much stronger in the case of a highly polarized carbonyl group, and thus the magnesium–carbon bond will be substantially weakened. This in turn would assist in the hydride transfer from the β carbon due to the increase in electron density on the carbon bonded to magnesium.

Addition at C═O *vs.* C≡N.—Addition of organomagnesium reagents occurs exclusively at carbonyl in both the aroyl and acyl cyanide systems. The nitrile functions only as an activating group and does not compete in electrophilic addition. Similarly, carbonyl cyanide suffers initial attack by isopropylmagnesium bromide exclusively at the carbonyl group. In contrast, however, phenylmagnesium bromide attacks predominantly (and phenyllithium exclusively) at the cyano group. These results can be explained as follows. The carbonyl group is undoubtedly the more electrophilic site in **6**, and in the absence of other factors addition occurs at this site. The generation of intermediate IVb (see eq 2) also removes the charge repulsion interactions present in **6**. In the case of phenyl Grignard addition, however, the stabilization of intermediate III renders addition at the cyano group competitive with addition at carbonyl, and both products are formed. This type of stabilization would be expected to be more important in the case of the more ionic lithium intermediate (III where MgBr is replaced by Li), and hence addition at the cyano group occurs exclusively.

It is apparent that these explanations do not provide complete support for the results described; other factors must be operating in the transition state complexes. It is interesting to note, however, that a consistent pattern emerges with spectral, experimental, and calculated data in agreement to support what we consider *a priori* to be surprising results.

Registry No.—**1**, 613-90-1; **2a** 2,4-DNP, 1677-87-8; **2c** 2,4-DNP, 1733-62-6; **3**, 631-57-2; **5**, 15657-96-2; **6**, 1115-12-4; **7**, 15344-34-0; **8**, 32861-42-0; methylmagnesium chloride, 676-58-4; isopropylmagnesium bromide, 920-39-8.

Formation of 1,1′-Oligomeric Ferrocenes from Mixed Ullmann Reactions of Haloferrocenes

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A series of 1,1′-oligomeric ferrocenes, including biferrocene, 1,1′-terferrocene, 1,1′-quaterferrocene, 1,1′-quinqueferrocene, and 1,1′-sexiferrocene, have been formed from a mixed Ullmann reaction between a haloferrocene and 1,1′-diiodoferrocene. Conditions were varied as to the haloferrocene, the ratio of haloferrocene to 1,1′-diiodoferrocene, and the type of copper used in order to ascertain the maximum yields of each oligomer. Mass spectra of all the 1,1′-oligomeric ferrocenes have been obtained.

Considerable interest has been focused recently on the thermal and conductivity properties of oligomeric ferrocenes;[1–4] yet the chemistry of ferrocene oligomers larger than biferrocene is virtually unknown. In the last 11 years, biferrocene (**1**) has been synthesized in many ways.[4–12] The most useful of these methods has utilized the Ullmann reaction.[7,12] Iodoferrocene is an extremely reactive compound in the Ullmann reaction, since a 97% yield of biferrocene can be obtained at temperatures as low as 60°.[12]

Nesmeyanov and coworkers[13] first isolated 1,1′-terferrocene (**2**) when they conducted a mixed Ullmann reaction with bromoferrocene (**7**) and 1,1′-dibromoferrocene to give a 57% yield of biferrocene, a 14% yield of 1,1′-terferrocene (**2**), and other higher oligomeric ferrocenes which were not separated. 1,1′-Terferrocene (**2**) has also been synthesized in an unequivocal manner from cyclopentadienylferrocene by Rinehart and coworkers.[14] More recently, Watanabe, *et al.*,[15] have described the formation of the 1,1′-oligomeric ferrocenes from biferrocene (**1**) to sexiferrocene (**5**), resulting from the treatment of a mixture of mono- and 1,1′-dilithioferrocenes with cobalt chloride. The yields were low and a number of butylated products, resulting from the excess *n*-butyllithium being present, were also isolated.

Results and Discussion

Based on our earlier successful studies on the Ullmann coupling of haloferrocenes,[12] and also on current interest in oligomeric ferrocenes, we decided to investigate in some detail the formation of this series of organometallic compounds *via* the Ullmann route. The mixed Ullmann reaction (eq 1) between a haloferrocene and 1,1′-diiodoferrocene (**9**) has indeed been found to give higher yields of the 1,1′-oligomeric ferrocenes than have the previous methods.[1,13,15,16] A reaction time of

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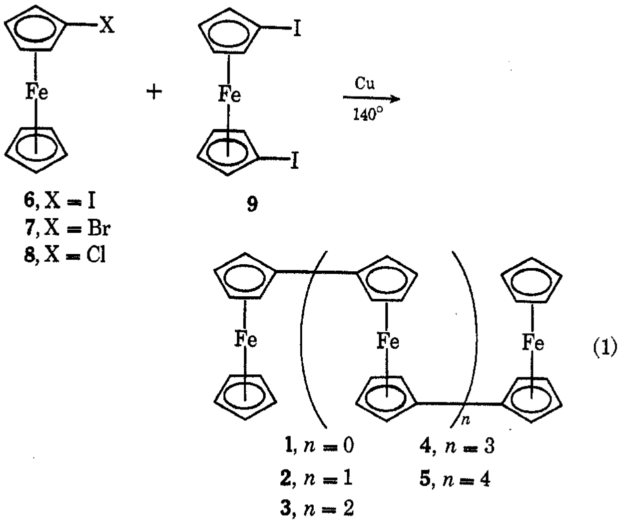
TABLE I

PERCENTAGE YIELDS[a] OF 1,1′-OLIGOMERIC FERROCENES

Run	$FeC_{10}H_9X$	Copper	Ratio[b]	**1**	**2**	**3**	**4**	**5**	Total
1	I	U. S.	2:1	37	10	2			49
2	I	U. S.	2:2	23	8	3	1		35
3	I[c]	U. S.	2:4	18	13	7	4	1	43
4	I	German	2:1	50	21	12	4	1	88
5	I	German	2:2	48	21	9	6	1	85
6	I	German	2:4	52	24	11	6	1	94
7	Br[c]	German	2:4	35	29	9	4	2	79
8	Cl	German	2:4	71	11	10	6	2	100

[a] Yields are based on the limiting reagent in each reaction. [b] This ratio represents the molar ratio of haloferrocene to 1,1′-diiodoferrocene used. [c] A duplicate run was made in this case, and the yields of all products were reproducible.



6, X = I
7, X = Br
8, X = Cl
9
1, $n = 0$
2, $n = 1$
3, $n = 2$
4, $n = 3$
5, $n = 4$

23 hr was used to ensure that total reaction between the haloferrocene and copper had taken place. The various oligomeric ferrocenes were separated by a combination of crystallization and chromatography on alumina.

As seen in Table I (runs 6–8), different product ratios were obtained depending on the haloferrocene used. These variations are undoubtedly related to the known gradation in reactivity of haloferrocenes under Ullmann conditions[12] and may possibly be accounted for as follows. Iodoferrocene (**6**), being very reactive in the Ullmann reaction, undergoes self-coupling (Scheme If) faster than mixed coupling (Scheme I a,b), thus giving the high yield of biferrocene (**1**). Bromoferrocene (**7**) evidently undergoes mixed coupling (Scheme Ia,b) more rapidly than does iodoferrocene (**6**), and thus the yields of the higher oligomers are slightly raised compared to the yield of biferrocene (**1**). Chloroferrocene (**8**), on the other hand, is known to be much less reactive than either bromoferrocene (**7**) or iodoferrocene (**6**) under Ullmann conditions. Self-coupling of 1,1′-diiodoferrocene (**9**) (Scheme Ic–e) evidently proceeds faster than mixed coupling (Scheme Ia,b). The remaining chloroferrocene (**8**) then undergoes self-coupling (Scheme If) to give a high yield of biferrocene (**1**).

SCHEME I[a]

$$\mathrm{FcX} + \mathrm{FcI_2} \longrightarrow \mathrm{Fc{-}Fcl{-}I} \qquad (a)$$

$$\mathrm{FcX} + \mathrm{I{-}Fcl{-}Fcl{-}I} \longrightarrow \mathrm{Fc{-}Fcl{-}Fcl{-}I} \qquad (b)$$

$$\mathrm{FclI_2} + \mathrm{FclI_2} \longrightarrow \mathrm{I{-}Fcl{-}Fcl{-}I} \qquad (c)$$

$$\mathrm{I{-}Fcl{-}Fcl{-}I} + \mathrm{FclI_2} \longrightarrow \mathrm{I{-}Fcl{-}Fcl{-}Fcl{-}I}, \text{ etc.} \qquad (d)$$

$$\mathrm{Fc{-}Fcl{-}I} + \mathrm{FclI_2} \longrightarrow \mathrm{Fc{-}Fcl{-}Fcl{-}I}, \text{ etc.} \qquad (e)$$

$$\mathrm{FcX} + \mathrm{FcX} \longrightarrow \mathrm{Fc{-}Fc} \qquad (f)$$

[a] Fc = ferrocenyl, $FeC_{10}H_9$; Fcl = 1,1′-ferrocenylene, $Fe(C_5H_4)_2$.

The copper powder used in the present studies was obtained from two different sources: the Schuchardt Co. (Germany) and the U. S. Bronze Powder Co., Inc. Table I shows that the overall percentage yields of the oligomers varies, depending on the source of copper used. The German copper was found superior to the U. S. copper in all Ullmann reactions attempted (compare runs 1–3 *vs.* runs 4–6), even though both powders had been activated in exactly the same manner.[17] An Ullmann reaction carried out on *o*-iodophenylferrocene gave, under identical conditions, 100% recovery of starting material with the U. S. copper and an 11% yield of 2,2′-diferrocenylbiphenyl with German copper. The difference in the reactivity of the two copper powders is not known at the present time. A variation in the molar ratio of monohaloferrocene to 1,1′-diiodoferrocene (**9**) did not significantly affect the product percentages when German copper was used (Table I). With the U. S. copper, however, there was a noticeable trend: as the ratio decreased the amount of higher oligomers increased. No 1,1′-biferrocenylene [bis(fulvalene)diiron] could be detected in these studies, even though it might have been an expected product on the basis of previous work.[1,18]

1,1′-Terferrocene (**2**) prepared in this study agrees in its properties with the 1,1′-terferrocene obtained by Motoyama, Watanabe, and Hata,[15] and its melting point indicates that the 1,1′-terferrocene reported by Nesmeyanov, *et al.*,[13] was perhaps slightly impure. The present 1,1′-terferrocene also showed the polymorphic properties reported by the Japanese workers.[15] The material of Rosenberg and Neuse[4] that melted at 224–226° can then also be assigned as 1,1′-terferrocene (**2**). The properties of the higher oligomers (**3**–**5**) obtained in our studies are in general agreement with those prepared by the Japanese workers.[15]

The mass spectra of the 1,1′-oligomeric ferrocenes are summarized in Table II. Each oligomer shows the expected parent ion peak as well as a doubly charged ion peak at $m/2e$, except in the case of 1,1′-sexiferrocene (**5**), where only the parent peak is observed. For 1,1′-quaterferrocene (**3**), a triply charged ion peak at $m/3e$ is observed. The mass spectrum of 1,1′-terferro-

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[17] A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Wiley, New York, N. Y., 1962, p 193.

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TABLE II

RELATIVE ABUNDANCE OF MASS SPECTRAL PEAKS OF 1,1′-OLIGOMERIC FERROCENES

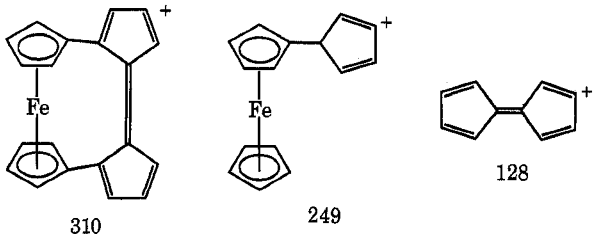
Peak, m/e	**1**	**2**	**3**	**4**	**5**
1106					2
922				6	7
738			61	12	4
554		100	5	1	5
489		10	29	5	2
461				2	
423		14	22	3	4
370	100	7	19	6	12
369	4	14	88	33	28
368	15	48	100	100	100
310		5	5	7	5
305	42	20	22	2	29
277		30	4		
249	6	8	4		8
246			6		
185	23				
184	6	5	6	90	15
128	4	5	4	7	19
121	27	17	9	4	28
56	20	7	6	15	30

cene (**2**) shows a metastable peak at m/e 431.6, which corresponds to a parent ion of m_1 554 and a daughter ion of m_2 489. This result indicates that a neutral fragment, cyclopentadienyl radical, is lost in the probe in a one-step process from the parent ion to form the daughter ion. No other metastable peaks were observed in the other spectra.

The fragmentation patterns of the 1,1′-oligomeric ferrocenes are very similar throughout the series and involve the loss of ferrocenyl units, cyclopentadienyl units, as well as iron and hydrogen atoms. Some plausible structures are given in Chart I for the fragments with their respective mass units. Of special interest is the fulvalene structure assigned to m/e 310. Such a structure is plausible for this ion and is in analogy with the formation of fulvalene in the fragmentation of ferrocene itself.[19] The 310 peak has almost the same relative abundance in the spectra of 1,1′-terferrocene to 1,1′-sexiferrocene, indicating that this substituted fulvalene is possibly a function of the 1,1′-oligomeric arrangement. Table III shows that the calculated values[20] and found values for the isotopic abundances of iron are in excellent agreement, and that the various 1,1′-oligomeric ferrocenes analyze well for the natural abundance distribution of iron and carbon.

CHART I

PROPOSED STRUCTURES FOR SOME IONS PRODUCED IN THE MASS SPECTRA OF 1,1′-OLIGOMERIC FERROCENES



Experimental Section

General.—Nmr spectra were recorded on a Varian A-60 spectrometer in 5–10% $CDCl_3$ solutions. Mass spectra were recorded either on an AEI MS-9 or a Hitachi RMU-6E mass spectrometer at 70 eV. The German copper used is Kupfer, KU300, Pulver mind. 99.75%; it was obtained from the Schuchardt Co., Munich, Germany. The U. S. copper used is Copper 4000, Lot 3767; it was obtained from the U. S. Bronze Powder Co., Inc., Flemington, N. J. Chloroferrocene,[21] bromoferrocene,[22] iodoferrocene,[10,23] and 1,1′-diiodoferrocene[24] were prepared by standard literature methods. The alumina of activity grade III used in this work was prepared by shaking 1 kg of neutral, activated CAMAG alumina (Alfa Inorganics) with 60 ml of water. All chromatographic columns were packed dry. The dimensions of the column were not considered important as long as the stated amount of alumina was used and the column was packed evenly. Melting points were taken on a Mel-Temp apparatus and are corrected. All microanalyses were carried out by Mr. Charles Meade of the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

1,1′-Oligomeric Ferrocenes.—A typical example (run 5) is given. In a 50-ml round-bottomed flask were melted 1.00 g (3.2 mmol) of iodoferrocene (**6**) and 1.41 g (3.2 mmol) of 1,1′-diiodoferrocene (**9**). Next was added 6.2 g (98 mmol) of activated German copper,[17] a glass stopper was inserted, and the mixture was shaken. The flask, flushed with nitrogen, was submerged in an oil bath to the depth of the bottom of the stopper, and the oil bath temperature was raised from 30 to 145° over 1.5 hr. The temperature was then maintained at 145° for an additional 21.5 hr. At the end of the heating period, the contents of the flask were extracted with benzene until the benzene extracts were colorless. The benzene was evaporated to yield substance A. The copper residue was further extracted with boiling toluene until the toluene extracts were colorless, and the toluene was evaporated to yield substance B. Finally, the copper residue was extracted with boiling bromobenzene, the extracts were allowed to cool, and the resulting precipitate was collected to give substance C.

Substance A was dissolved in 25 ml of benzene and 25 ml of hexane was added. A precipitate formed and was collected to yield 0.05 g of a yellow product. This product was crystallized from benzene and was identified as 1,1′-quinqueferrocene (**4**), mp (sealed under N_2) 262–264° dec (lit.[15] mp 240–245°).

Anal. Calcd for $C_{50}H_{42}Fe_5$: C, 65.13; H, 4.59; Fe, 30.28; mol wt, 922. Found: C, 64.90; H, 4.89; Fe, 30.2; mol wt, 922 (mass spectrometry).

The filtrate was placed on a column of 300 g of alumina (activity grade III) and the column was eluted with hexane to yield 0.01 g of ferrocene, mp 170–172°. Elution with hexane–benzene (8:2 by volume) gave 0.26 g of biferrocene (**1**), mp (sealed under N_2) 238–240° dec (lit.[12] mp 238–239°). *Anal.* Calcd: mol wt, 370. Found: mol wt, 370 (mass spectrometry).

The third band was eluted with hexane-benzene (6:4) to yield 0.18 g of a yellow material, which was crystallized from a mixture of hexane–benzene. This material was 1,1′-terferrocene (**2**): mp (sealed under N_2) 224–226° dec (lit.[15] 226.5–227.2° dec); nmr ($CDCl_3$) singlet at τ 6.04 [10 H, unsubstituted cyclopentadienyl ring protons), multiplet at 5.70–5.95 (16 H, α and β protons on the substituted rings).

Anal. Calcd for $C_{30}H_{26}Fe_3$: C, 65.03; H, 4.73; Fe, 30.24; mol wt, 554. Found: C, 65.10; H, 4.88; Fe, 30.2; mol wt, 554 (mass spectrometry).

The last band was eluted with benzene to give 0.09 g of a red-orange compound, which was crystallized from benzene to yield 1,1′-quaterferrocene (**3**), mp (sealed under N_2) 279–281° dec (lit.[15] mp 280°).

Anal. Calcd for $C_{40}H_{34}Fe_4$: C, 65.09; H, 4.64; Fe, 30.27; mol wt, 738. Found: C, 65.20; H, 4.92; Fe, 30.0; mol wt, 738 (mass spectrometry).

Substance B was purified in a manner similar to substance A to yield 0.02 g of biferrocene, 0.01 g of 1,1′-terferrocene, 0.01 g of 1,1′-quaterferrocene, and 0.01 g of 1,1′-quinqueferrocene.

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TABLE III

ISOTOPIC ABUNDANCES[a,b] FOR THE 1,1′-OLIGOMERIC FERROCENES

	1		2		3		4		5	
Peak	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
M + 4	0.0	0	0.2	0	0.5	1	1.1		1.4	2
M + 3	0.5	0	1.4	1	3.1	3	5.8	5	9.3	9
M + 2	4.2	4	9.0	9	15.4	16	23.2	24	31.5	32
M + 1	27.2	27	40.4	40	53.2	53	65.1	64	75.7	75
M	100.0	100	100.0	100	100.0	100	100.0	100	100.0	100
M − 1	3.1	4	7.2	8	12.8	14	19.6	20	27.3	28
M − 2	12.7	15	18.8	19	24.8	25	30.4	30	35.5	42
M − 3	0.1	0	0.4	0	1.2	1	2.4		4.2	5
M − 4	0.4	0	1.2	1	2.3	3	3.8		5.5	8

[a] All found isotopic abundances are the average of two or more spectra. [b] The isotopic abundances were calculated on a computer by an appropriate expansion of the expression, $(a + b + c + d)^m (e + f)^n$, where $a = 5.82\%$ natural abundance of ^{54}Fe, $b = 91.66\%$ ^{56}Fe, $c = 2.19\%$ ^{57}Fe, $d = 0.33\%$ ^{58}Fe, $e = 98.89\%$ ^{12}C, $f = 1.11\%$ ^{13}C, m = number of iron atoms, and n = number of carbon atoms. Hydrogen was disregarded since the natural abundance of deuterium is low (0.015%).

Substance C was extracted with boiling benzene until the extracts were colorless. The benzene was allowed to cool to yield 0.01 g of a yellow-brown material, 1,1′-sexiferrocene (**5**), mp (sealed under N_2) 270–272° dec (lit.[15] mp 252–256°).

Anal. Calcd for $C_{60}H_{50}Fe_6$: C, 65.15; H, 4.56; Fe, 30.29; mol wt, 1106. Found: C, 65.15; H, 4.63; Fe, 30.3; mol wt, 1106 (msss spectrometry).

The residue remaining after the benzene extraction of substance C was in turn extracted with toluene to give 0.01 g of a substance with the following analysis.

Anal. Found: C, 63.80, 63.20; H, 4.67, 5.05.

The total amounts and percentage yields of oligomeric ferrocenes from this reaction follow: biferrocene (**1**), 0.28 g (48%); 1,1′-terferrocene (**2**), 0.19 g (21%); 1,1′-quaterferrocene (**3**), 0.10 g (9%); 1,1′-quinqueferrocene (**4**), 0.06 g (6%); 1,1′-sexiferrocene (**5**), 0.01 g (1%). Yields of products from other runs are summarized in Table I.

Thin layer chromatography (tlc), using 6:4 hexane–benzene as eluent and silica gel as adsorbant, was very useful in identifying the oligomers. The approximate R_f values under these conditions are as follows: ferrocene 0.7, biferrocene (**1**) 0.5, 1,1′-terferrocene (**2**) 0.4, 1,1′-quaterferrocene (**3**) 0.3, and 1,1′-quinqueferrocene (**4**) 0.2. 1,1′-Sexiferrocene (**5**) was too insoluble for tlc studies. All oligomers after separation and purification were found to be pure by tlc.

2,2′-Diferrocenylbiphenyl.—In a Schlenk tube under nitrogen were placed 1.20 g (3.1 mmol) of *o*-iodophenylferrocene[25] and 5.5 g (86.5 mmol) of activated German copper.[16] This mixture was heated at 147° in an oil bath for 22 hr. The reaction mixture was then extracted with ethyl ether and the ether evaporated. The residue was dissolved in hexane and placed on a column of 75 g of alumina. The first band was eluted with an 8:2 mixture of hexane–benzene. An nmr spectrum of the material indicated it to be a mixture of starting material and phenylferrocene. The second band was eluted with 1:1 hexane–benzene. Crystallization from hexane yielded 0.09 g (11%) of 2,2′-diferrocenylbiphenyl: mp 172.5–174°; nmr ($CDCl_3$) apparent singlet at τ 5.99 (18 H, ferrocenyl protons), multiplet at 2.6–3.2 (6 H, protons meta and para to the ferrocenyl group), multiplet at 2.1–2.4 (2 H, protons ortho to the ferrocenyl group).[26]

Anal. Calcd for $C_{32}H_{26}Fe_2$: C, 73.59; H, 5.02. Found: C, 73.40; H, 5.18.

In a similar run with the U. S. copper, no 2,2′-diferrocenylbiphenyl was obtained.

Registry No.—**1**, 1287-38-3; **2**, 1273-59-2; **3**, 1299-15-6; **4**, 1299-19-0; **5**, 1299-20-3; 2,2′-diferrocenylbiphenyl, 12597-74-9.

Acknowledgments.—The authors are grateful to the donors to the Petroleum Research Fund, administered by the American Chemical Society, for a grant in support of this research program. They also wish to thank Drs. A. Siegel and D. Hunt for assistance in obtaining the mass spectra, Dr. D. Garrett for writing the computer program, and the U. S. Bronze Powder Co. for a gift of the copper powder.

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