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Two Substrates, Three Products: Reactions Between Ferrocene-carboxaldehyde and Dioxaphospholene, Characterization and Crystal Structures of Oxygenated C_3- and C_4-Chain Containing Ferrocenes

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ABSTRACT

Reactions of aldehydes RCHO with 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene are known to form trimethylbiacetyl-aldehyde-phosphite adducts which upon methanolysis gave rise to the corresponding symmetrical 3-R-2,4-pentanediones (R = aryl, alkyl). Reactions between ferrocenecarboxaldehyde and the biacetyl-trimethylphosphite adduct, whatever the experimental conditions used, afforded three new oxygenated C_3 and C_4 side-chain containing ferrocenyl complexes, namely, 1-ferrocenyl-1,2-propanedione (**1**, Fc-C(O)C(O)CH_3); Fc = (η^5-C_5H_5)Fe(η^5-C_5H_4)), 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (**2**, Fc-CH(OCH_3)C(CH_3)(OH)C(O)CH_3) as a single diastereoisomer, and the ferrocenyl enone 4-ferrocenyl-3-methyl-3-buten-2-one (**3**, Fc-CH=C(CH_3)C(O)CH_3) with the enone portion adopting the *s-trans* confrormation in the solid state. The compounds readily purified by silica gel packed column chromatography were isolated in 31-44% yields, and their constitution is in agreement with elemental analyses, IR and multinuclear NMR spectroscopy, and electrospray mass spectrometry. Their molecular identity and geometry have been confirmed by single-crystal X-ray diffraction.

Keywords: ferrocene; α-diketone; hydroxyketone; enone; X-ray structure

1. Introduction

β-diketones RC(=O)CH(R')C(=O)R'', that can be functionalized in the three sites of the molecule, are attractive building blocks for the construction of polydentate Schiff bases, and both the parent derivative 2,4-pentanedione (R = R'' = CH_3, R' = H) and its organometallic counterpart ferrocenoylacetone (R = Fc, R' = H, R'' = CH_3) have been widely employed to prepare Schiff base half-units (Fc =(η^5-C_5H_5)Fe(η^5-C_5H_4)) [1-4]. Mono-condensation of such organic or organometallic β-diketones with an appended O, N or S donor group containing primary amine leads to the formation of tridentate Schiff bases, also called "half unit", through the imine and amine nitrogen atoms and the carbonyl oxygen [1]. Their deprotonated forms, the monoanionic O,N,X-donor Schiff bases (X = O, N, S) can be considered as "pincer-like" ligands. They could, therefore, serve as good chelating ligands for transition metals with for instance, potential applications in catalysis [5].

It is noteworthy that inspite of the availability of variously substituted ferrocenyl containing 1,3-dione unit (R = Fc, R' = H, R'' = CF_3 [6], CCl_3 [7], C_6H_5 [8], Fc [7]; R = R'' = CH_3, R' = $FcCH_2$ [9], FcCH [10]), no corresponding O,N,X-tridentate metalloligands were reported starting from those β-diketone precursors. This is presumably due to the easy access to the 1-ferrocenyl-1,3-butanedione [3a]. Recently, we designed and structurally characterized the new 4-hydroxyphenyl substituted β-diketone derivative , Fc-C(O)CH=C(OH)(*p*-C_6H_4OH), which upon monocondensation with diaminoethane gives the ferrocene containing O,N,N-tridentate enaminone functionalized with a phenolic group [11].

In the pursue of our research work aimed at extending the scope of acyclic Schiff base metalloligands, in particular into ferrocenyl-containing O,N,N-tridentate ones, we decided to synthetize the 3-ferrocenyl-2,4-pentanedione Fc-CH($C(O)CH_3$)$_2$, and further study some monocondensation reactions with different primary diamines. Such symmetrically 3-substituted 2,4-pentanedione RCH($C(O)CH_3$)$_2$ (R = CH_3 [12], arylhydrazones (Ar-NHN=) [13], $FcCH_2$ [9], FcCH [10]) are usually prepared by reaction of the acetylacetonate anion (acac) with the appropriately designed electrophile reagent. To prepare our target molecule, we attempted the organic methodology developped in the 1960s by Ramirez and co-workers [14], starting from ferrocenecarboxaldehyde (FcCHO). Ramirez' procedure involves the condensation of the biacetyl-trimethyl phosphite 1:1 adduct (Scheme 1, **A**) [15] with aliphatic or aromatic aldehydes (RCHO) to form essentially one diastereomeric form of the 2,2,2-trimethoxy-4-methyl-4a-acetyl-5a-R-1,3,2-dioxaphospholane (Scheme 1, **B**), a cyclic saturated oxyphosphorane structure with the 1,3-dioxaphospholane ring system. Methanolysis of this trimethyl-biacetyl-aldehyde-phosphite adduct gave the desired 3-R-2,4-pentanedione

(Scheme 1, **C**) through an intramolecular rearrangement involving the 1,2 shift of an acetyl group during the loss of the trimethylphosphate [14b]. This methodology has recently been successfully used by Pariya *et al.* [16] to prepare organosilicon-based multifunctional β-diketone building blocks designed for the synthesis of structurally defined metal-organic frameworks (MOFs).

Scheme 1

Ferrocene is well-known to behave as an aromatic molecule [17]. However, contrary to what is observed with benzaldehyde or its substituted derivatives [14,16], treatment of ferrocenecarboxaldehyde with the biacetyl-trimethylphosphite adduct followed by methanolysis does not provide the expected symmetrically 3-substituted acac, $FcCH(C(O)CH_3)_2$. Instead, the α-diketone product 1-ferrocenyl-1,2-propanedione (**1**, $Fc\text{-}C(O)C(O)CH_3$) was formed, and when slight modifications of Ramirez' experimental conditions were applied, two new C_4 side-chain containing ferrocenyl complexes, 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (**2**, $Fc\text{-}CH(OCH_3)C(CH_3)(OH)C(O)CH_3$) formed diastereoselectively, and the ferrocenyl enone, 4-ferrocenyl-3-methyl-3-buten-2-one (**3**, $Fc\text{-}CH{=}C(CH_3)C(O)CH_3$), were obtained (see formulae in Scheme 2). Herein, we wish to present their isolation, full analytical and spectroscopic characterization, as well as their molecular and crystal structures.

2. Experimental

2.1. General Experimental Methods

Reactions were performed under dry nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled under dinitrogen by standard methods prior to use. All chemicals were purchased from commercial sources and used without further purification. The phospholene 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene was prepared using the literature method [15]. IR spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrophotometer, in the range 4000-450 cm^{-1}. ^{1}H and ^{13}C NMR spectra were

recorded on a 400 MHz Bruker Avance III 400 spectrometer at 298 K. Chemical shifts (δ) are reported in parts per million (ppm) and referenced to the residual deuterated solvent peaks ($CDCl_3$: ^1H δ = 7.26 ppm, ^{13}C δ = 77.16 ppm). Coupling constants (J) are expressed in Hertz (Hz). High resolution electrospray mass spectra (HR-ESI-MS) were collected on a Bruker Q-Tof 2 spectrometer at the Centre Régional de Mesures Physiques de l'Ouest (CRMPO, Rennes). Microanalyses were conducted on a Thermo-FINNIGAN Flash EA 1112 CHNS/O analyzer by the Microanalytical Service of the CRMPO at the University of Rennes 1. Cyclic voltammetry (CV) measurements were performed using a Radiometer Analytical model PGZ 100 all-in one potentiostat, using a three-electrode CEMM with glassy carbon working, Ag/AgCl reference and platinum wire auxiliary electrodes. The ferrocene/ferrocenium ($FcH^{0/+}$) couple was located at $E_{½}$ = 0.507 V, where $E_{1/2}$ was calculated from the average of the oxidation and reduction peak potentials. Migration coefficients (Rf) were determined on silica gel TLC. Melting points were measured in evacuated capillaries on a Kofler Bristoline melting point apparatus and are uncorrected.

2.2. Synthesis of 1-ferrocenyl-1,2-propanedione (1)

To a Schlenk tube loaded with 500 mg (2.34 mmol) of ferrocenecarboxaldehyde were added dropwise by syringe, under dry dinitrogen, 0.60 mL (2.7 mmol) of freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene. The reaction mixture was stirred for 5 days at room temperature (rt), then 5.0 mL of methanol were added and the solution was stirred and refluxed for 4 h. The resulting solution was then evaporated under reduced pressure and the crude oil was purified by column chromatography (3 x 24 cm) using silica gel (70-230 mesh) and a 4:1 mixture of hexane/ethyl acetate as eluent. The ferrocenyl-α-diketone was clearly observed as a purple band on the column (Rf = 0.6). Removal of the solvents and drying under vacuum yielded 180 mg (0.7 mmol, 31%) of **1** as a dark powder. Diffraction-quality single crystals of **1** were obtained as red plates upon cooling a saturated pentane solution for 4 days at -30 °C. M.p. 90-91 °C. HRMS positive ESI, [*m/z*] calcd for $C_{13}H_{12}O_2{}^{56}Fe$: 256.01867; found: 256.0194 (relative error: 3 ppm) $[M]^{\cdot+}$. IR (KBr, cm^{-1}): 3096(vw) ν(C-H arom); 2962 (w), 2918(w), 2849(w), ν(C-H aliph); 1708 (vs), 1643 (vs) ν(C=O). ^1H NMR (400 MHz, $CDCl_3$): 2.48 (s, 3H, CH_3), 4.23 (s, 5H, C_5H_5), 4.70 (t, J_{HH}=1.83 Hz, 2H, C_5H_4), 5.03 (t, J_{HH}= 1.83 Hz, 2H, C_5H_4). ^{13}C chemical shifts were deduced from HMQC and HMBC spectra: 25.5 (CH_3), 70.2 (C_5H_5), 71.1 (C_5H_4), 73.9 (C_5H_4), 98.8 (C_{ipso} C_5H_4), 194.1 (COC_5H_4), 199.2 ($COCH_3$).

2.3. Synthesis of 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (2)

To a three necked 100 mL round bottomed flask fitted with a water cooled condenser, containing a magnetic stirbar and 0.60 mL (2.7 mmol) of freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene, were added dropwise by syringe, under dry dinitrogen, a solution of ferrocenecarboxaldehyde (500 mg, 2.34 mmol) in methanol (5.0 mL). The reaction mixture was stirred for 5 min at rt, and then refluxed for 4 h. Upon cooling to rt, 15 mL of CH_2Cl_2 were added and the organic phase was washed with water and dried over $MgSO_4$. After evaporation of the solvents under reduced pressure, the crude oil was purified by chromatography under the same conditions as those described above in section 2.2. Compound **2** was clearly observed as a yellow fraction on the column (Rf = 0.4). Removal of the solvents and drying under vacuum yielded 284 mg (0.90 mmol, 39%) of **2** as a yellow powder. Diffraction-quality single crystals of **2** were obtained as light orange blocks by slow evaporation of a saturated diethyl ether solution for 3 days at rt. M.p. 101-102 °C. Anal. Calc. for $C_{16}H_{20}FeO_3$ (316.17 g mol^{-1}): C, 60.78; H, 6.38. Found: C, 61.14; H, 6.46%. IR (KBr, cm^{-1}): 3438 (vs) ν(O-H); 3096(vw) ν(C-H arom); 2974 (vw), 2940(vw), 2912(vw), 2842 (vw) ν(C-H aliph); 1708 (vs) ν(C=O). ^{1}H NMR (400 MHz, $CDCl_3$): 1.25 (s, 3H, CH_3), 2.03 (s, 3H, COCH_3), 3.41 (s, 1H, C*H*), 3.70 (s, 3H, OCH_3), 4.07 (s, 1H, C*H*), 4.23 (s, 9H, C_5H_4 + C_5H_5). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): 21.20 (CH_3), 26.53 (CO*C*H_3), 60.84 (OCH_3), 66.71 (C_5H_5), 67.25 (C_α C_5H_4), 68.09 (C_β C_5H_4), 68.82 (C-H), 82.11 (*C*-OH), 85.36 (C_{ipso} C_5H_4), 212.54 (C=O). CV: $E_{1/2}$ = 531 mV.

2.4. Synthesis of 4-ferrocenyl-3-methyl-3-buten-2-one (3)

To a Schlenk tube loaded with 500 mg (2.34 mmol) of ferrocenecarboxaldehyde were added dropwise by syringe, under dry dinitrogen, 0.60 mL (2.7 mmol) of freshly prepared 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene. The reaction mixture was stirred for 2 weeks at rt. Then, 10 mL of CH_2Cl_2 were added and the organic phase was washed with water, and dried over $MgSO_4$. After evaporation of the solvents under reduced pressure, the crude oil was subjected to chromatographic purification under the same conditions as those described above in section 2.2. The ferrocenylenone was clearly observed as a red band on the column (Rf = 0.7). Removal of the solvents and drying under vacuum afforded 280 mg (1.04 mmol, 44%) of **3** as a red powder. Diffraction-quality single crystals of **3** were obtained as orange blocks by slow evaporation of a saturated hexane solution for 3 days at rt. M.p. 64-65

°C. Anal. Calc. for $C_{15}H_{16}FeO$ (268.13 g mol^{-1}): C, 67.19; H, 6.01. Found: C, 66.72; H, 5.91%. HRMS positive ESI, [*m/z*] calc. for $C_{15}H_{16}O^{56}Fe$: 268.05505; found: 268.0559 (relative error: 3 ppm) $[M]^{\cdot+}$. IR (KBr, cm^{-1}): 3096(vw) ν(C-H arom); 2988 (vw), 2960 (vw), 2924 (vw) ν(C-H aliph); 1652 (vs) ν(C=O), 1620 (VS) ν(C=C).^{1}H NMR (400 MHz, $CDCl_3$): 1.89 (s, 3H, CH_3), 2.31 (s, 3H, COCH_3), 4.06 (s, 5H, C_5H_5), 4.40 (s, 2H, H_β C_5H_4), 4.46 (s, 2H, H_α C_5H_4), 7.22 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 11.8 (CH_3), 24.7 (COCH_3), 68.4 (C_5H_5), 69.7 (C_α C_5H_4), 69.9 (C_β C_5H_4), 78.1 (C_{ipso} C_5H_4), 132.7 (=*C*-CH_3), 139.4 (=CH), 198.2 (C=O). CV: $E_{1/2}$ = 555 mV.

2.5. Crystal structure determinations

X-ray data for complexes **1-3** were collected at 150(2) K on a Bruker APEXII AXS diffractometer, equipped with a CCD detector, using Mo-Kα radiation (λ = 0.71073 Å). For each compound, a crystal of appropriate size was coated in Paratone-N oil and mounted on a Kaptan loop. The loop was transferred to the diffractometer, centered in the beam, and cooled by a nitrogen flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. The structures were solved by direct methods using *SIR97* [18], and then refined with full-matrix least-square methods based on F^2 (*SHELXL-97*) [19], with the aid of *WINGX* [20], with all non-hydrogen atoms being refined anisotropically. The hydrogen atoms were included in calculated positions and were refined as riding atoms with isotropic displacement parameters. A summary of the details about crystal data, collection parameters and refinement are documented in Table 1, and additional crystallographic details are in the CIF files. ORTEP and Ball-and-Stick views are generated using OLEX2 [21].

Table 1 Crystallographic data, details of data collection and structure refinement parameters for compounds **1-3**

	1	**2**	**3**
Empirical Formula	$C_{13}H_{12}FeO_2$	$C_{16}H_{20}FeO_3$	$C_{15}H_{16}FeO$
Formula mass, g mol^{-1}	256.08	316.17	268.13
Collection T, K	150(2)	150(2)	150(2)
crystal system	Monoclinic	Triclinic	Monoclinic
space group	P 2_1/a	P-1	P 2_1/a
a (Å)	7.2915(14)	8.7953(11)	11.3633(5)
b (Å)	18.688(4)	9.2619(13)	7.6689(4)
c (Å)	8.4140(16)	9.5556(12)	14.8531(7)
α (°)	90	103.201(5)	90
β (°)	110.881(9)	94.868(5)	105.966(2)
γ (°)	90	107.267(5)	90
V (Å^3)	1071.2(4)	713.87(16)	1244.43(10)

Z	4	2	4
D_{calcd} (g cm^{-3})	1.588	1.471	1.431
Crystal size (mm)	0.37 x 0.28 x 0.07	0.51 x 0.32 x 0.17	0.41 x 0.32 x 0.24
F(000)	528	332	560
abs coeff (mm^{-1})	1.386	1.060	1.191
θ range (°)	3.18 to 27.48	3.57 to 27.48	3.61 to 27.47
range h,k,l	-9/9, -23/18, -10/10	-10/11, -12/12, -12/11	-9/14, -9/9, -19/19
No. total refl.	8152	7921	9798
No. unique refl.	2418	3238	2809
Comp. to θ_{max} *(%)*	98.4	99.0	98.7
Max/min transmission	0.908/0.675	0.835/0.743	0.751/0.689
Data/Restraints/Parameters	2418/0/146	3238/0/186	2809/0/156
Final R	R1 = 0.0300	R1 = 0.0285	R1 = R1 =
[I>2σ(I)]	wR2 = 0.0697	wR2 = 0.0745	0.0273 wR2 = 0.0690
R indices (all data)	R1 = 0.0354 wR2 = 0.0720	R1 = 0.0319 wR2 = 0.0767	R1 = 0.0319 wR2 = 0.0718
Goodness of fit / F^2	1.031	1.055	1.037
Largest diff. Peak/hole (eÅ^{-3})	0.441 and -0.349	0.360 and -0.311	0.349 and -0.272

3. Results and Discussion

Each substituted ferrocene derivative **1**-**3** was generated from the same starting materials by reactions between ferrocenecarboxaldehydes (FcCHO) and 2,2,2-trimethoxy-4,5-dimethyl-1,3,2-dioxaphospholene upon varying the experimental conditions as depicted in Scheme 2. They were isolated as crystalline colored solids, air stable and moisture insensitive on storage under ordinary conditions. Compound **1** is poorly soluble in common organic solvents, whereas **2** and **3** are very soluble in diethyl ether and dicloromethane, but slightly soluble in n-hexane or pentane. Their composition and identity were deduced from elemental analysis, FT-IR and multinuclear and 2D NMR spectroscopy, and mass spectrometry (see Sections 2.2-2.4 for details). Additionally, the crystal and molecular structures of the three complexes **1**-**3** were determined by single crystal X-ray diffraction analysis.

Scheme 2 Conditions: (a) 5 days at rt and then 4 h reflux in methanol, (b) 5 min at rt and then 4 h reflux in methanol, (c) 2 weeks at rt.

3.1. Isolation, characterization and X-ray diffraction study of 1-ferrocenyl-1,2-propanedione (1)

Upon attempting to prepare the 3-ferrocenyl-acac by reaction of ferrocenylcarboxaldehyde with a slight excess of neat freshly prepared biacetyl-trimethyl phosphite 1:1 adduct for five days at room temperature before addition of methanol and refluxing for four hours (Scheme 2, path a), the dark oily residue formed after evaporation of the reaction mixture was chromatographed on silica gel to give 1-ferrocenyl-1,2-propanedione (**1**, Fc-C(O)C(O)CH_3) as the principal isolated product (for details see Section 2.2). The metallocenic α-diketone **1** was isolated as a purple solid in 35% yield.

The solid state IR spectrum of **1** showed two very intense C=O stretching bands at 1708 and 1643 cm^{-1}, supporting the presence of a α-diketone unit. Besides the two downfield shifted triplets at 4.70 (2 H) and 5.03 (2 H) ppm attributed to the protons of the substituted cyclopentadienyl ring, the ^{1}H NMR spectrum exhibited a set of two singlets integrating for 3 and 5 H at 2.48 and 4.23 ppm assigned to the methyl and free cyclopentadienyl protons, respectively. Owing to its insolubility, no ^{13}C NMR spectrum of **1** can be recorded; however, data obtained from HMQC and HMBC spectra provided additional information on the

structure of complex **1** with the two signals in the low field region at 194.1 and 199.2 ppm, which were assigned to the ferrocenoyl and acetyl carbonyl carbons, respectively. Furthermore, high resolution ESI-MS of **1** gave an exact mass of M/z=256.01867 for $[M]^+$ that matched the calculated value of 256.0194, and the expected isotopic distribution for the molecular ion peak. Such spectroscopic features are in agreement with that reported for their arylated ferrocenyl α-diketone counterparts, Fc-C(O)C(O)-Ar [22].

Red plate-shaped X-ray quality crystals of 1-ferrocenyl-1,2-propanedione (**1**) were obtained upon cooling a saturated pentane solution. Complex **1** crystallizes in the monoclinic centrosymmetric space group $P2_1/a$ with a single molecule in the asymmetric unit. The molecular structure of **1** with the atom labeling scheme is presented in Fig. 1 with selected bond distances and angles given in the caption. Complex **1** consists of a ferrocenyl core substituted with a methyl glyoxal fragment, forming monomeric units that are separated by normal van der Waals distances. The ferrocenyl group with almost eclipsed cyclopentadienyl rings (torsional angle 6.2°) features a typical linear metallocene structure with a ring centroid-iron-ring centroid angle of 177.17°. The ring centroid-iron distances of 1.652 and 1.658 Å for the ring with and without the side chain indicate that there is a Fe(II) oxidation state [23].

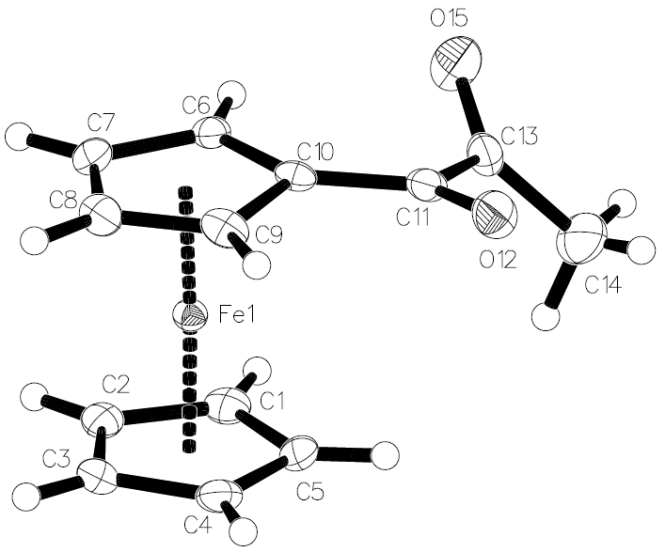


Fig. 1 Molecular structure of **1** with the atom numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) and angles (°): C(10)-C(11) 1.452(3), C(11)-O(12) 1.227(2), C(11)-C(13) 1.545(3), C(13)-O(15) 1.203(2), C(13)-C(14) 1.484(3), avg Fe(1)-C(C_5H_5) = 2.0531(19), avg Fe(1)-C(C_5H_4) = 2.0504(19); C(10)-C(11)-O(12) 124.28(17), O(12)-C(11)-C(13) 117.74(17), C(11)-C(13)-O(15) 119.95(17), O(15)-C(13)-C(14) 123.79(19).

Within complex **1** the fragment C(10)-C(11)-O(12) is almost coplanar with the substituted cyclopentadienyl ring with a dihedral angle of 13.1°, as typically observed in other structurally characterized ferrocenylarylglyoxal derivatives [22] and in the symmetrical 1,2-diferrocenylethanedione [22b]. The torsional angle O(12)-C(11)-C(13)-O(15) takes the values 131.9(2)°. This value is slightly larger than that found in 1,2-diferrocenylethanedione (126.0(8)°) [22b], but much smaller than 180° in butane-2,3-dione ($CH_3C(O)C(O)CH_3$) which is centrosymmetric in the solid state and hence adopt the *trans*-planar conformation [24]. The C(11)-C(13) distance, 1.545(3) Å, is very similar to the lengths measured in its symmetrical counterparts, that is 1.541(10) Å in 1,2-diferrocenylethanedione [22b], and 1.540(6) Å in butane-2,3-dione [24]. The other intramolecular bond lengths and angles are unexceptional and do not deserve further specific comments.

3.2. Isolation, characterization and X-ray diffraction study of 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (2)

When the reaction of freshly prepared biacetyl-trimethylphosphite 1:1 adduct and ferrocenecarboxaldehyde was carried out in a single step, *i.e.* reacting immediately the two reagents in the presence of the methanol, under reflux for 4 h (Scheme 2, path b), the formation of compound **1** was no more observed. Instead, the organometallic hydroxyketone 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (**2**, Fc-$CH(OCH_3)C(CH_3)(OH)C(O)CH_3$) was stereospecifically formed as a single diastereoisomer and isolated as a yellow solid upon chromatography on silica gel (see Section 2.3) in 39% yield.

The solid state FT-IR spectrum of **2** showed two intense bands at 3438 and 1708 cm^{-1}, attributed to the ν(O-H) and ν(C=O) stretching modes, respectively. The former band is shifted to a lower energy as a consequence of a O-H···O intramolecular hydrogen bonding interaction (see below). The ^{1}H NMR spectrum of **2** displayed only a set of signals. The three different methyl groups of the alcoholic, methoxy and acetyl functionalities of the C_4 ferrocenyl side-chain appeared as singlets, integrating each for 3 H, at 1.25, 2.03 and 3.70 ppm, respectively. The β-CH unit gave rise to a singlet at 4.07 ppm, whereas the hydroxyl proton involved in hydrogen bonding interaction with the ether oxygen atom (*vide infra*) was not observed. The presence of only one diastereoisomer in solution is also attested by the ^{13}C NMR spectrum which exhibited a single sharp resonance for each chiral carbon atom at 68.82 (*C*(H)OCH_3), and 82.11 (*C*(OH)CH_3), one signal at 85.36 ppm for the C_{ipso} carbon atom of the

substituted C_5-ring, and one low field resonance at 212.54 ppm for the acetyl carbonyl carbon. Additionaly, the number of signals for the CH_3, C_5H_4 and C_5H_5 groups, and their respective chemical shifts testified to structure **2**, that was further unambiguously confirmed by X-ray crystallographic analysis (see below). The high diastereoselectivity observed in the formation of compound **2** is quite remarkable and can presumably be attributed to a ferrocenyl-mediated transformation of the cyclic saturated oxyphosphorane intermediate **B** in Scheme 1, with R = Fc, which is formed in essentially one diastereomeric form as reported by Ramirez and co-workers [14,15].

Light orange block-shaped X-ray quality crystals of 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (**2**) were obtained by slow evaporation of a saturated diethyl ether solution. Complex **2** crystallizes in the triclinic centrosymmetric space group P-1 with a single molecule in the asymmetric unit. The molecular structure of **2** with the atom labeling scheme is displayed in Fig. 2 with selected bond distances and angles given in the caption. Compound **2** consists of a ferrocene linked to a 3-oxobut-1-yl chain substituted by methoxy groups at the 1-position and by hydroxyl and methyl groups at the 2-position, forming monomeric units that are separated by normal van der Waals distances. Like for **1**, the ferrocenyl entity with slightly stagered cyclopentadienyl rings (torsional angle 14.1°) features a typical linear metallocene structure with a ring centroid-iron-ring centroid angle of 177.92°, and ring centroid-iron distances of 1.650 and 1.651 Å for the free and substituted ring.

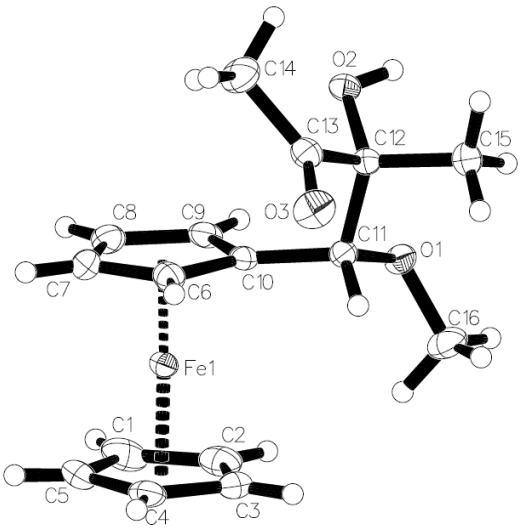


Fig. 2 Molecular structure of **2** with the atom numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) and angles (°): C(10)-C(11) 1.5032(19), C(11)-O(1) 1.4302(16), O(1)-C(16) 1.4082(18), C(11)-C(12) 1.551(2), C(12)-

O(2) 1.4206(17), C(12)-C(15) 1.526(2), C(12)-C(13) 1.529(2), C(13)-O(3) 1.2113(19), C(13)-C(14) 1.492(2), avg Fe(1)-C(C_5H_5) = 2.0450(16), avg Fe(1)-C(C_5H_4) = 2.0392(15); C(10)-C(11)-O(1) 110.51(11), C(11)-O(1)-C(15) 114.98(11), O(1)-C(11)-C(12) 106.71(11), O(2)-C(12)-C(11) 109.58(11), O(2)-C(12)-C(16) 111.59(12), O(2)-C(12)-C(13) 108.08(12), O(3)-C(13)-C(12) 119.12(14), O(3)-C(13)-C(14) 122.13(14).

The X-ray diffraction analysis confirms the diastereoselective formation of **2**, only the diasteroisomer with the R(C11) S(C12) configuration is found in the crystal. The lengths of the C-C, single and double C-O bonds in the side-chain, and of the C-C and C-Fe bonds in the ferrocene sandwiches fall all within the range of standard values [25]. The bond angles at the chiral carbons C(11) and C(12) averaging 109.49(11) and 109.38(12)°, respectively, are idealized values for sp^3-hybridized atoms, whereas the acetyl O(3)-C(13)-C(14) angle of 122.13(14)° is similar to that measured for **1** (123.79(19)°). Finally, an intramolecular hydrogen bond is formed between the hydroxy and ether oxygen atoms (O(1)···O(2) 2.732 Å), thus closing a five-membered heterocycle. The torsion angles between the C-O units of the chain are of 117.74° for O(1)-C(11)-C(12)-O(2), and of 179.63° for O(2)-C(12)-C(13)-O(3) with a O(2)···O(3) separation of 3.515 Å.

3.3. Isolation, characterization and X-ray diffraction study of 4-ferrocenyl-3-methyl-3-buten-2-one (3)

An attempt to isolate the expected intermediate **B** of Scheme 1 (R = Fc) was carried out by reacting neat, for two weeks at room temperature, equimolar amounts of freshly prepared biacetyl-trimethylphosphite 1:1 adduct and ferrocenecarboxaldehyde (Scheme 2, path c). The reaction proven unsuccessful because after extraction and chromatographic purification (see Section 2.4), the known α,β-unsaturated ketone, 4-ferrocenyl-3-methyl-3-buten-2-one (**3**, Fc-CH=C(CH_3)$COCH_3$) [26], was obtained as a red solid in 44% yield. Ferrocenyl-enone **3** was first reported in 1969 as the minor product of the piperidine-catalysed condensation of ferrocenecarboxaldehyde with methyl ethyl ketone in methanol, and as such was partially characterized [26]. Aldol condensation between the same reagents under solvent-free dry conditions gave also **3** as the side product in 10% yield [27]. Compound **3** belongs to the Fc-CH=CH-COR class of ferrocenyl chalcones for which considerable interest has been focused on their broad range of biological activities and especially their role in antimalarial activity [28].

Complex **3** was characterized by satisfactory elemental analysis and its molecular peak at 268.0559 ($M^{\cdot+}$) in the positive ESI mass spectrum (calcd for $C_{15}H_{16}FeO$: 268.05505), with the expected characteristic isotopic distribution pattern of the molecular ion.

The FT-IR spectrum of 4-ferrocenyl-3-methyl-3-buten-2-one (**3**) in a KBr disk showed two strong bands, at 1652 and 1620 cm^{-1}, due to the carbonyl and ethylenic stretching vibrations respectively. This small difference between these two absorption maxima (32 cm^{-1}) is diagnostic of the presence of the *s-trans* rotational isomer, according to a conformational IR study of a series of ferrocenyl-α,β-unsaturated ketones, where differences between carbonyl and olefinic absorption maxima of 34-50 cm^{-1} were attributed to *s-trans* isomers [29]. The ^{1}H NMR spectrum of compounds **3** displays two singlets at 1.89 and 2.31 ppm for the ethylenic and acetyl methyl protons, respectively, one singlet at 7.22 ppm for the olefinic proton, and three resonances for protons of the ferrocenyl fragment. The ^{13}C NMR spectrum confirmed the structure of **3** with the three signals of the enone system at 132.7 (=*C*CH_3), 139.4 (=CH) and 198.2 (C=O), in accordance with chemical shifts reported for 3-Ferrocenyl-2-methyl-1-phenylprop-2-enone having the same substituted α,β-unsaturation [30]. In addition, resonances for carbon nuclei of the ferrocenyl unit and two methyl substituents are present in the ^{13}C NMR spectrum (see Section 2.4).

Although 4-ferrocenyl-3-methyl-3-buten-2-one (**3**) is known for a long time [26], its X-ray diffraction analysis has not been published till now. Thus, we report here its structural characterization by X-ray crystallography. Orange block-shaped X-ray quality crystals of **3** were obtained by slow evaporation of a saturated hexane solution. Complex **3** crystallizes in the monoclinic centrosymmetric space group $P2_1/a$ with a single molecule per asymmetric unit. The molecular structure of **3** with the atom labeling scheme is presented in Fig. 3 with selected bond distances and angles given in the caption. Compound **3** consists of a ferrocene core bearing a 3-oxo-2-methylbut-1-enyl substituent forming monomeric units that are separated by normal van der Waals distances. The ferrocenyl and acetyl substituents adopt the *trans*-conformation about the olefinic linkage. The ferrocenyl entity with eclipsed cyclopentadienyl rings (torsional angle = 1.2°) features a typical linear metallocene structure with a ring centroid-iron-ring centroid angle of 179.70°, and ring centroid-iron distances of 1.644 and 1.646 Å for the free and substituted ring.

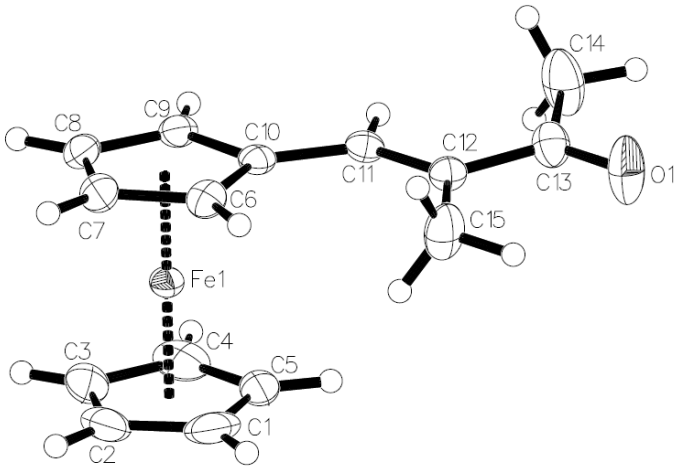


Fig. 3 Molecular structure of **3** with the atom numbering scheme. The thermal ellipsoids are drawn at the 40% probability level. Selected bond distances (Å) and angles (°): C(10)-C(11) 1.461(2), C(11)-C(12) 1.344(2), C(12)-C(13) 1.485(2), C(12)-C(15) 1.499(2), C(13)-O(1) 1.221(2), C(13)-C(14) 1.500(3), avg Fe(1)-C(C_5H_5) = 2.0360 (18), avg Fe(1)-C(C_5H_4) = 2.0444(16); C(10)-C(11)-C(12) 129.46(14), C(11)-C(12)-C(13) 119.93(14), O(1)-C(13)-C(12) 120.17(16), O(1)-C(13)-C(14) 119.35(16).

As expected from the solid state IR data of **3** (see above), the two double bonds of the enone portion, C(11)=C(12) and C(13)=O(1), separated by the C(12)-C(13) single bond are in the *s-trans* conformation, as clearly shown in Fig. 3. This spatial arrangement of the enone unit was also found for its benzoyl counterpart Fc-CH=C(CH_3)-COPh [30], and for the *E*-Fc-CH=CH-CO(Anthryl) derivative [31]. All the other structurally characterized ferrocenyl chalcones of type Fc-CH=CH-COAr (Ar = aryl or heteroaryl) showed the *s-cis* conformation of the enone linkage [32]. The enone unit in **3** is essentially planar with a torsion angle C(11)-C(12)-C(13)-O(1) of 179.36(17)° and is almost co-planar with the substituted cyclopentadienyl ring with a dihedral angle of 8.55°. All the bond lengths and angles are within the normal range found for such ferrocenyl chalcones in previous studies [28, 30-32]. For instance, the ethylenic and ketonic bond lengths are 1.344(2) and 1.221(2) Å, respectively, whereas like in **1** and **2**, the bond angle at the acetyl carbonyl carbon, O(1)-C(13)-C(14), is 119.35(16)°, again very close to the ideal value of 120°.

3.4. Cyclic voltammetry

The electrochemical features of compounds **2** and **3** were investigated by cyclic voltammetry in dichloromethane solution containing 0.1 M *n*-Bu_4NPF_6 as supporting electrolyte. All measurements were carried out in 10^{-3} M solutions at room temperature in the potential range +1.5 to -1.0 V with scan rate 100 mV s^{-1}. Cyclic voltammograms (CV) of solutions containing **2** and **3** show a chemically reversible oxidation process with current ratio i_{pa}/i_{pc} equal to unity, at $E_{1/2}$ = 0.024 and 0.048 V *vs* FcH/FcH^+ couple. The anodic to cathodic peak-to-peak separations are similar to that observed for ferrocene under identical conditions, indicating that it is likely a one-electron oxidation to the respective ferrocenium species $\mathbf{2}^+$ and $\mathbf{3}^+$ at the electrode. In the two cases, the $E_{1/2}$ values are positively shifted with respect to that of free ferrocene, thus featuring some electron withdrawing ability of the side chain. However, compared to the $E_{1/2}$ = 0.25 V *vs* FcH/FcH^+ found for acetylferrocene [33], both C_2 linkers of **2** and **3** switch off the strong electron withdrawing effect of the acetyl fragment, albeit in a lesser extent for the ferrocenyl-containing enone **3**.

4. Conclusion

In this report we have shown that: firstly, although ferrocene is known to react, in many instances, as an organic aromatic compound, in the present work it failed to adopt the similar reaction pathway reported with benzaldehyde or its derivatives [14-16], and secondly, that slightly changing the experimental conditions dramatically modify the outcome of the reaction between the biacetyl trimethylphosphite 1:1 adduct and the ferrocenecarboxaldehyde, leading to the formation of either 1-ferrocenyl-1,2-propanedione (**1**), or 4-methoxy-4-ferrocenyl-3-hydroxy-3-methyl-2-butanone (**2**) as a single diastereoisomer, or 1-(3-oxo-2-methylbut-1-enyl)ferrocene (**3**) with a s-trans conformation of the enone unit. These complexes have been fully characterised by various spectroscopic techniques, elemental analysis, and X-ray diffraction experiments. These three compounds presumably arise from the same intermediate **B** of Scheme 1 (R = Fc) as each of them are made of both [ferrocenyl-C_α] and the acetyl fragments coming from the starting reagents. No attempts were made to try to generate the other complexes starting from isolated **1**, **2** or **3** in refluxing methanol. With aromatic organic aldehydes, it has been postulated that the driving force of the conversion of the oxyphosphorane intermediate **B** (R = Ph) to the final symmetric β-diketone products by methanol could be the loss of trimethylphosphate with the incipient formation of a benzyl carbonium ion [14,15]. In such a rearrangement, the well-known stabilization of the

carbonium ion in α-position by ferrocene, through the fulvene mesomeric form [34], would favor the observed different reaction pathways, depending on the experimental conditions used.

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Appendix A. Supplementary material

CCDC 893249 (for **1**), 893248 (for **2**), and 893250 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.as.uk/data_request/cif.

References

[1] (a) G. Cros, J.-P. Costes, C. R. Acad. Sci. Paris, Ser. IIIc 294 (1982) 173;
(b) G. Bett, D.E. Fenton, J.R. Tate, Inorg. Chim. Acta 54 (1981) L101;
(c) J.-P. Costes, D.E. Fenton, J. Chem. Soc., Dalton Trans. (1983) 2235;
(d) J.-P. Costes, Polyhedron 6 (1987) 2169 and references cited therein.

[2] P. Hu, L. Zhang, X. Zhu, X. Liu, L. Ji, Y. Chen, Polyhedron 8 (1989) 2459.

[3] (a) M. Fuentealba, J.-R. Hamon, D. Carrillo, C. Manzur, New J. Chem. 31 (2007) 1815;
(b) A. Trujillo, S. Sinbandhit, L. Toupet, D. Carrillo, C. Manzur, J.-R. Hamon, J. Inorg. Organomet. Polym. Mater. 18 (2008) 81;
(c) M. Fuentealba, A. Trujillo, J.-R. Hamon, D. Carrillo, C. Manzur, J. Mol. Struct. 881 (2008) 76.

[4] (a) Y.-C. Shi, H.-M. Yang, H.-B. Song, C.-G. Yan, X.-Y. Hu, Polyhedron 23 (2004) 567;
(b) Y.-C. Shi, C.-X. Sui, H.-B. Song, P.-M. Jian, J. Coord. Chem. 58 (2005) 363;

(c) Y.-C. Shi, S.-H. Zhang, H.-J. Cheng, W.-P. Sun, Acta Crystallogr. C62 (2006) m407;
(d) Y.-C. Shi, Acta Crystallogr. E61 (2005) m811;
(e) Y.-C. Shi, H.-J. Cheng, S.-H. Zhang, Polyhedron 27 (2008) 3331;
(f) Y.-C. Shi, H.-M. Yang, W.-B. Shen, C.-G. Yan, X.-Y.Hu, Polyhedron 23 (2004) 15;
(g) Y.-C. Shi, H.-M. Yang, W.-B. Shen, C.-G. Yan, X.-Y. Hu, Polyhedron 23 (2004) 1541.

[5] (a) M. Muthu Tamizh, B. F.T. Cooper, C. L.B. Macdonald, R. Karvembu, Inorg. Chim. Acta 394 (2013) 391;
(b) M. Muthu Tamizh, K. Mereiter, K. Kirchner, R. Karvembu, J. Organomet. Chem. 700 (2012) 194.

[6] V. Weinmayr, Naturwissenschaften 45 (1958) 311.

[7] W.C. Du Plessis, T.G. Vosloo, J.C. Swarts, J. Chem. Soc., Dalton Trans. (1998) 2507.

[8] C.R. Hauser, J.K. Lindsay, J. Org. Chem. 22 (1957) 482.

[9 C.M. Zakaria, C.A. Morrison, D. McAndrew, W. Bell, C. Glidewell, J. Organomet. Chem. 485 (1995) 201.

[10] E. I. Klimova, T. Klimova, J. M. Méndez Stivalet, C. Alvarez Toledano, R. Alfredo Toscano, S. Hernández Ortega, L. Ruíz Ramírez, L. V. Bakinovsky, M. Martínez García, Eur. J. Org. Chem. (2004) 1714.

[11] S. Celedon, M. Fuentealba, T. Roisnel, J.-R. Hamon, D. Carrillo, C. Manzur, Inorg. Chim. Acta 390 (2012) 184.

[12] D. Kalaitzakis, J.D. Rozzell, I. Smonou, S. Kambourakis, Adv. Synth. Catal. 348 (2006) 1958.

[13] (a) E.V. Shchegol'kov, Y.V. Burgart, O.G. Khudina, V.I. Saloutin, O.N. Chupakhin, Russ. Chem. Rev. 79 (2010) 31;
((b) M. N. Kopylovich, M. J. Gajewska, K. T. Mahmudov, M. V. Kirillova, P. J. Figiel, M. F. C. Guedes da Silva, B. Gil-Hernández, J. Sanchiz, A. J. L. Pombeiro, New J. Chem. 36 (2012) 1646.

[14] (a) F. Ramirez, A.V. Patwardhan, N. Ramanathan, N.B. Desai, C.V. Greco, S.R. Heller, J. Am. Chem. Soc. 87 (1965) 543;
(b) F. Ramirez, S.B. Bhatia, A.V. Patwardhan, C.P. Smith, J. Org. Chem. 32 (1967) 3547.

[15] F. Ramirez, N. Ramanathan, N.B. Desai, J. Am. Chem. Soc. 84 (1962) 1317.

[16] a) C. Pariya, Y.S. Marcos, Y. Zhang, F.R. Fronczek, A.W. Maverick, Organometallics 27 (2008) 4318;
(b) C. Pariya, C.R. Sparrow, C.K. Back, G. Sandí, F.R. Fronczek, A.W. Maverick, Angew. Chem., Int. Ed. 46 (2007) 6305.
[17] For example, ferrocene can be easily acetylated with acetyl chloride in the presence of $AlCl_3$: R.B. Woodward, M. Rosenblum, M.C. Whiting, J. Am. Chem. Soc. 74 (1952) 3458.
[18] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
[19] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
[20] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[21] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, J. Appl. Crystallogr. 42 (2009) 339.
[22] (a) Ar = Ph: C. Glidewell, M. J. Gottfried, J. Trotter, G. Ferguson, Acta Crystallogr. C52 (1996) 773;
(b) Ar = 4-biphenylyl: C. Glidewell, S. Z. Ahmed, M. Gottfried, P. Lightfoot, B. J.L. Royles, J. P. Scott, J. Wonnemann, J. Organomet. Chem. 530 (1997) 177.
(c) Ar = 5-nitrothien-2-yl : I.-Y. Wu, J. T. Lin, C.-S. Li, W. C. Wang, T. H. Huang, Y. S. Wen, T. Chow, C. Tsai, Tetrahedron 55 (1999) 13973.
[23] J.D. Dunitz, L.E. Orgel, A. Rich, Acta Crystallogr. 9 (1956) 373.
[24] K. Eriks, T. D. Hayden, S. Hsi Yang, I. Y. Chan, J. Am. Chem. Soc. 105 (1983) 3940.
[25] (a) F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. (1987) S1;
(b) A.G. Orpen, L. Brammer, F.H. Allen, D. Kennard, D.G. Watson, R. Taylor, J. Chem. Soc., Dalton Trans. (1989) S1.
[26] H. Kono, M. Shiga, I. Motoyama, K. Hata, Bull. Chem. Soc. Jpn. 42 (1969) 3273.
[27] W.-Y. Liu, Q.-H. Xu, B.-H. Chen, Y.-X. Ma, Synth. Commun. 32 (2002) 171.
[28] R. Arancibia, C. Biot, G. Delaney, P. Roussel, A. Pascual, B. Pradines, A.H. Klahn, J. Organomet. Chem. 723 (2013) 143 and references cited therein.
[29] H. Kono, M. Shiga, I. Motoyama, K. Hata, Bull. Chem. Soc. Jpn. 43 (1970) 1435.
[30] D.I. Mendez, E. Klimova, T. Klimova, L. Fernando, S.O. Hernandez, M.G. Martinez, J. Organomet. Chem. 679 (2003) 10.
[31] Y. Jung, K.-I. Son, Y. Eui Oh, D.-Y. Noh, Polyhedron 27 (2008) 861.

[32] (a) S. Attar, Z. O'Brien, H. Alhaddad, M. L. Golden, A. Calderón-Urrea, Bioorg. & Med. Chem. 19 (2011) 2055;
(b) S.-K. Lee, Y.-S. Noh, K.-I. Son, D.-Y. Noh, Inorg. Chem. Commun. 13 (2010) 1343;
(c) K.-I. Son, D.-Y. Noh, J. Korean Chem. Soc. 51 (2007) 591;
(d) X. Wu, E. R.T. Tiekink, I. Kostetski, N. Kocherginsky, A. L.C. Tan, S. Beng Khoo, P. Wilairat, M.-L. Go, Eur. J. Pharm. Sci. 27 (2006) 175;
(e) M.-Y. Teng, X.-B. Mao, Q.-B. Song, E. R. T. Tiekink,Acta Crystallogr. E62 (2006) m968;
(f) V. Kudar, V. Zsoldos-Mády, K. Simon, A. Csámpai, P. Sohár, J. Organomet. Chem. 690 (2005) 4018.
[33] N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.
[34] D. Astruc, Organometallic Chemistry and Catalysis, Springer, Heidelberg, 2007, pp. 251-288.