Preparation and some properties of Mn(I) metallocenylacetylide and the related complexes

Masaru Sato *, Emiko Mogi

Chemical Analysis Center, Saitama University, Urawa, Saitama 338, Japan

Abstract

The reaction of lithium ferrocenyl- or ruthenocenylacetylide and $MnBr(CO)_5$ at low temperature gave the corresponding Mn(I) metallocenylacetylide complex in a moderate yield. In the presence of excess methyllithium, (tetracarbonyl)(1-ferrocenyl-buten-3-one-1-η^1,O) manganese and 4,6-diferrocenyl-α-pyrone were isolated, in addition to the Mn(I) ferrocenylacetylide complex. The former was also obtained in the reaction of $MnMe(CO)_5$ with $FcC\equiv CH$. The structures of these two complexes were determined by a single crystal X-ray analysis.

Keywords: Ferrocene; Manganese complex; α-Pyrone; Ruthenocene; Acetylide complex; Metallacycle

1. Introduction

It has been well known for a long time that ferrocenylacetylene reacted with transition-metal complexes to give cyclic oligomers [1]. From the viewpoint of developing a new functionalized material, the chemistry of ferrocenylacetylene has recently been revived. Ferrocenylacetylene reacted with rutheniumdodecacarbonyl to give a new type of trinuclear complex [2]. Ru(II) [3], Fe(II) [4], Ni(II) [5], Pd(II) [5] and Pt(II) ferrocenylacetylide complexes [6] have been reported. The reaction of Re(I) phenylacetylide and ferrocenylacetylene was also reported [7]. The reaction product of silver ferrocenylacetylide with $BrMn(dppe)(CO)_3$ was reported to have potential for non-linear optics [8]. In contrast, ruthenocenylacetylide complex is rarely reported [9]. We report here on the preparation of Mn(I) ferrocenyl- and ruthenocenylacetylides and the related complexes.

2. Results and discussion

The reaction of ferrocenylacetylene, $FcC\equiv CH$ (1), with MeLi in THF followed by addition of a somewhat

excess of $MnBr(CO)_5$ at low temperature gave Mn(I) ferrocenylacetylide complex, $FcC\equiv CMn(CO)_5$ (3), in 60% yield, which was unstable in solution and was then purified as orange crystals by sublimation under vacuum. The IR spectrum of 3 showed the $C\equiv C$ stretching vibration at 2112 cm^{-1} and the $C\equiv O$ stretching vibration at 2135, 2078, 2032, 1982, and 1946 cm^{-1}. Complex 3 afforded the signals attributed to the ferrocenyl ring protons as a singlet at δ 4.16 (5H) and triplets at δ 4.06 (2H) and 4.32 (2H) in the ^1H NMR spectrum, and the acetylenic carbon signals at 82.69, 113.34 and the carbonyl carbon at 206.92 ppm in the ^{13}C NMR spectrum. These spectral data confirmed the structure of complex 3. In a similar reaction of ruthenocenylacetylene, $RcC\equiv CH$ (2), Mn(I) ruthenocenylacetylide complex, $RcC\equiv CMn(CO)_5$ (4), was obtained in a similar yield. These results were in contrast to the fact that the reaction of $MnBr(dppe)(CO)_3$ with $FcC\equiv CLi$ did not take place at all under similar conditions. A mixture of 1 and $MnBr(CO)_5$ was treated with 1.6 equivalents of MeLi in THF at $-78°C$, followed by warming to room temperature and stirring for 1 h, to give a complex mixture. Four products were isolated after the chromatography of the reaction mixture on silica gel besides the recovered starting material (22%). The first of them was the acetylide complex (3) (20%) and the second product was 1,4-diferrocenylbutadiyne (3.3%). The third product (5), isolated as red crystals (12%), showed a

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* Corresponding author.
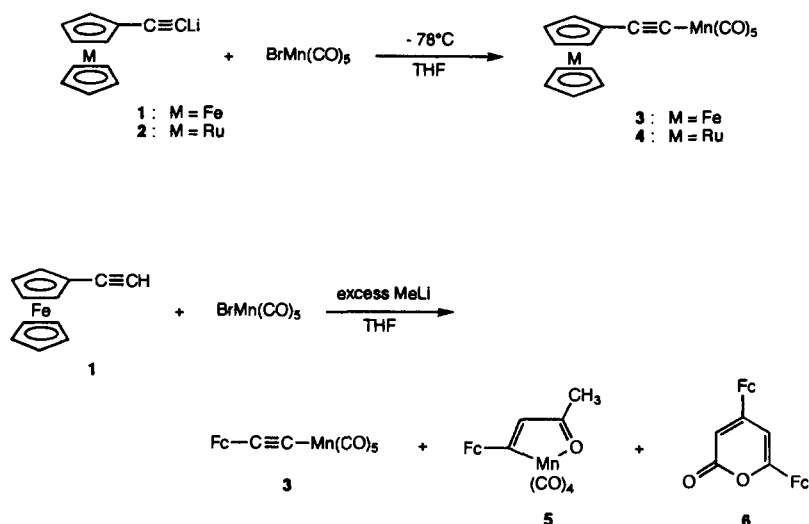
singlet of methyl protons at δ 2.25, a singlet of an olefinic proton at δ 7.11, and signals of ferrocenyl ring protons at δ 4.22 (5H), 4.62 (2H), and 4.79 (2H) in the ^{1}H NMR spectrum. The chemical shift of the methyl and olefinic protons in 5 is very similar to those of the product (7) in the reaction of MeMn(CO)$_5$ with phenyl-acetylene [10]. Then, the structure of 5 is assigned as (tetracarbonyl)(1-ferrocenyl-2-buten-3-one-1-η^1,O)

manganese, which was confirmed by a single crystal X-ray diffraction analysis (vide infra). Otherwise, ferro-cenylacetylene 1 reacted with MnMe(CO)$_5$ in THF at room temperature overnight to give the same complex 5 in 76% yield. Similarly, the reaction of ruthenocenyl-acetylene 2 with MnMe(CO)$_5$ gave the ruthenocenyl analog (8) in a good yield. The final product (6) (2%) was unexpected. The IR spectrum of 6 confirmed the

Table 1
Crystal and intensity collection data for 5 and 6

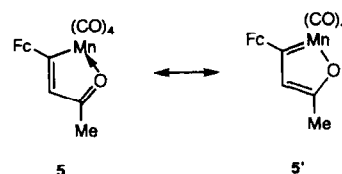|	5	6
Mol formula	C$_{18}$H$_{13}$O$_5$MnFe	C$_{25}$H$_{20}$O$_2$Fe$_2$
Mol weight	420.086	464.10
Crystal system	monoclinic	monoclinic
Space group	$P21/n$ (No. 14)	$P21/a$ (No. 14)
a (Å)	16.215(9)	12.620(5)
b (Å)	12.111(5)	13.001(5)
c (Å)	8.865(4)	12.397(4)
β (deg)	98.73(4)	104.32(3)
V (Å^3)	1721(1)	1971(1)
Z	4	4
D_{cal} (g cm^{-3})	1.62	1.56
Crystal dimensions (mm^3)	0.24 × 0.26 × 0.18	0.50 × 0.50 × 0.26
Radiation (λ (Å))	Mo K α (0.71073)	Mo K α (0.71073)
Reflection (hkl) limits	$0 < h < 21$, $-9 < k < 15$, $-11 < l < 11$	$-7 < h < 16$, $-1 < k < 16 - 16 < l < 15$
Total reflections measured	4424	5095
Unique reflections	3958	4529
Linear abs coeff (cm^{-1})	15.776	14.898
Reflections used in L.S.	2926	3065
L.S. parameters	278	342
R	0.0365	0.0349
Rw	0.0386	0.0376
Max peak in final Fourier map (e Å^{-3})	0.55	0.39
Min peak in final Fourier map (e Å^{-3})	−0.45	−0.35
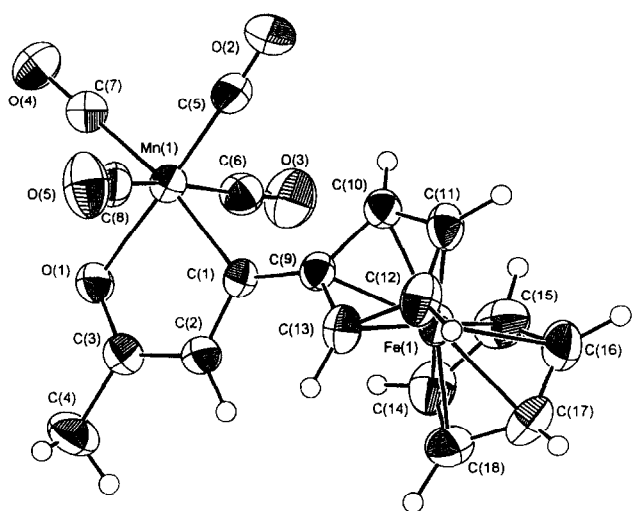
Fig. 1. ORTEP view of complex 5.

presence of a carbonyl group (1696 cm^{-1}). In the ^{1}H NMR spectrum, 6 showed two olefinic proton signals at δ 6.17 and 6.34 and two pairs of signals assigned to the ferrocenyl ring protons. The ^{13}C NMR spectrum of 6 afforded the carbonyl carbon signal at δ 157.49 and the four olefinic carbon signals at δ 99.09, 103.23, 163.15, and 163.35. The olefinic carbon atoms due to the two signals observed at a lower field are conjugated with the carbonyl group and are also connected to the ferrocenyl group because the carbons are a quaternary one. In the MS spectrum of 6, the molecular ion was observed at m/z 464. On the basis of these spectral data, the structure of 4,6-diferrocenyl-α-pyrone is offered for complex 6. A single crystal X-ray diffraction analysis of 6 confirmed this assignment (vide infra). Complex 6 was also isolated in 8.3% yield, when the reaction of 1 with MnBr(CO)$_5$ in the presence of excess of MeLi was carried out in ethyl ether instead of THF.

The crystallographic data of 5 and 6 are collected in Table 1. The ORTEP-view of 5 is shown in Fig. 1 and the selected bond distances and bond angles are summa-

rized in Table 2. The Mn atom takes a cis configuration of the octahedral arrangement in complex 5. This is in agreement with the observation of three signals for the terminal carbonyl carbon in the ^{13}C NMR spectrum (vide infra). The Mn–CO distance (1.799(5) Å) trans to the coordinated oxygen atom of the carbonyl group is considerably shorter than those of other Mn–CO distances (1.849(4)–1.865(5) Å), probably because of the weak trans influence due to weak coordination of the carbonyl oxygen atom to the Mn atom. The main point of interest is the metallacycle ring which contains the C–O, Mn–O, and Mn–C bonds. The C–O (1.264(5) Å) and Mn–C bonds (2.055(4) Å) of 5 are comparable with those for the complexes which have a similar five-membered ring (1.29 (C–O) and 1.99 Å (Mn–C) in 9 [11] and 1.244 (C–O) and 2.042 Å (Mn–C) in 10 [12]). This suggests that extensive delocalization is possible through the resonance 5 ↔ 5' in the five-membered ring of 5. The limited structure 5' would contribute to the increased C(1)–C(2) distance (1.361(6) Å) and the decreased C(2)–C(3) distance (1.413(6) Å). The metallacycle containing the Mn atom is nearly planar, the plane of which is inclined by ca. 26° to the substituted cyclopentadienyl ring of the ferrocenyl group. On the basis of the above structure, the signal at δ 25.91 is assigned as the methyl carbon, signals at δ 132.34 and 250.64 as the olefinic carbons, the signals at δ 210.90, 214.01, and 220.38 as the terminal carbonyl ligand, and the signal at δ 210.63 as the carbonyl carbon in the ^{13}C NMR spectrum of 5. The shift of the carbonyl carbon to a lower field (ca. Δ20 ppm) agrees with the coordina-

Table 2
Selected bond lengths (Å) and bond angles (deg) for 5

| Bond lengths			
Mn–(1)	2.055(4)	Mn–C(5)	1.799(5)
Mn–C(6)	1.865(5)	Mn–C(7)	1.849(4)
Mn–C(8)	1.859(5)	Mn–O(1)	2.050(3)
C(1)–C(2)	1.361(6)	C(2)–C(3)	1.413(6)
C(3)–C(4)	1.491(7)	C(3)–O(1)	1.264(5)
C(1)–C(9)	1.458(5)		
Bond angles			
C(1)–Mn–O(1)	49.8(2)	C(1)–Mn–C(5)	99.8(2)
C(1)–Mn–C(7)	169.0(2)	C(1)–Mn–C(6)	88.7(2)
C(1)–Mn–C(8)	83.4(2)	O(1)–Mn–C(7)	89.4(2)
O(1)–Mn–C(5)	179.2(2)	O(1)–Mn–C(6)	91.9(2)
O(1)–Mn–C(8)	90.6(2)	Mn–C(1)–C(9)	127.6(3)
Mn–C(1)–C(2)	110.9(3)	Mn–O(1)–C(3)	113.9(3)
C(1)–C(2)–C(3)	116.8(4)	C(2)–C(3)–O(1)	118.6(4)

tion of the carbonyl group to the metal center, and the appearance of one of the olefinic carbons in the very low field (δ 250.64) seems to be explained by the fact that the C(1) atom has a partial carbenic α-carbon character in the limited structure 5'. Also, the observation of three signals for the terminal carbonyl (strength ratio, 2:1:1) is coincident with the formation of the metallacycle in complex 5. The ORTEP view of 6 is shown in Fig. 2 and the selected bond distances and angles are summarized in Table 3. No doubtful point is observed in the α-pyrone ring in 6. Interestingly, the α-pyrone ring and the substituted cyclopentadienyl rings of two ferrocenyl groups, however, are coplanar to each other. This seems to be due to the conjugation of the ferrocenyl groups with the carbonyl group in the α-pyrone ring. Also, the Fe atoms of the two ferrocenyl groups are on the same side toward the plane of the

α-pyrone ring, i.e. syn-conformation. This may suggest that there is some interaction between the two ferrocenyl groups. The cyclic voltammogram of 6 measured in CH_3CN showed only one quasi-reversible wave corresponding to the two-electron redox at +0.17 V, although 6 contained two ferrocenyl groups in the molecule. This suggests that the iron atoms of the ferrocenyl ring in 6 scarcely interact with each other. The two cyclopentadienyl rings in the ferrocenyl group in 6 adopt an eclipsed form in both ferrocenyl groups (3.6 and 0.0°). These features probably do not depend on the steric or electronic factors in the molecule but seem to be due to the crystal packing.

The formation of 5 and 6 in the reaction of 1 with $BrMn(CO)_5$ in the presence of excess of MeLi may be explained as follows (Scheme 1): methyllithium first reacts with $BrMn(CO)_5$ to give $MeMn(CO)_5$ which then

Table 3
Selected bond lengths (Å) and bond angles (deg) for 6

Bond lengths			
C(21)–C(22)	1.423(7)	C(21)–O(1)	1.405(6)
C(21)–O(2)	1.207(7)	C(22)–C(23)	1.341(7)
C(23)–C(24)	1.429(6)	C(23)–C(1)	1.467(6)
C(24)–C(25)	1.348(6)	C(25)–O(1)	1.356(5)
C(25)–C(11)	1.462(6)		
Bond angles			
C(22)–C(21)–O(1)	115.8(5)	O(1)–C(21)–O(2)	115.7(5)
C(22)–C(21)–O(2)	128.5(5)	C(21)–C(22)–C(23)	123.0(4)
C(22)–C(23)–C(24)	118.3(4)	C(22)–C(23)–C(1)	122.4(4)
C(24)–C(23)–C(1)	119.3(4)	C(23)–C(24)–C(25)	119.8(4)
C(24)–C(25)–O(1)	121.6(4)	C(24)–C(25)–C(11)	125.8(4)
O(1)–C(25)–C(1)	112.6(4)	C(21)–O(1)–C(2)	121.4(4)
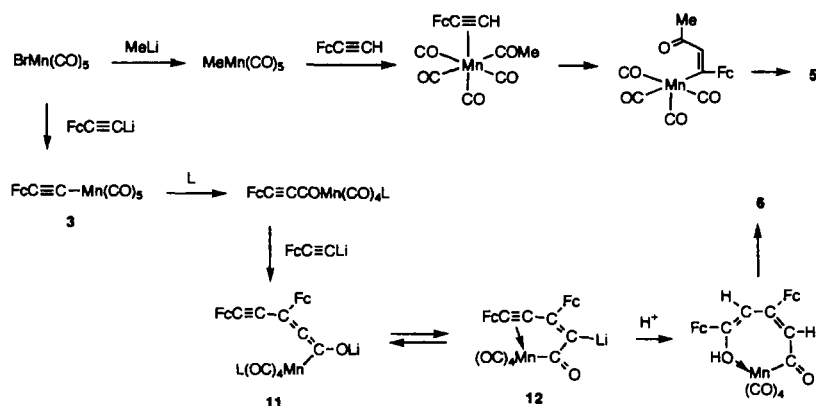
Scheme 1.
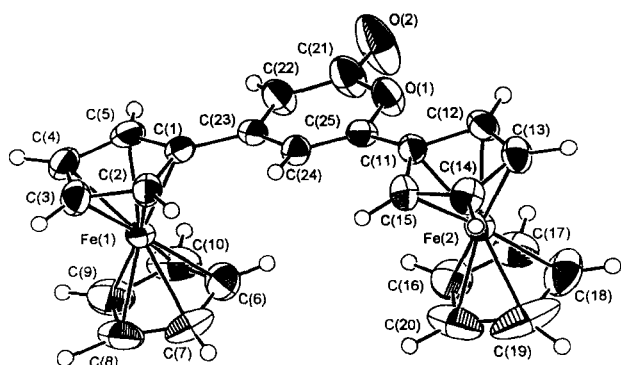
Fig. 2. ORTEP view of complex 6.

reacted with 1 to result in 5. In coincidence to this, the reaction of 1 with MeMn(CO)$_5$ gave 5 in good yield (vide supra). According to the pathway proposed for the reaction of phenylacetylene with MeMn(CO)$_5$ by Booth and Hargreaves [10], the CO insertion to MeMn(CO)$_5$ forms the acyl complex, MeCOMn(CO)$_4$L, and then the insertions of FcC≡CH to the Mn–COMe bond, followed by the coordination of the carbonyl oxygen atom to the Mn atom give complex 5. No reaction of complex 3 with 1 proceeded in ethyl ether at all; however, 3 reacted with lithium ferrocenylacetylide to give 6, although in very low yield, in similar conditions along with the high recovery of 1 (90%). The reaction resulting in 6 may be slow, because 6 was obtained in 24% yield when the reaction of 1 with 3 was carried out in the presence of aqueous LiOH at room temperature overnight. Therefore, the precursor in the formation of 6 is considered to be the acetylide complex 3 generated from the reaction of FcC≡CLi with BrMn(CO)$_5$. Complex 3 successively undergoes carbonyl insertion to result in the acyl complex FcC≡CCOMn(CO)$_4$L. The 1,4-addition of an additional FcC≡CLi to the unsaturated carbonyl part forms FcC≡C–C(Fc)=C=C(–O–)Mn(CO)$_4$L (11) which is stabilized by the equilibrium with the cyclized complex (12). Protonation and the addition of H$_2$O to the coordinated C≡C bond in 12, followed by cyclization, gives complex 6. In order to confirm this process, the quenching of the reaction with D$_2$O was attempted. The intensity of the H-3 and H-5 of the pyrone ring in 6 was reduced to 60% and 20% respectively, supporting the above process.

In summary, lithium ferrocenyl- and ruthenocenyl-acetylide reacted with MnBr(CO)$_5$ at low temperature to respectively give FcC≡CMn(CO)$_5$ and RcC≡CMn(CO)$_5$ in good yield. Moreover, in the reaction of ferrocenylacetylene with MnBr(CO)$_5$ in the presence of an excess of MeLi, the metallacycle complex 5 and the cyclic product 6 were also isolated. The formation of 6 is unprecedented in this kind of carbonylation. Interestingly, two ferrocenyl groups took a syn-confomation in the α-pyrone derivative 6.

3. Experimental

3.1. General

All reactions were carried out under a nitrogen atmosphere and the workup was carried out in air. Ferrocenyl- [13], ruthenocenylacetylene [14], and MnMe(CO)$_5$ [15] were prepared by literature methods. All the other chemicals were reagent grade and were used as-received from common commercial sources. Solvents were dried by standard procedures. IR spectra were recorded as KBr pellets on a Perkin–Elmer System 2000 spectrometer. NMR spectra (in CDCl$_3$) were recorded on a Bruker AM400 or ARX400 instrument, using TMS as an internal standard. Electrochemical measurements were by cyclic voltammetry in a solution of 0.1 M (n-Bu)$_4$NClO$_4$ in acetonitrile under nitrogen at 25°C, using a standard three-electrode cell on a BAS CV-27 analyzer. All potentials referenced to FcH/FcH$^+$, which had a potential of +0.14 V vs. Ag/AgNO$_3$ in this medium. The scan rate was 100 mV s^{-1}.

3.2. Procedure

3.2.1. FcC≡CMn(CO)$_5$ (3)

Ferrocenylacetylene (1) (210 mg, 1.0 mmol) was dissolved in dry THF (2 ml) and cooled −78°C. To the solution was added MeLi (0.7 ml of 1.14 M solution in ethyl ether, 0.8 mmol). After stirring for 30 min at −78°C, a solution of MnBr(CO)$_5$ (275 mg, 1.0 mmol) in THF (13 ml) was added and the mixture was stirred for 1 h at this temperature. Then the reaction mixture was poured into water and the mixture was extracted with CH$_2$Cl$_2$. The extract was dried over MgSO$_4$ and evaporated. The residue was chromatographed on silica gel column by using CH$_2$Cl$_2$–hexane (1 : 3) as an eluent. FcC≡CMn(CO)$_5$ (3) (248 mg, 61%) was obtained. Sublimation under reduced pressure gave an analytical sample. Orange crystals, m.p. ca. 104°C (dec.). Anal. Found: C, 50.73; H, 2.23. C$_{17}$H$_9$FeMnO$_5$. Calc.: C, 50.54; H, 2.25%. IR (KBr): 2135, 2078, 2032, 1982, 1946 (C≡O), and 2111 cm^{-1} (C≡C). ^{1}H NMR (CDCl$_3$): δ 4.06 (t, *J* = 1.8 Hz, 2H, Cp-β), 4.16 (s, 5H, Cp-unsub.), 4.32 (t, *J* = 1.6 Hz, 2H, Cp-α). ^{13}C NMR (CDCl$_3$): δ 67.41 (Cp-β), 69.63 (Cp-unsub.), 70.26 (Cp-α), 70.99 (Cp-ipso), 82.69 (C≡C), 113.34 (C≡C), 206.92 (C≡O).

3.2.2. [RcC≡CMn(CO)$_5$] (4)

This complex was prepared according to the procedure described above. Yellow crystals (49%), m.p. ca. 125°C (dec.). Anal. Found: C, 45.55; H, 2.01. C$_{17}$H$_9$MnO$_5$Ru. Calc.: C, 45.45; H, 2.02%. IR (KBr):

2135, 2078, 2032, 1982, 1946 (C=O), and 2111 cm^{-1} (C≡C). ^{1}H NMR (C$_6$D$_6$): δ 4.31 (bs, 2H, Cp-β), 4.53 (s, 5H, Cp-unsub.), 4.94 (bs, 2H, Cp-α). ^{13}C NMR (C$_6$D$_6$): δ 70.02 (Cp-β), 71.82 (Cp-unsub.), 74.08 (Cp-α), 74.43 (Cp-ipso), 82.49 (C≡C), 113.07 (C≡C), 207.15 (C=O).

3.2.3. Reaction of FcC≡CH with MnBr(CO)$_5$ in the presence of MeLi

Compound 1 (210 mg, 1.0 mmol) and MnBr(CO)$_5$ (275 mg, 1.0 mmol) were dissolved in dry THF (15 ml) and cooled −78°C. To the solution was added MeLi (1.4 ml of 1.14 M solution in ethyl ether, 1.6 mmol). After stirring for 2 h at −78°C, the solution was poured into water and the mixture was extracted with CH$_2$Cl$_2$. The extract was dried over MgSO$_4$ and evaporated. The residue was chromatographed on silica gel column by using CH$_2$Cl$_2$–hexane (1:3) as an eluent. The first yellow fraction gave 1 (47 mg, 22%). The second fraction was 1,4-diferrocenylbutadiyne (14 mg, 3.3%). The third dark-red fraction afforded (tetracarbonyl)(1-ferrocenyl-buten-3-one-1-η^1,O)manganese(I) (5) (48 mg, 12%). From the fourth fraction complex 3 (84 mg, 20%) was obtained, which was purified by sublimation under reduced pressure. The fifth fraction gave 4,6-di-ferrocenyl-α-pyrone (6) (9.3 mg, 2%). Recrystallization of 5 and 6 from CH$_2$Cl$_2$–hexane gave an analytical sample as dark-red and red-orange crystals respectively.

5. Dark-red crystals (12%), m.p. 114–116°C. Anal. Found: C, 51.71; H, 3.13. C$_{18}$H$_{13}$FeMnO$_5$. Calc.: C,

Table 4
Fractional atomic coordinates and U_{iso} for complex 5

Atom	x	y	z	U_{iso}
Fe(1)	0.85170(3)	0.03924(4)	0.13759(6)	0.036
Mn(1)	0.66596(3)	0.00634(5)	−0.34965(6)	0.038
O(1)	0.58122(16)	−0.10505(22)	−0.29056(30)	0.043
O(2)	0.7851(2)	0.1685(3)	−0.4364(4)	0.066
O(3)	0.8040(2)	−0.1586(3)	−0.3190(4)	0.076
O(4)	0.5977(2)	−0.0279(3)	−0.6786(3)	0.067
O(5)	0.5546(2)	0.1954(3)	−0.3031(5)	0.075
C(1)	0.6929(2)	0.0147(3)	−0.1159(4)	0.035
C(2)	0.6410(2)	−0.0517(3)	−0.0494(4)	0.042
C(3)	0.5824(2)	−0.1143(3)	−0.1482(4)	0.042
C(4)	0.5213(4)	−0.1906(5)	−0.0926(7)	0.063
C(5)	0.7396(3)	0.1057(3)	−0.4001(5)	0.045
C(6)	0.7497(3)	−0.1005(3)	−0.3336(5)	0.048
C(7)	0.6240(2)	−0.0165(3)	−0.5531(5)	0.047
C(8)	0.5940(2)	0.1222(3)	−0.3249(5)	0.046
C(9)	0.7533(2)	0.0863(3)	−0.0247(4)	0.037
C(10)	0.8310(2)	0.1271(3)	−0.0633(5)	0.043
C(11)	0.8684(3)	0.1950(3)	0.0580(5)	0.052
C(12)	0.8168(3)	0.1985(3)	0.1713(5)	0.052
C(13)	0.7458(3)	0.1314(3)	0.1230(5)	0.044
C(14)	0.8573(3)	−0.1298(4)	0.1459(6)	0.060
C(15)	0.9344(3)	−0.0860(4)	0.1146(6)	0.063
C(16)	0.9661(3)	−0.0174(4)	0.2372(6)	0.061
C(17)	0.9096(3)	−0.0188(4)	0.3436(5)	0.061
C(18)	0.8422(3)	−0.0876(4)	0.2864(6)	0.060

Table 5
Fractional atomic coordinates and U_{iso} for complex 6

Atom	x	y	z	U_{iso}
Fe(1)	0.14550(4)	0.16851(4)	−0.14659(4)	0.034
Fe(2)	0.32860(4)	0.15941(4)	0.44739(4)	0.035
O(1)	0.4914(2)	0.1579(3)	0.2407(2)	0.054
O(2)	0.5908(3)	0.0634(4)	0.1541(3)	0.107
C(1)	0.2799(3)	0.2483(3)	−0.0660(3)	0.039
C(2)	0.1840(3)	0.3106(3)	−0.0765(3)	0.041
C(3)	0.1335(4)	0.3214(3)	−0.1922(3)	0.047
C(4)	0.1969(4)	0.2664(4)	−0.2527(3)	0.051
C(5)	0.2869(3)	0.2205(4)	−0.1769(3)	0.048
C(6)	0.1426(5)	0.0420(4)	−0.0522(5)	0.072
C(7)	0.0431(5)	0.0963(4)	−0.0672(5)	0.073
C(8)	−0.0055(4)	0.0992(4)	−0.1817(5)	0.064
C(9)	0.0621(5)	0.0498(4)	−0.2377(5)	0.068
C(10)	0.1546(4)	0.0140(4)	−0.1581(6)	0.075
C(11)	0.3970(3)	0.2503(3)	0.3500(3)	0.037
C(12)	0.4756(3)	0.2259(3)	0.4518(3)	0.042
C(13)	0.4342(4)	0.2635(3)	0.5402(3)	0.045
C(14)	0.3325(4)	0.3110(3)	0.4947(3)	0.046
C(15)	0.3086(3)	0.3027(3)	0.3784(3)	0.041
C(16)	0.2607(5)	0.0362(4)	0.3529(5)	0.064
C(17)	0.3473(4)	0.0046(3)	0.4362(5)	0.061
C(18)	0.3269(7)	0.0291(5)	0.5378(5)	0.082
C(19)	0.2234(8)	0.0783(5)	0.5153(8)	0.110
C(20)	0.1839(4)	0.0817(4)	0.3985(7)	0.081
C(21)	0.5122(4)	0.1191(5)	0.1422(4)	0.066
C(22)	0.4378(3)	0.1503(4)	0.0414(3)	0.054
C(23)	0.3532(3)	0.2134(3)	0.0387(3)	0.040
C(24)	0.3362(3)	0.2497(3)	0.1420(3)	0.038
C(25)	0.4049(3)	0.2204(3)	0.2386(3)	0.038

51.47; H, 3.12%. IR (KBr): 2080, 2012, 1984, 1918 cm^{-1} (C=O). ^{1}H NMR (CDCl$_3$): δ 2.25 (s, 3H, CH_3), 4.22 (s, 5H, Cp-unsub.), 4.62 (t, J = 1.8 Hz, 2H, Cp-β), 4.79 (t, J = 1.8 Hz, 2H, Cp-α), 7.11 (s, 1H, butene-H_2). ^{13}C NMR (CDCl$_3$): δ 25.91 (CH_3), 70.29 (Cp-β), 71.01 (Cp-α), 72.18 (Cp-unsub.), 91.28 (Cp-ipso), 132.34 (butene-C$_2$), 210.63 (butene-C$_1$), 210.90 (C=O), 214.01 (C=O), 220.38 (C=O), 250.64 (butene-C$_3$).

6. Red crystals (2%), m.p. ca. 210°C (dec.). Anal. Found: C, 64.50; H, 4.39. C$_{25}$H$_{20}$Fe$_2$O$_2$. Calc.: C, 64.69; H, 4.34%. IR (KBr): 1696 (C=O), 1622 and 1537 cm^{-1} (C=C). ^{1}H NMR (CDCl$_3$): δ 4.15 (s, 5H, Cp-unsub.), 4.21 (s, 5H, Cp-unsub.), 4.48 (t, J = 1.8 Hz, 2H, Cp), 4.53 (t, J = 1.8 Hz, 2H, Cp), 4.69 (t, J = 1.8 Hz, 2H, Cp), 4.84 (t, J = 1.8 Hz, 2H, Cp), 6.17 (d, J = 1.4 Hz, 1H, pyrone-H), 6.34 (d, J = 1.4 Hz, 1H, pyrone-H). ^{13}C NMR (CDCl$_3$): δ 66.81 (Cp-sub.), 67.58 (Cp-sub.), 70.07 (Cp-unsub.), 70.30 (Cp-unsub.), 70.80 (Cp-sub.), 71.54 (Cp-sub.), 75.97 (Cp-ipso), 78.29 (Cp-ipso), 99.09 (pyrone-C), 103.23 (pyrone-C), 157.49, 163.15, 163.35 (C=O or pyrone-C). MS (75 eV): m/z 121, 165, 464(M$^+$).

Methyllithium solution (1.0 ml of 1.14 M solution in ethyl ether, 1.1 mmol) was added to a solution of 1 (42 mg, 0.2 mmol) and MnBr(CO)$_5$ (55 mg, 0.2 mmol) in ethyl ether (10 ml) at −78°C and the solution was

stirred for 10 min. Then the reaction mixture was warmed to room temperature and stirred for 1 h. After hydrolysis, the mixture was extracted with ethyl ether and the extract was dried over $MgSO_4$ and then evaporated. The residue was chromatographed on Al_2O_3 to give complex 5 (11.2 mg, 8.3%).

To a solution of lithium ferrocenylacetylide prepared from 1 (25 mg, 0.12 mmol) and n-BuLi (0.1 ml, 0.15 mmol) in anhydrous THF (5 ml) on an ice–salt bath, 3 (48 mg, 0.12 mmol) was added. The solution was stirred for 1 h and then was poured into water. The mixture was extracted with CH_2Cl_2 and the extract was dried over $MgSO_4$. After evaporation, the residue was chromatographed on SiO_2 by elution of CH_2Cl_2–hexane. Complex 1 was recovered in 88% yield and complex 6 was obtained in 3% yield.

To a solution of 1 (16 mg, 0.075 mmol) and 3 (30 mg, 0.075 mmol) in anhydrous THF, an aqueous saturated solution of $LiOH \cdot H_2O$ (one drop) was added. The solution was stirred at room temperature overnight. After the ordinary work-up, 1 was recovered in 25% yield and 6 was obtained in 24% yield.

3.2.4. (Tetracarbonyl)(1-ferrocenyl-buten-3-one-1-η^1,O)manganese(I) (5)

A solution of 1 (42 mg, 0.2 mmol) and $MnMe(CO)_5$ (42 mg, 0.2 mmol) in anhydrous THF (saturated with N_2) (5 ml) was stirred overnight at room temperature under an atmosphere of nitrogen. After evaporation, the residue was chromatographed on silica gel by elution of CH_2Cl_2 to give 5 (64 mg, 76%).

3.2.5. (Tetracarbonyl)(1-ruthenocenyl-buten-3-one-1-η^1,O)manganese(I) (7)

A similar treatment of 2 (51 mg, 0.2 mmol) with $MnMe(CO)_5$ gave 7 (67 mg, 72%) as yellow-orange crystals. M.p. 119–120°C. Anal. Found: C, 46.86; H, 2.81. $C_{18}H_{13}MnO_5Ru$. Calc.: C, 46.46; H, 2.82%. IR (KBr): 2080, 2012, 1984, 1918 cm^{-1} (C≡O). ^{1}H NMR (CDCl$_3$): δ 2.21 (s, 3H, CH_3), 4.61 (s, 5H, Cp-unsub.), 4.84 (t, J = 1.7 Hz, 2H, Cp-β), 5.08 (t, J = 1.7 Hz, 2H, Cp-α), 7.03 (s, 1H, butene-H_2). ^{13}C NMR (CDCl$_3$): δ 25.95 (CH_3), 72.20 (Cp-β), 72.24 (Cp-unsub.), 73.20 (Cp-α), 96.75 (Cp-ipso), 131.95 (butene-C_2), 211.15 (C≡O), 211.56 (butene-C_1), 213.94 (C≡O), 247.21 (butene-C_3).

3.3. Structure determination

The crystallographic data and the position parameters are listed in Table 1 and Tables 4 and 5 respectively. Data collection was performed at room temperature on a Mac Science MXC18K diffractometer with graphite monochromated Mo K α radiation and an 18 kW rotating anode generator. The structure was solved with the Dirdif-Patty method in CRYSTAN-GM (software-package for structure determination) and refined by full-matrix least squares procedure. Absorption correction with the ψ-scan method and anisotropical refinement for non-hydrogen atoms were carried out.

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