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Reductive coupling of ferrocenyl arones by low-valent titanium reagents. Synthesis and characterization of some 1,2-diferrocenylethenes and 1,2-diferrocenylethanes

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Abstract

Ferrocenyl arones react with low-valent titanium reagents ($TiCl_4/Zn$/pyridine and $TiCl_4/LiAlH_4/Bu_3N$) to give 1,2-diferrocenyl-1,2-diarylethenes (**1**) and 1,2-diferrocenyl-1,2-diarylethanes (**2**) albeit in low yields. Mass spectra in combination with ^1H and ^{13}C NMR spectra prove the correctness of the proposed structures. The configuration of compounds **1** is *E*, that of **2** is *meso* (achiral). Proton chemical shifts of the cyclopentadienyl units, interpreted in terms of diamagnetic shielding exercised by the *cis*-positioned phenyl rings, allow us to infer the preferred conformations. In **1** the cyclopentadienyl and phenyl rings are approximately perpendicular to the plane of the ethylene group. In **2** the conformation is staggered with the Cp–Fe–Cp axis approximately parallel to the HC–aryl bond. A tentative assignment of ^{13}C chemical shifts is given.

Introduction

Three recent reviews [1–3] show that low-valent titanium species, generated *in situ* by reduction of $TiCl_4$ or $TiCl_3$ using suitable reducing agents, are widely used in organic synthesis, particularly to couple ketones and aldehydes to olefins. In contrast, the coupling is less often employed with organometallic carbonyl compounds. We wish to present here the results of coupling reactions of eight ferrocenyl arones (**3**) with $TiCl_4/LiAlH_4/Bu_3N$ and $TiCl_4$/Zn/pyridine systems [4, 5] (Fig. 1).

To the best of our knowledge the only other examples in this field are the coupling of formylferrocene, acetylferrocene [6] and 1-ethyl-1′-acetylferrocene [7]. In addition, some ferrocenophane derivatives have also been prepared by this coupling [8].

Results and discussion

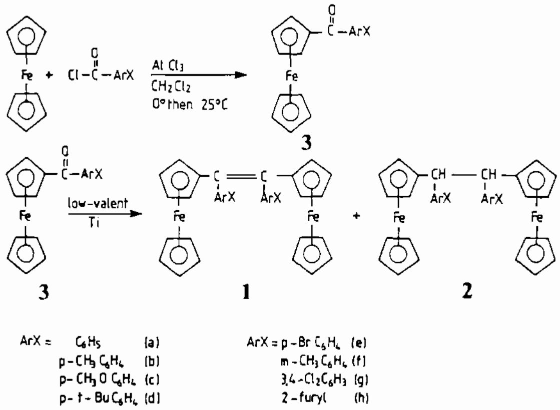

Fig. 1. Reaction scheme.

The ferrocenyl arones (**3**) to be coupled were readily prepared by reaction of ferrocene with aromatic acid chlorides as described [9]. Results are collected in Table 1. The MS, IR and IR spectra of the arones **3** are compatible with literature data [10–13].

The reductive coupling of the arones **3** was achieved by low-valent titanium species, generated by reduction of $TiCl_4$ using zinc dust or $LiAlH_4$. The major products are 1,2-diferrocenyl-1,2-diarylethenes (**1**) and 1,2-diferrocenyl-1,2-diarylethanes (**2**). Table 2 shows some experimental details, while three general comments may be given. First, Br and Cl substituents on the phenyl ring remain unaffected under the

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TABLE 1. Physical and spectral data for some ferrocenylarones, $C_5H_5FeC_5H_4COArX$ (**3**)

ArX	Colour	Yield (%)	Melting point (°C)	Mass spectroscopy		For C–O		For C_5H_5		Reference
				$[M]^+(m/z)$	Relative intensity	IR (cm^{-1})	^{13}C NMR	^1H NMR	^{13}C NMR	
C_6H_5	dark red	70	108–109	290	100	1624	198.66	4.17	70.06	11
p-$CH_3C_6H_4$	dark red	59	127–128	304	100	1636	198.30	4.16	70.12	12
p-$CH_3OC_6H_4$	blood red	30	78–80	320	100	1624	196.83	4.14	70.06	11
p-t-BuC_6H_4	dark red	45	124–126	346	100	1630	198.54	4.22	70.18	this work
p-BrC_6H_4	red–brown	37	116–118	368	100	1638	197.99	4.19	70.30	this work
m-$CH_3C_6H_4$	dark red	26	69–71	304	100	1637	198.17	4.11	69.94	12
3,4-$Cl_2C_6H_3$	red	50	143–145	358	100	1635	196.35	4.21	70.36	this work
2-Furyl	red	47	81–83	280	100	1637	184.53	4.16	70.06	12

TABLE 2. Synthetic details of products isolated after reductive coupling[a] of arones **3**

ArX	Reflux time (h)	Product	Colour	Melting point (°C)	Yield (%)
C_6H_5[b]	17	**1a**	red–brown	276–277[c] (dec.)	23
p-$CH_3C_6H_4$	20	**1b**	red	245 (dec.)	10
		2b	yellow	233 (dec.)	18
p-$CH_3OC_6H_4$	37	**2c**	yellow	188	15
p-tert-BuC_6H_4	24	**2d**	light yellow	271–273	16
p-BrC_6H_4	24	**2e**	orange	206 (dec.)	8
m-$CH_3C_6H_4$	37	**1f**	orange	250 (dec.)	7
		2f	yellow	200–202 (dec.)	16
3,4-$Cl_2C_6H_3$	24	**1g**	red	220 (dec.)	8
2-Furyl	18	**1h**	orange	216–218	17

[a] Coupled using $TiCl_4$/Zn/pyridine, unless stated otherwise. [b] Coupled using $TiCl_4/LiAlH_4/Bu_3N$. [c] 275–280 °C (ref. 14).

experimental conditions, as was also observed by others [14] in titanium-mediated couplings of purely organic ketones. Second, 1,2-diferrocenyl-1,2-diarylethenes (**1**) and 1,2-diferrocenyl-1,2-diarylethanes (**2**) show severe steric crowding, particularly in the central part of the molecule. This crowding causes the coupling to proceed with low yields and also causes the occurrence of ethanes **2** next to ethenes **1**. These observations are again parallel to previous results with purely organic compounds [6, 15]. Third, if the Ti-mediated reductive coupling and the Zn/Hg-mediated reductive coupling (abnormal Clemmensen reduction) follow mechanistically similar pathways, then the ethenes **1** will have the *E* configuration and the ethanes **2** the achiral, *meso* configuration [16]. These assignments are supported by comparing the melting points (Table 2) with those of similar compounds of known configuration [17].

Despite the low yields the titanium mediated coupling provides a reasonable alternative to the Clemmensen reductive coupling [17], which also leads to low yields of **1** and **2**, as well as to more complex reaction mixtures. The structure of the products (Table 2) was confirmed by IR, MS, ^1H and ^{13}C NMR spectra. IR spectra showed absorptions at 1104–1107 and 999–1003 cm^{-1}, attributed [11, 16] to unsubstituted cyclopentadienyl rings and ferrocenyl moieties, respectively, as well as the disappearance of the carbonyl absorption, which occurs in the arones **3** at 1630±5 cm^1. Electron impact (70 eV) mass spectral data are collected in Table 3. The ethene derivatives **1**, all exhibit intense molecular ions, while often a double charged *M* ion is also seen. Fragment peaks include $[M-C_5H_5]$, $[M-Fe(C_5H_5)_2]$, $[Fe(C_5H_5)]$ and [Fe] ions, so characteristic of ferrocene structures. In compound **1g** we observed isotopic molecular ion peaks at $m/z = 684$, 686, 688 and 690 with an intensity ratio 8:10:5:1, showing the presence of four chlorine atoms in the molecule and proving that during the coupling the chlorine substituents on the phenyl ring remain unaffected. The molecular ion of the ethane derivatives **2** does not show itself or is very weak. In contrast, a strong signal (base peak) occurs at half the molecular weight. The lability of M^+ and an easy fragmentation into 1/2 M^+ species is a well known phenomenon with tetra-arylethanes. Further fragmentation leads again to $[FeC_5H_5]^+$ and Fe^+ ions.

TABLE 3. M/z Values and relative abundances (% of base peak) in parentheses of major fragments of coupled ethene derivatives **1** and ethane derivatives **2**. Electron impact spectra at 70 eV

ArX		M^+	$M^+/2$	$M-C_5H_5$	$M-FeCp_2$	C_5H_5Fe	Fe	Other ions
C_6H_5	**1a**	548(100)		483(19)	362(33)			
p-$CH_3C_6H_4$	**1b**	576(63)		511(8)	390(25)	121(24)	56(3)	153(14)
m-$CH_3C_6H_4$	**1f**	576(100)	288(16)	511(19)	390(25)	121(4)		
3,4-$Cl_2C_6H_3$	**1g**	684(79)	342(20)	619(5)		121(18)	56(7)	493(14) $M-FeCl_2Cp$; 428(30)$M-FeCp_2$-2HCl; 186(31) $FeCp_2$
2-Furyl	**1h**	528(100)	264(10)		342(9)	121(7)	56(4)	
ArX		M^+	$M^+/2$	C_5H_5Fe	Fe	Other ions		
p-$CH_3C_6H_4$	**2b**	578(4)	289(100)	121(25)	56(3)	168(10) $1/2M-FeCp$; 153(18)"168"-CH_3		
p-$CH_3OC_6H_4$	**2c**	610(14)	305(100)	121(3)	56(10)	290(11) $1/2M-CH_3$; 196(23) $M-CH_3OPh$-H; 184(50) $1/2M-FeCp$		
p-tert-BuC_6H_4	**2d**	662(4)	331(100)	121(3)				
p-BrC_6H_4	**2e**	706[a]						
m-$CH_3C_6H_4$	**2f**		289(100)	121(18)	56(7)			

[a] FAB spectrum.

Since the electron impact spectrum of **2e** failed to show the molecular ion, its FAB spectrum was recorded, showing isotopic M peaks at $m/z = 706$, 708 and 710 with an approximate intensity ratio 1:2:1. It proves the presence of two bromine atoms in **2e**. Hence the bromine substituent on phenyl is left unaffected during the coupling reaction.

NMR data are presented in Tables 4 and 5. Because of poor solubility in $CDCl_3$ some ^{13}C NMR signals of the ethenes **2** were too weak to be detected. In the ethene derivatives **1** the ten protons of the unsubstituted cyclopentadienyl rings give rise to an apparent singlet at $\delta = 4.07 \pm 0.1$ ppm, while the eight protons of the substituted cyclopentadienyl rings appear as two well resolved triplets at $\delta = 4.01 \pm 0.1$ and $\delta = 3.10 \pm 0.1$ ppm. They can be described as A_2X_2 patterns. Compared to the protons in ferrocene ($\delta = 4.00$–4.04 ppm) [13] the α-protons of the substituted cyclopentadienyl rings in derivatives **1** resonate ($\delta = 3.10$ ppm) at higher field. The upfield shift is ascribed to the diamagnetic anisotropic shielding exercised by the phenyl rings in *cis*-position to the ferrocenyl units. The exclusion of other potential causes follows from the observation [18] that the NMR spectra of vinylferrocene, 1-ferrocenyl-1-phenylethene and *trans*-1-ferrocenyl-2-phenyl-ethene all exhibit two apparent triplets downfield from the C_5H_5 resonance peak. The ferrocenyl moiety in turn affects the phenyl protons. The effect, however, is rather deshielding, because all phenyl protons and even the methyl protons resonate at higher chemical shifts than calculated from standard substituent increments [19, 20]. The phenomenon can be rationalized if the phenyl and cyclopentadienyl rings in **1** are more or less perpendicular to the plane of the ethylene group (see Fig. 3). This is corrobated by the conformations observed in X-ray analyses of E-1,2-bis(1'-ethyl-1-ferrocenyl)-1,2-dimethylene [7] and tetraphenylethene [21]. The ^1H NMR spectrum of E-1,2-diferrocenyl-1,2-di(2'-furyl)ethene (**1h**) can be explained in a similar way.

In the ethane derivatives **2** the ten protons of the unsubstituted cyclopentadienyl rings exhibit an apparent singlet at $\delta = 3.7 \pm 0.1$ ppm, while the eight protons of the substituted cyclopentadienyl together with the two protons of the central CH give rise to a multiplet centered around 3.9 ± 0.1 ppm. Thus, all cyclopentadienyl protons in **2** resonate upfield compared to ferrocene, but now the unsubstituted cyclopentadienyl ring protons have the lowest chemical shift. In other words, the unsubstituted cyclopentadienyl protons are more shielded than the protons of the substituted cyclopentadienyl. Such a behaviour is compatible with the conformation shown in Fig. 4.

TABLE 4. ^1H chemical shifts (ppm, relative to TMS) of coupled products in $CDCl_3$ solution (see Fig. 2 for numbering)

ArX	Product	C_5H_5	C_5H_4	Aryl ring	Other protons
C_6H_5	**1a**	4.05(s,10H)	3.97(t,4Hβ); 3.14(t,4Hα)	7.17–7.51(m,10H)	
p-$CH_3C_6H_4$	**1b**	4.07(s,10H)	4.00(t,4Hβ); 3.12(t,4Hα)	7.34(m,8H)	2.54(CH_3)
m-$CH_3C_6H_4$	**1f**	4.10(m)	4.10(m)	7.31(m,8H)	2.53(CH_3)
3,4-$Cl_2C_6H_3$	**1g**	4.04(s,10H)	3.95(t,4Hβ); 3.22(t,4Hα)	7.72(s,2H(2)); 7.62(d,2H(6)); 7.32(d,2H(5))	
2-Furyl	**1h**	4.18(s,10H)	3.98(t,4Hβ); 3.64(t,4Hα)	7.60(m,2H(5)); 6.50(m,2H(3) + 2H(4))	
p-$CH_3C_6H_4$	**2b**	3.68(s,10H)	~3.84(m; 4Hα + 4Hβ + 2HCsp^3)	7.0–7.2(m,8H)	2.32(CH_3)
p-$CH_3OC_6H_4$	**2c**	3.72(s,10H)	~3.80(m; 4Hα + 4Hβ + 2HCsp^3)	7.04(d,4H(2)); 6.82(d,4H(3))	3.80(OCH_3)
p-tert-BuC_6H_4	**2d**	3.67(s,10H)	~3.88(m, 4Hα + 4Hβ + 2HCsp^3)	7.27(d,4H(2)); 7.07(d,4H(3))	1.36($C(CH_3)_3$)
p-BrC_6H_4	**2e**	3.73(s,10H)	~3.97(m; 4Hα + 4Hβ + 2HCsp^3)	7.44(d,4H(3)); 7.02(d,4H(2))	
m-$CH_3C_6H_4$	**2f**	3.70(s,10H)	~3.85(m; 4Hα + 4Hβ + 2HCsp^3)	7.12(m,8H)	2.35(CH_3)

TABLE 5. ^{13}C chemical shifts (ppm, relative to TMS) of coupled products in $CDCl_3$ solution (see Fig. 2 for numbering)

ArX	Product	C_5H_5	C_5H_4			Aryl ring						Other carbons
			i	α	β	C1	C2	C3	C4	C5	C6	
C_6H_5	**1a**	69.3	70.1	69.5	68.5	134.9	130.3	128.5	127.0			87.2(Csp^2)
p-$CH_3C_6H_4$	**1b**	69.4	n.o.[a]	69.6	68.5	n.o.	130.1	129.2	136.5			21.4(CH_3)
3,4-$Cl_2C_6H_3$	**1g**	69.3	n.o.	69.5	68.5	131.5	132.1	133.4	132.7	130.6	129.3	85.7(Csp^2)
2-Furyl	**1h**	69.6	70.7	68.8	68.5	–	151.1	109.1	111.1	140.8		85.4(Csp^2)
p-$CH_3C_6H_4$	**2b**	68.3	69.2	67.9	67.1	140.6	128.1	129.3	135.4			54.6(Csp^3); 21.1(CH_3)
p-$CH_3OC_6H_4$	**2c**	68.3	69.2	67.9	66.5	135.9	130.4	112.8	157.9			55.2(Csp^3); 25.7(OCH_3)
p-tert-BuC_6H_4	**2d**	68.3	69.3	67.0	66.2	140.9	129.0	124.2	148.8			54.2(Csp^3); 34.4(C), 31.5(CH_3)
p-BrC_6H_4	**2e**	68.4	69.9	68.9	67.4	142.3	130.7	131.0	120.1			54.7(Csp^3)
m-$CH_3C_6H_4$	**2f**	68.3	69.6	67.8	67.1	143.7	127.6	136.7	126.6	127.0	126.2	54.7(Csp^3); 21.5(CH_3)

[a] n.o. = not observed.

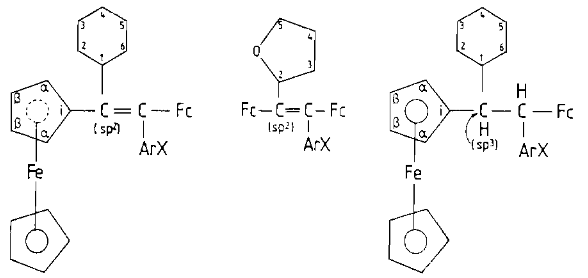

Fig. 2. Numbering of atoms. Fc signifies $C_5H_5FeC_5H_4$. Ar is aryl, and X a substituent.

The ^{13}C NMR data are collected in Table 5. To the best of our knowledge no ^{13}C chemical shifts of diferrocenylethenes nor diferrocenylethanes have been reported before. The assignments must be considered tentative, because they are only only based on general rules concerning signal intensities [22] and additivity of standard substituent increments [19]. Furthermore the influence of the complex substituents (Fc)C = C(Fc)aryl and (Fc)CH–CH(Fc)aryl on a phenyl ring is assumed comparable to the influence of $-CH=CH_2$ and $-CH_2-CH_3$ groups, respectively. Nevertheless, the procedure gives satisfactory agreement between observed and calculated

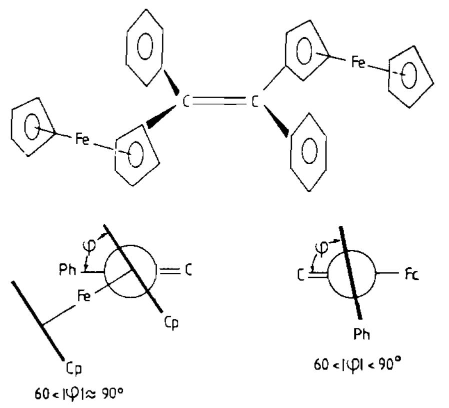

Fig. 3. Proposed conformation of 1,2-diferrocenyl-1,2-diphenylethenes. The group $C_5H_5FeC_5H_4$ is abbreviated as Fc, cyclopentadienyl as Cp, phenyl as Ph.

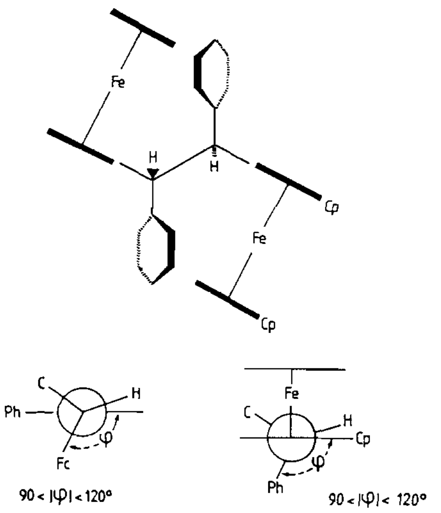

Fig. 4. Proposed conformation of 1,2-diferrocenyl-1,2-diphenylethanes. The group $C_5H_5FeC_5H_4$ is abbreviated as Fc, cyclopentadienyl as Cp, phenyl as Ph.

shifts of the aryl carbons. The ten equivalent carbon atoms of the unsubstituted cyclopentadienyl rings are expected to give the most intense signal in the 60–80 ppm range, and the atoms C(i) of the substituted cyclopentadienyl are expected to give the least intense signal. The assignment of the medium intense signals to C(α) and C(β) of the substituted cyclopentadienyl ring is based on the expectation that the substituents on the phenyl rings cause a larger effect on C(α) than on C(β), in other words that the range of shift values observed for C(α) would be larger than the range observed for C(β). The same way of reasoning is used by Gronowitz *et al.* [23] in their assignment of aryl substituted ferrocenes and by Nesmeyanov *et al.* [24] in their analysis of phenylferrocene.

The signals of CH_3, OCH_3, $C(CH_3)_3$ as well as of –CH–CH– are all found near their expected shift values [19]. This leaves in the ethenes **1** only the signal near $\delta = 85$ ppm for the central olefinic carbon atoms.

Experimental

Commercial reagents (Janssen Chimica) were used without further purification. Tetrahydrofuran was dried on sodium sand and distilled from $LiAlH_4$ prior to use. Nitrogen gas protection was employed during the coupling procedure. Ferrocenyl arones, FcCOAr (**3**) were synthesized as described by Reeves [9]. IR spectra were recorded on a Nicolet 5DxB infrared spectrophotometer using a diffuse reflectance cell (DRIFT Cell, Spectra Tech.) with KBr as background. Proton and carbon nuclear magnetic resonance spectra were obtained on a Jeol NMR PS-100 and a Jeol NMR FX100 spectrometer, respectively. $CDCl_3$ was used as solvent and TMS as internal standard.

Mass spectra were measured on a Jeol OI-SG-II with an electron impact source (70 eV) and direct probe inlet. The FAB spectrum of **2e** was recorded on a VG 70-SEQ hybrid mass spectrometer using glycerol as matrix.

Coupling procedure

Method A with $TiCl_4/LiAlH_4/Bu_3N$

Into a solution of 9.49 g (50 mmol) $TiCl_4$ in 200 ml THF with ice cooling and stirring was added powdered 0.97 g (26 mmol) $LiAlH_4$ in small portions under N_2. A black slurry was formed immediately during the addition. The mixture was warmed to room temperature and then heated to reflux for 2 h while stirring. A 50 ml THF solution of 2.9 g (10 mmol) benzoylferrocene and 1.85 g (10 mmol) tributylamine was added dropwise to the black slurry at room temperature, and then refluxed for 17 h. After being cooled, the reaction was quenched by adding 150 ml of 20% K_2CO_3 aqueous solution and filtered. The filtrate was extracted wth 3×50 ml CH_2Cl_2. The combined organic extracts were washed with 2×50 ml water and dried over anhydrous $MgSO_4$. Filtration and concentration gave a reddish brown solid which was recrystallized from heptane, yielding 0.62 g (23%) 1,2-diphenyl-1,2-diferrocenylethene.

Method B with $TiCl_4/Zn/pyridine$

Under N_2 protection, while stirring and cooling with ice, 14.2 g (75 mmol) $TiCl_4$ was dropped into 250 ml THF. Then 10 g (150 mg-atom) zinc dust was added in small portions and the gray mixture formed was refluxed for 2 h. During this time it became black due to the formation of low-valent titanium species. After cooling to room temperature 5 ml pyridine and 20 ml THF solution containing 1.52 g (5 mmol) *p*-methylbenzoyl-ferrocene was added and refluxed for 20 h while stirring. The mixture was cooled to room temperature, 150 ml of a 10% K_2CO_3 solution was added, and then it was extracted with 5×50 ml pentane. The combined organic extracts were washed with 2×50 ml water, dried over $MgSO_4$, filtered and concentrated. Red crystals (0.149 g, 10%) of 1,2-di-(*p*-methylphenyl)-1,2-diferrocenylethene (**1b**) were obtained. From the residue 0.26 g (18%) 1,2-di-(*p*-methylphenyl)-1,2-diferrocenylethane (**2b**) was isolated by column chromatography (length column 40 cm; width 3 cm) on silica gel (Merck 60; 0.063–0.200 mm) using pentane as eluens.

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