica gel. A yellow band, eluted with an acetone–dichloromethane, gave yellow crystals of the *product*. Yield, 75%. I.r. (acetone): 1 958 cm^{-1}.

[1/032 *Received*, 9*th January*, 1981]

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