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Note

Catalytic addition of ferrocenyl ketones to olefins with the aid of $Ru(H)_2(CO)(PPh_3)_3$

Hongguang Du [a,*], Qun Liu [b], Shujian Shi [a], Shiwei Zhang [b]

[a] *Department of Applied Chemistry, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China*
[b] *Institute of Physical Chemistry, Department of Chemistry, Beijing University, Beijing 100871, People's Republic of China*

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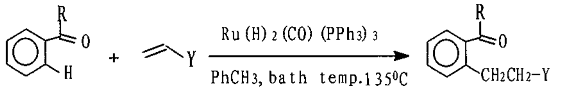
Abstract

The catalytic addition reactions of ferrocenyl ketones with terminal olefins in the presence of $Ru(H)_2(CO)(PPh_3)_3$ as catalyst have been studied. Benzoylferrocene reacts with triethoxyvinylsilane, styrene and vinylferrocene, respectively, to give 1:1 coupling products I–III in high yields. C–H bond cleavage takes place at the carbon atom of the benzene ring at the *ortho* position of the carbonyl group and C–C bond formation takes place at the terminal carbon atom of the olefins. 2-Furoylferrocene reacts with vinylferrocene to give a 1:1 coupling product IV and the C–H bond cleavage takes place at the carbon atom of the furan ring at the *ortho* position of the carbonyl group and the C–C bond formation takes place at the terminal carbon atom of vinylferrocene. The new products I–IV have been characterized by elemental analysis, ^{1}H-NMR and MS. The X-ray crystal structure of IV has been determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Ferrocene; $Ru(H)_2CO(PPh_3)_3$; C–H bond cleavage; Crystal structures; Catalysis; Catalytic C–H/olefin coupling

1. Introduction

Carbon–hydrogen bonds are ubiquitous in organic chemistry. The activation of the C–H bond using transition metals is a very interesting area in organometallic chemistry. Although extensive studies have been performed and there have already appeared a number of reviews and papers, the ability to react sp^2- and sp^3-hybridized C–H bonds is limited. A few years ago, Murai and co-workers [1–6] found a very efficient catalytic addition of a C–H bond in aromatic ketones to olefins with the aid of ruthenium complexes. The new catalytic reaction permits the one-step addition of C–H bonds in aromatic ketones to terminal olefins and a new C–C bond is formed between the carbon atom at the *ortho* position of the carbonyl group and the terminal carbon atom of the olefin (Eq. (1)).



(1)

R = CH_3, C_2H_5, $C(CH_3)_3$, C_6H_5, etc.   Y = $Si(OC_2H_5)_3$, C_6H_5, etc.

The new reaction is unique because it is characterized by very high efficiency, high regioselectivity and wide applicability [7].

In this paper we report our studies of the catalytic addition of ferrocenyl ketones to olefins with the aid of $Ru(H)_2(CO)(PPh_3)_3$ for the synthesis of new ferrocene derivatives and the characterization of the new products.

2. Results and discussion

2.1. Reaction of ferrocenyl ketones with olefins

The results of the coupling reactions are listed in Table 1.

Acetylferrocene, 1,1′-diacetylferrocene and formylferrocene did not react with triethoxyvinylsilane using

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* Corresponding author. Fax: +86-10-64435312.
E-mail address: dhg@buct.edu.cn (H. Du).

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$Ru(H)_2(CO)(PPh_3)_3$ as a catalyst even when an excess of catalyst and a longer reaction time were used.

In the work of Murai and co-workers [4] 1-indanone, a five-membered ketone, did not undergo a coupling reaction at all while α-tetralone (a six-membered ketone) and a seven-membered ketone did undergo the coupling reaction. We think that the relative site of the oxygen atom of the carbonyl group and the *ortho* C–H bond may affect the reaction; therefore, we studied the action of ferrocenyl cyclic ketones such as 1,2-(α-oxotetramethylene)ferrocene and 2,3-ferrocoindenone with olefins such as triethoxyvinylsilane and vinylferrocene. We found that they did not react at all, even when the amounts of olefin and $Ru(H)_2(CO)(PPh_3)_3$ were increased and the reaction time extended.

Benzoylferrocene does react with terminal olefins such as triethoxyvinylsilane, styrene and vinylferrocene in the presence of $Ru(H)_2(CO)(PPh_3)_3$ to give the 1:1 coupling products I–III in high yields (Runs 1–3). The C–H bond cleavage takes place at the carbon atom of the benzene ring at the *ortho* position of the carbonyl group and the C–C bond formation takes place at the terminal carbon atom of the olefins. 2-Furoylferrocene reacts with vinylferrocene to give the 1:1 coupling product IV. The C–H bond cleavage takes place at the carbon atom of the furan ring at the *ortho* position of the carbonyl group and the C–C bond formation takes place at the terminal carbon atom of vinylferrocene (Run 4). The structural formulas for compounds I–IV are shown in Fig. 1.

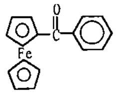
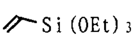
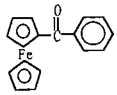
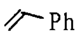
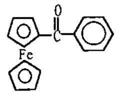
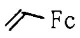
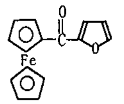
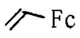
All the results show no evidence for the C–H bond in the cyclopentadienyl ring at the *ortho* position of the carbonyl group in ferrocenyl ketones for coupling with olefins by $Ru(H)_2(CO)(PPh_3)_3$.

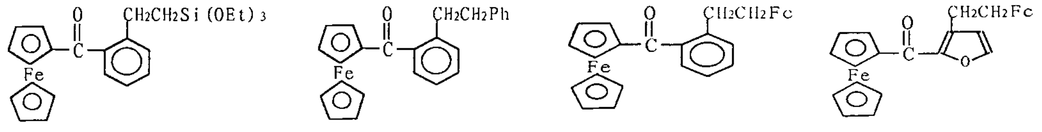
Murai and co-workers believe [1–4] that the reaction mechanism may involve coordination of the ruthenium complex with the ketone group on the aromatic ring. Accordingly, we examined the reactions of *N*,*N*-dimethylaminomethylferrocene with styrene, ferrocenylmethanol and α-hydroxyethylferrocene with triethoxyvinylsilane using $Ru(H)_2(CO)(PPh_3)_3$ as catalyst. In all cases, no reactions were observed.

2.2. Characterization of products I–IV

Products I–IV are new derivatives of ferrocene. They are all air-stable compounds, and are characterized by elemental analysis, ^{1}H-NMR spectra and MS spectra.

Table 1
Catalytic addition reaction of ferrocenyl ketones with olefins

Run	Ketone	Olefin	Ket./Ole./Cat. (mmol)	Time (h)	Product and Yield (%)
1			2/2/0.04	1	I 91
2			2/2/0.04	4	II 98
3			2/2/0.04	4	III 93
4			2/2/0.04	4	IV 80



I II III IV

Fig. 1. The structural formulas for compounds I–IV.

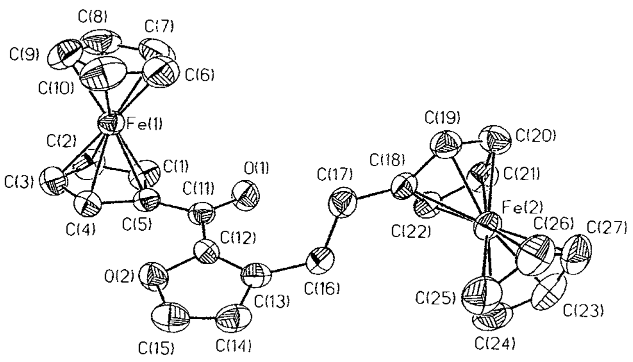


Fig. 2. Molecular structure of product IV.

Table 2
Selected bond lengths (Å) and bond angles (°) for compound IV

Bond lengths			
C(1)–C(2)	1.417(4)	C(19)–C(20)	1.417(4)
C(2)–C(3)	1.393(5)	C(20)–C(21)	1.415(5)
C(3)–C(4)	1.410(5)	C(21)–C(22)	1.422(4)
C(4)–C(5)	1.437(4)	Fe(1)–C(1)	2.026(3)
C(5)–C(1)	1.434(4)	Fe(1)–C(2)	2.049(3)
C(5)–C(11)	1.469(4)	Fe(1)–C(3)	2.048(3)
C(11)–O(1)	1.232(3)	Fe(1)–C(4)	2.035(3)
C(11)–C(12)	1.453(4)	Fe(1)–C(5)	2.029(3)
C(12)–C(13)	1.367(4)	Fe(1)–C(6)	2.016(3)
C(12)–O(2)	1.389(3)	Fe(1)–C(7)	2.020(3)
C(13)–C(14)	1.417(4)	Fe(1)–C(8)	2.016(3)
C(13)–C(16)	1.500(4)	Fe(1)–C(9)	2.041(4)
C(14)–C(15)	1.334(4)	Fe(1)–C(10)	2.026(4)
C(15)–O(2)	1.354(4)	Fe(2)–C(18)	2.051(3)
C(16)–C(17)	1.530(4)	Fe(2)–C(19)	2.045(3)
C(17)–C(18)	1.503(4)	Fe(2)–C(20)	2.041(3)
C(18)–C(22)	1.425(4)	Fe(2)–C(21)	2.036(3)
C(18)–C(19)	1.424(4)	Fe(2)–C(22)	2.039(3)
Bond angles			
C(2)–C(1)–C(5)	108.0(3)	C(12)–C(13)–C(16)	127.4(3)
C(4)–C(5)–C(11)	131.2(3)	C(14)–C(13)–C(16)	126.7(3)
C(1)–C(5)–C(11)	121.9(3)	C(13)–C(14)–C(15)	107.5(3)
C(1)–C(5)–C(4)	106.7(3)	C(14)–C(15)–O(2)	111.0(3)
O(1)–C(11)–C(5)	120.2(3)	C(15)–0(2)–C(12)	106.2(2)
O(1)–C(11)–C(12)	118.1(3)	C(13)–C(16)–C(17)	112.6(3)
C(5)–C(11)–C(12)	121.7(2)	C(16)–C(17)–C(18)	113.5(3)
C(11)–C(12)–C(13)	131.5(3)	C(17)–C(18)–C(19)	126.0(3)
O(2)–C(12)–C(11)	119.0(2)	C(17)–C(18)–C(22)	126.5(3)
C(13)–C(12)–O(2)	109.3(2)	C(22)–C(18)–C(19)	107.3(3)
C(12)–C(13)–C(14)	105.9(3)	C(18)–C(19)–C(20)	108.3(3)

The results show that the catalytic reaction of benzoylferrocene and 2-furoylferrocene with terminal olefins yield 1:1 coupling products.

The ^{1}H-NMR spectra of compounds I–IV display two symmetrical singlets of two protons for each between 4.50 and 5.30 ppm, which indicate the presence of a single-substituted cyclopentadienyl ring. This is consistent with the C–H bond cleavage at the carbon atom of the benzene ring and the furan ring, but not at the *ortho* position of the carbonyl group on the cyclopentadienyl ring. The ^{1}H-NMR spectra also display a singlet at δ 3.80 ppm for compound I, a singlet at δ 3.03 ppm for compound II, two symmetrical multiplets between δ 2.45 and 3.05 ppm for compound III and two symmetrical multiplets between δ 2.57 and 3.25 ppm for compound IV. It is obvious that the C–C bond formation takes place at the terminal carbon atom of the olefins.

2.3. X-ray crystal structure of compound IV

The structure of compound IV has been confirmed by an X-ray crystal diffraction study. An ORTEP diagram of the structure of IV is shown in Fig. 2, selected bond lengths and bond angles are listed in Table 2.

The dihedral angle of C(12)–C(13)–C(16)–C(17) is 100.7°. The ferrocene connected with C(17) has an antiprismatic conformation with a torsion angle C(20)–center–center–C(27) of 11.2°.

The furan ring is at an angle of 4.5° to the C(12)–C(11)–C(5)–O(1) mean plane, which shows that the two planes are almost coplanar. This contributes to the conjugative effect. The dihedral angle of C(12)–C(11)–C(5)–C(4) is 14.8°, which results from the cooperation of the conjugative effect and the steric effect. The ferrocene connected with C(5) has a prismatic conformation with a torsion angle C(6)–center–center–C(5) of 1.1°, which is unusual. This may be due to the result of packing of molecule IV in the crystal.

3. Experimental

3.1. Instruments and materials

Melting points were determined on a microscopic apparatus and were uncorrected. Elemental analyses were performed with a Carlo Erba 1106 elemental analyzer. ^{1}H-NMR spectra were recorded on a Bruker AC 80 Spectrometer, using $CHCI_3$-*d* as solvent and TMS as an internal standard. The MS analyses were measured on a VG70 SE GC/MS gas chromatography mass spectrometer.

Toluene and triethoxyvinylsilane were distilled under nitrogen from CaH_2. Styrene was distilled under reduced pressure. Vinylferrocene [8], benzoylferrocene [9], 2-furoylferrocene [10], acetylferrocene [11], 1,1′-diacetylferrocene[12], formylferrocene [13], 1,2-(α-oxotetramethylene)ferrocene [14], 2,3-ferrocoindenone [15], *N*,*N*-dimethylaminomethylferrocene [16], ferrocenylmethanol [16] and α-hydroxyethylferrocene [17] were prepared according to the literature procedures.

3.2. Preparation of $Ru(H)_2(CO)$ $(PPh_3)_3$

$Ru(H)_2(CO)(PPh_3)_3$ was prepared by a modified method from the literature [18]. The reaction was performed under oxygen-free nitrogen. Hydrated ruthenium trichloride (0.52 g, 2 mmol) in ethanol (20 ml), aqueous formaldehyde (22 ml, 37% w/v solution) and potassium hydroxide (82% content, 0.74 g, 10 mmol) in ethanol (20 ml) were added quickly and successively to a stirred solution of triphenylphosphine (3.14 g, 12 mmol) in boiling ethanol (140 ml). The mixture was heated under reflux for 30 min, and then cooled. The resultant gray precipitate was filtered off, and washed with ethanol, deionized water, ethanol and petroleum ether (b.p. 40–60°C). The crude product was recrystallized from benzene–methanol twice. The precipitate was filtered off, washed with methanol and petroleum ether, and dried in vacuo. The colorless solids were used for the catalytic reaction.

3.3. Preparation of the products I–IV

3.3.1. General procedure for the synthesis

A 25-ml two-necked round-bottom flask, equipped with a reflux condenser, a nitrogen inlet, a magnetic stirring bar and a tube sealed with a rubber septum, was flushed with dry nitrogen, and then the apparatus was flame dried under a flow of dry nitrogen. In the flask was placed $Ru(H)_2(CO)(PPh_3)_3$, ferrocenyl ketone, olefin and toluene under a flow of nitrogen. The mixture was heated under vigorous reflux (at 135°C, oil bath temperature) with stirring for an appropriate reaction period under nitrogen atmosphere. The mixture was allowed to cool to room temperature, and then was passed through a short neutral alumina or silica gel column with petroleum ether–ethyl acetate as eluent. The effluent was concentrated on a rotary evaporator and followed by an evaporation of the solvent in vacuo. The products were characterized as follows.

3.3.2. [2-(2-Triethoxysilylethyl)benzoyl] ferrocene (I)

The product was isolated by silica gel column chromatography with petroleum ether–ethyl acetate(v/v 4:1) as eluent. Brownish red liquid. Yield 91%. Anal. Found: C, 62.31; H, 6.92. Calc. for $C_{25}H_{32}O_4SiFe$: C, 62.50; H, 6.71%. ^{1}H-NMR (δ ppm): 1.20 (s, 9H, CH_3), 2.72 (s, 6H, OCH_2), 3.80 (s, 4H, CH_2CH_2), 4.20–4.66 (m, 9H, Fc), 7.30 (s, 4H, Ph). MS m/z (% relative intensity): 480 (100), 446 (56), 415 (15), 318 (17), 149 (19), 57 (32).

3.3.3. [2-(2-Phenylethyl) benzoyl]ferrocene (II)

Product II was isolated by neutral alumina column chromatography with petroleum ether–ethyl acetate (v/v 20:1) as eluent. Brownish red liquid. Yield 98%. Anal. Found: C, 75.92; H, 5.77. Calc. for $C_{25}H_{22}OFe$: C, 76.15; H, 5.62%. ^{1}H-NMR (δ ppm): 3.03 (s, 4H, CH_2), 4.27 (s, 5H, unsubstituted Cp), 4.56 (s, 2H, substituted Cp), 4.79 (s, 2H, substituted Cp), 7.30–7.70 (m, 9H, Ph). MS m/z (% relative intensity): 394 (100), 311 (37), 236 (12), 178 (7), 153 (12), 121 (13).

3.3.4. [2-(2-ferrocenylethyl) benzoyl]ferrocene (III)

Product III was isolated by neutral alumina column chromatography with petroleum ether–ethyl acetate (v/v 5:1) as eluent. Red liquid. Yield 93%. Anal. Found: C, 69.59; H, 5.39. Calc. for $C_{29}H_{26}OFe_2$: C, 69.36; H, 5.22%. ^{1}H-NMR (δ ppm): 2.45–3.05 (two symmetrical multiplets, 4H, CH_2), 4.03–4.77 (m, 18H, Cp), 7.20–7.60 (m, 4H, Ph).

3.3.5. 3-(2-Ferrocenylethyl)-2-ferrocenoylfuran (IV)

The product was isolated by neutral alumina column chromatography with petroleum ether–ethyl acetate (v/v 10:1) as eluent. Red plates. Yield 80%. m.p. 118–120°C. Anal. Found: C, 65.78; H, 5.01. Calc. for $C_{27}H_{24}O_2Fe_2$: C, 65.89; H, 4.92%. ^{1}H-NMR (δ ppm): 2.57–3.25 (two symmetrical multiplets, 4H, CH_2), 4.14 (s, 5H, unsubstituted Cp), 4.55 (s, 2H, substituted Cp), 5.21 (s, 2H, substituted Cp), 6.40 (s, 1H, β-H of oxygen in furan ring), 7.45 (s, 1H, α-H of oxygen in furan ring). MS m/z (% relative intensity): 492 (100), 427 (62), 362 (37), 297 (13), 246 (11), 199 (39), 121 (28).

Table 3
Crystal data and structure refinement for compound IV

Chemical formula	$C_{27}H_{24}Fe_2O_2$
Formula weight	492.16
Crystal size (mm)	$0.2 \times 0.4 \times 0.6$
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	17.166(3)
b (Å)	9.462(2)
c (Å)	14.801(3)
α (°)	90
β (°)	115.44(3)
γ (°)	90
V (Å^3)	2170.9(7)
Z	4
D_{calc} (g cm^{-3})	1.506
μ (mm^{-1})	1.358
F(000)	1016
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Theta range for data collection (°)	2.52–26.00
Index ranges	$-18 \le h \le 21$, $-11 \le k \le 0$, $-18 \le l \le 0$
Reflections measured	4308
Unique reflections	4229
R_{int}	0.0121
Completeness to $2\theta = 26.00$ (%)	92.9
Data/restraints/parameters	4229/0/281
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0364$, $wR_2 = 0.0911$
R indices(all data)	$R_1 = 0.0650$, $wR_2 = 0.1016$
Goodness-of-fit	1.040
Extinction coefficient	0.0027(3)
Highest peak and deepest hole (e Å^{-3})	0.345, -0.419

3.4. Crystallography

The crystal used for X-ray diffraction was grown in ethanol. The red plate crystal of IV was mounted on a Rigaku AFC6S diffractometer. Unit cell parameters were determined with θ angles in the range of 2.52–26.00° and refined with the full-matrix least-squares method. Intensities were collected with graphite monochromated Mo–K_{α} radiation by using the ω-scan technique. A total of 4308 reflections were measured and 4229 reflections were considered as observed applying the condition $I > 2\sigma(I)$. Data were corrected for the Lorentz and polarization effects. All calculations were performed using the SHELXL-93 program. The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included but not refined. Crystal data and structure refinement are summarized in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC no. 150793. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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