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Cyclisation of diferrocenylbutadiyne dicobalt hexacarbonyl mono-adduct to novel ferrocenotropones

Gerhard Laus [a], Herwig Schottenberger [b,*], Josef Lukasser [b], Klaus Wurst [b], Johannes Schütz [c], Karl-Hans Ongania [d], László Zsolnai [b]

[a] *Immodal Pharmaka GmbH, Bundesstrasse 44, 6111 Volders, Austria*
[b] *Institute of Inorganic Chemistry, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria*
[c] *Department of Pharmaceutical Chemistry, Institute of Pharmacy, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria*
[d] *Institute of Organic Chemistry, University of Innsbruck, Innrain 52a, 6020 Innsbruck, Austria*

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Abstract

Treatment of 1,4-diferrocenyl-1,3-butadiyne dicobalt hexacarbonyl complex **(1)** [CARN: 178388-65-3] with trifluoroacetic acid resulted in cyclisation with concomitant CO insertion to give the green 2,3-ferroceno-7-ferrocenyl-4,5-dehydrotropone dicobalt hexacarbonyl (**2**), which in turn was converted by trifluoroacetic acid to red 2,3-ferroceno-7-ferrocenyltropone (**3**). The first step implied the involvement of a second dicobalt hexacarbonyl complex as a CO source. The molecular structures of **2** and **3** were determined by single crystal X-ray analysis, and pairs of enantiomers with different conformations were observed in **3**.

Keywords: Alkyne dicobalt hexacarbonyl; Alkynyl ferrocene; Crystal structure; HPLC; Tropone

1. Introduction

In earlier work, we reported on allyl, allenyl and fluorenyl cations stabilised by adjacent organotransition-metal donor groups, and even polyferrocenyl-substituted cumulenic carbocations [1]. Another area of interest were ferrocene-derived alkynes [2], and it appeared compelling to expand our research into the field of vinyl cations. Vinyl cations are readily generated in trifluoroacetic acid (TFA) by protonation of alkynes [3]. Previously, it was shown that these cations can be captured by solvent molecules to give trifluoroacetoxycarbenium ions, and the corresponding ketones were isolated after hydrolysis [3]. In the case of ferrocenylvinyl cations, the rate of solvent capture was found to be sensitive to alkyl substitution in the ferrocene rings, and when the β-vinyl position was sterically obstructed the cation was extremely resistant to nucleophilic addition [4]. ^{1}H NMR spectroscopical observation of vinyl cations and their TFA adducts was reported [4].

Moreover, inter- and intra-molecular trapping may occur. Thus, intra-ionic cyclisation of ferrocenyl-stabilised vinyl cations was observed when a neighbouring π-system was available [5]. As an alkyne dicobalt hexacarbonyl group is known to possess less cation-stabilising capacity than a ferrocene group [6], it was anticipated that, in a disubstituted alkyne with competing donors, α-ferrocenyl cationic sites would prevail over Co-complexed propargyl cations [7]. In view of possible Pauson–Khand reactions [8] and other cobalt-mediated cyclisations with multiple carbon–carbon bond formations [9], it seemed to be of interest to explore the chemistry of a ferrocenyl-stabilised vinyl

* Corresponding author. Tel.: +43 512 507 5118; fax: +43 512 507 2934.
E-mail address: herwig.schottenberger@uibk.ac.at (H. Schottenberger).

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cation with an additional neighbouring cobalt carbonyl cluster.

2. Results and discussion

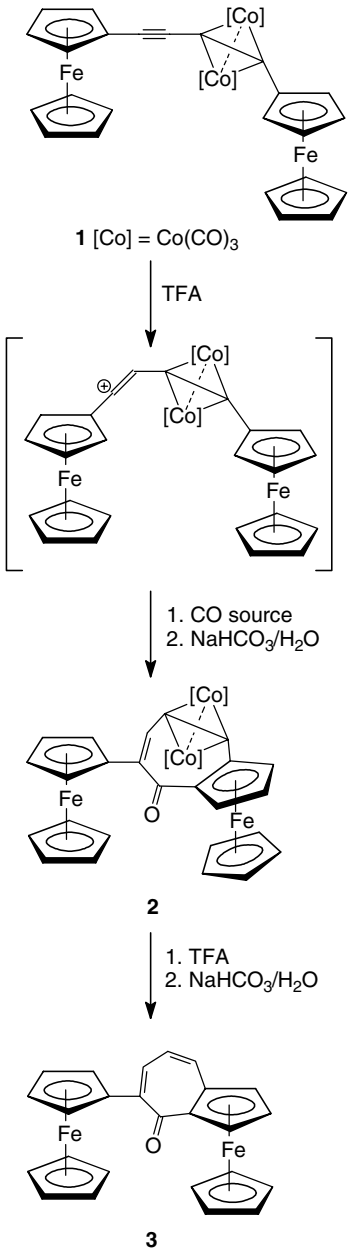
1,4-Diferrocenyl-1,3-butadiyne dicobalt hexacarbonyl (**1**) was treated with TFA to create the corresponding vinyl cation and to study the subsequent reactions. Formation of the cation adjacent to the ferrocene group was expected [6], but all attempts to observe the vinyl cation or its TFA adduct by ^{1}H NMR were futile. The NMR signals collapsed within a few minutes, possibly due to the formation of intermediate paramagnetic species. Obviously, no solvent addition took place, since no ketones were formed upon immediate hydrolysis, and only starting material was recovered, confirming that this cation was sterically shielded from nucleophilic attack. However, when the reaction was terminated after 3 hours, the green dicobalt hexacarbonyl complex of 2,3-ferroceno-7-ferrocenyl-4,5-dehydrotropone (**2**) was isolated. Thus, a formal [6 + 1] cyclisation with incorporation of carbon monoxide has occurred, with another molecule acting as the source of the CO. This explained the rather modest yield, but the structure of the product also confirmed the expected site of protonation. The rate of reaction was found to be quite variable, and therefore the transformation had to be monitored by TLC to get acceptable preparative results.

A different product was obtained after prolonged reaction time. The dicobaltatetrahedrane completely decomposed in TFA to give the red ferrocenotropone **3** (Scheme 1). Such a decomplexation usually requires reductive conditions to afford alkenes.

The X-ray diffraction data of the products revealed some notable features. In compound **2**, the average torsion angle of the fused ferrocene subunit is 26°, whereas that of the σ-bonded subunit is 12° (Fig. 1); the Co–Co bond length is 2.473(1) Å, and the C(30)–C(31) bond length in the tetrahedrane is 1.337(8) Å, the shortest of all ring bonds. The pivotal angles C(29)–C(30)–C(31) and C(30)–C(31)–C(32) are 130.7(5)° and 135.0(5)°, respectively, showing extreme deviation from sp hybridisation. Both compounds display planar chirality. Interestingly, in the crystal of compound **3**, with two molecules in the asymmetric unit, one enantiomer displays an average torsion angle of the fused ferrocene subunit of 19° and that of the σ-bonded of 7°; in the other enantiomer the fused subunit is virtually eclipsed (<2°), and the σ-bonded unit is twisted by only 3° (Fig. 2). Such enantiomers with different conformations have been also called conformational diastereomers.

Details of the data collection, cell dimensions and structure refinement are given in Table 1.

A kinetic study of the reaction starting with **1** by HPLC was not conclusive, most likely due to the poor solubility of **1** in TFA. However, the conversion of isolated **2** in TFA to **3** clearly followed a pseudo-first order rate law, as derived from a linear plot of ln*c* vs. *t* up to a degree of reaction of 0.95. It was also found that HBF_4 or concentrated H_2SO_4 were not effective for this transformation, giving inseparable mixtures.



Scheme 1.

A related TFA-mediated cyclisation of alkyne dicobalt hexacarbonyl complexes with concomitant CO insertion to the corresponding Pauson–Khand cyclopentenone has been reported previously [10]. Dicobalt hexacarbonyl complexes of silylalkynes have been also reported to give alkenes upon TFA treatment in a protonolysis of C–Co bonds [10]. Only one other ferrocene-anellated tropone was found in the literature, i.e., 4,5-ferrocenotropone,

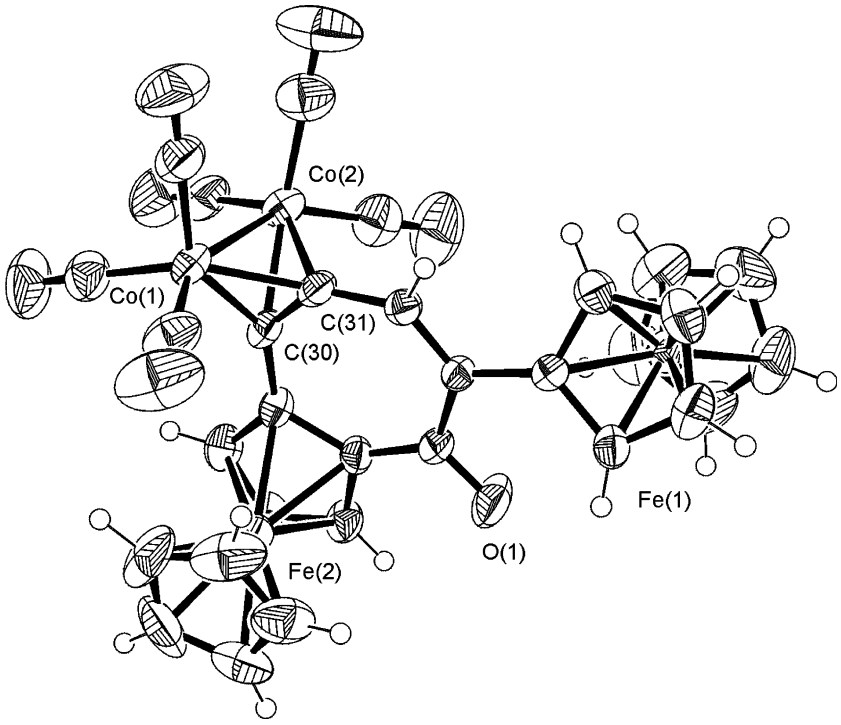


Fig. 1. ORTEP View of **2** drawn with 50% displacement ellipsoids.

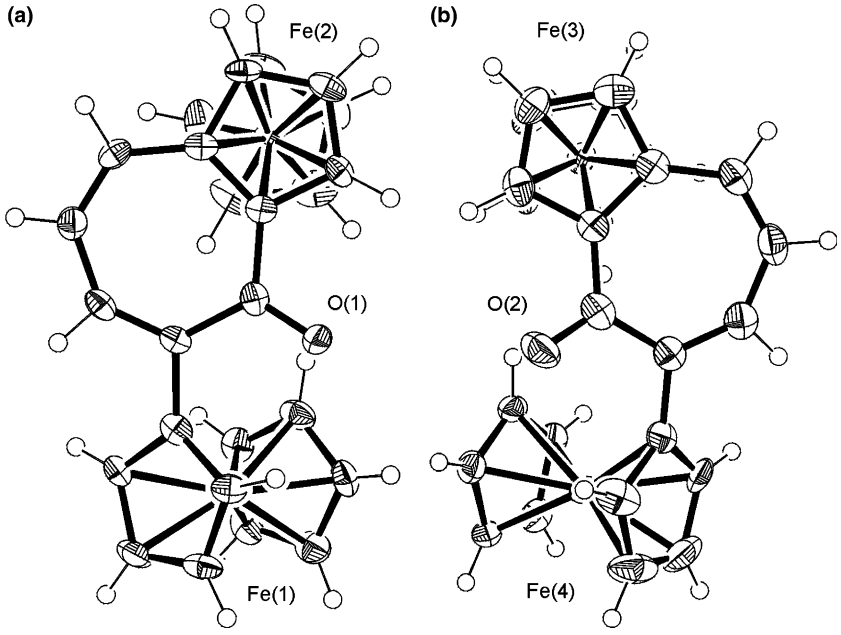


Fig. 2. ORTEP View of **3** drawn with 50% displacement ellipsoids; the fused *Fc* subunits of the two enantiomers are (a) twisted and (b) nearly eclipsed.

which was obtained by a trivial condensation of ferrocene-1,2-dicarbaldehyde with acetone [11].

Although the mechanistic picture is only tentative at the moment, the reactions described here should be of interest for further mechanistic studies. Certainly, the use of a CO atmosphere or, possibly, a metal carbonyl catalysed version are among the synthetic variations worthwhile to be explored. In a preliminary experiment, the conversion of **1** to **2** was attempted in the presence of gaseous CO, but the expected product was accompanied by at least two new byproducts. It was decided not to pursue this matter at this stage.

Table 1
Crystal data and structure refinement for compounds **2** and **3**

	2	**3**
Molecular formula	$C_{31}H_{18}Co_2Fe_2O_7$	$C_{25}H_{20}Fe_2O$
M_r	732.0	448.1
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Unit cell dimensions		
a (pm)	1636.1(2)	1922.2(8)
b (pm)	1311.6(1)	2137.3(9)
c (pm)	1379.3(2)	1325.9(5)
α (°)	90	90
β (°)	108.64(1)	137.92(2)
γ (°)	90	90
V (nm^3)	2.8046(6)	3.6505(26)
Z	4	8
T (K)	293	200
D_{calc} (g cm^{-3})	1.734	1.631
Absorption coefficient (mm^{-1})	2.224	1.602
F (000)	1464	1840
Color, habit	Green prism	Red prism
Crystal size (mm)	$0.7 \times 0.3 \times 0.25$	$0.2 \times 0.3 \times 0.3$
θ Range for data collection (°)	4.05–24.77	1.58–24.06
Index ranges	$-18 \leqslant h \leqslant 18$, $-15 \leqslant k \leqslant 1$, $-1 \leqslant l \leqslant 15$	$0 \leqslant h \leqslant 21$, $0 \leqslant k \leqslant 24$, $-14 \leqslant l \leqslant 14$
Reflections collected	5340	5722
Independent reflections	4296(R_{int} = 0.0453)	5541 (R_{int} = 0.0588)
Reflections with $I > 2\sigma(I)$	2582	3905
Absorption correction	ψ-scan	ψ-scan
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4295/0/379	4990/0/509
Goodness-of-fit on F^2	1.028	1.055
Final R indices [$I > 2(I)$]	R_1 = 0.0500, wR_2 = 0.0785	R_1 = 0.0521, wR_2 = 0.1190
R indices (all data)	R_1 = 0.1099, wR_2 = 0.0965	R_1 = 0.0876, wR_2 = 0.1395
Largest difference peak and hole (e nm^{-3})	362 and −318	631 and −615

3. Experimental

All reactions were carried out using standard Schlenk techniques. Solvents were deoxygenated, purified and dried prior to use. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200 and Varian Gemini 200 spectrometers. Chemical shifts are quoted relative to Me_4Si. Infrared spectra were measured as KBr pellets on a Nicolet 510 FT-IR spectrometer. High resolution mass spectra were obtained with a Finnigan MAT 95 instrument. Diffraction data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation. The HPLC equipment consisted of a Merck-Hitachi L-6200A pump and an L-4250 UV–Vis detector.

1,4-Diferrocenyl-1,3-butadiyne dicobalt hexacarbonyl (**1**) [CARN: 178388-65-3] [12–14] was obtained from 1,4-diferrocenyl-1,3-butadiyne [CARN: 1273-18-3] along with 1,4-diferrocenyl-1,3-butadiyne bis(dicobalt hexacarbonyl) [CARN: 178388-66-4] [12,14,15]. 1,4-Diferrocenyl-1,3-butadiyne was prepared by strictly following the procedure for the synthesis of the analogous 1,4-diphenyl-1,3-butadiyne [16], providing an extremely easy workup by precipitation compared with earlier protocols.

3.1. rac-2 3-Ferroceno-7-ferrocenyl-4,5-dehydrotropone dicobalt hexacarbonyl (2)

1,4-Diferrocenyl-1,3-butadiyne dicobalt hexacarbonyl (**1**) (1.0 g, 1.42 mmol) was suspended in degassed TFA (25 ml) and stirred under argon at room temperature. The reaction was monitored by TLC (silica, diethyl ether–pentane 1:2). After approximately 3 h, the solvent was evaporated, saturated sodium bicarbonate solution was added, and the mixture was extracted with diethyl ether. Column chromatography (silica gel 60) of the crude product using diethyl ether–pentane (1:2) as eluent yielded 220 mg (21%) of the green product. M.p. 145°C (dec.). IR (KBr): 2087, 2052, 2023, 1997, 1607 cm^{-1}. ^{1}H NMR ($CDCl_3$, TMS): 4.16 (s, 5H), 4.20 (s, 5H), 4.40 (m, 2H), 4.75 (m, 1H), 4.82 (m, 2H), 4.94 (m, 1H), 5.19 (m, 1H), 7.94 (s, 1H) ppm. ^{13}C NMR ($CDCl_3$, TMS): 68.8, 69.3, 69.6, 69.8, 70.6, 70.7, 71.4, 71.8, 73.7, 84.2, 87.9, 129.0, 131.0, 133.3, 141.7, 192.8,

198.2, 199.6 ppm. HRMS (FAB): 732.8502 (M + H), $C_{31}H_{19}Co_2Fe_2O_7$ requires 732.8488.

3.2. rac-2 3-Ferroceno-7-ferrocenyltropone (3)

1,4-Diferrocenyl-1,3-butadiyne dicobalt hexacarbonyl (**1**) (1.0 g, 1.42 mmol) was suspended in degassed TFA (25 ml) and stirred under argon at room temperature for 24 h. The reaction was monitored by TLC (silica, diethyl ether–pentane 1:2). The solvent was evaporated, saturated sodium bicarbonate solution was added, and the mixture was extracted with diethyl ether. Column chromatography (silica gel 60) of the crude product using diethyl ether–pentane (1:2) as eluent yielded 150 mg (24%) of the red product. M.p. 122°C. IR (KBr): 1620, 1603 cm^{-1}. ^1H NMR ($CDCl_3$, TMS): 4.05 (s, 5H), 4.13 (s, 5H), 4.34 (m, 2H), 4.56 (m, 1H), 4.74 (m, 1H), 4.80 (m, 1H), 4.90 (m, 1H), 5.43 (m, 1H), 6.30 (dd, 1H, $J = 11.0$, $J = 9.3$), 7.19 (d, 1H, $J = 11.0$), 7.39 (d, 1H, $J = 9.3$) ppm. ^{13}C NMR ($CDCl_3$, TMS): 68.7, 69.1, 69.6, 70.2, 71.7, 72.3, 73.3, 83.8, 85.3, 86.2, 121.6, 128.8, 130.9, 132.7, 137.3, 138.4 ppm. HRMS (FAB): 449.0254 (M + H), $C_{25}H_{21}Fe_2O$ requires 449.0286.

The same product **3** was obtained by treatment of **2** with TFA (10 mg/ml). The reaction was monitored by HPLC analysis of aliquots (10 μl) sampled from the mixture (containing 10 mg/ml formylferrocene as internal standard) in suitable time intervals. After hydrolysis (1 ml sat. aq. $NaHCO_3$), the sample was subjected to solid-phase extraction on a preconditioned (2 ml CH_3CN, 2 ml H_2O) RP-18 LiChrolut (200 mg, endcapped) column (Merck), washed (1 ml H_2O), and eluted (1 ml CH_3CN). The eluate was diluted (1 ml H_2O) and chromatographed on a LiChrospher 100 RP-18 column (125 × 4 mm, 5 μm, Merck) using a gradient program (0–1 min CH_3CN–H_2O 60:40, 1–2 min to 95:5, 2–7 min 95:5) with a flow of 2 ml min^{-1} at 25 °C and detection at 220 nm. Retention time of **2** was 5.0 min, of **3** 3.7 min. Formylferrocene was eluted at 1.2 min, and traces of **1** could be observed at 6.0 min.

4. Crystallographic data

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 216576 for compound **2** and CCDC No. 216577 for compound **3**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, United Kingdom; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

References

[1] (a) R.H. Herber, B. Bildstein, P. Denifl, H. Schottenberger, Inorg. Chem. 36 (1997) 3586;
(b) J. Lukasser, H. Angleitner, H. Schottenberger, H. Kopacka, M. Schweiger, B. Bildstein, K.-H. Ongania, K. Wurst, Organometallics 14 (1995) 5566;
(c) M. Buchmeiser, H. Schottenberger, Organometallics 12 (1993) 2472.
[2] H. Schottenberger, K. Wurst, M. Buchmeiser, J. Organomet. Chem. 584 (1999) 301.
[3] D. Kaufman, R. Kupper, J. Org. Chem. 39 (1974) 1438.
[4] (a) T.S. Abram, W.E. Watts, J. Chem. Soc., Perkin Trans. 1 (1977) 1522;
(b) T.S. Abram, W.E. Watts, J. Organomet. Chem. 87 (1975) C39;
(c) T.S. Abram, W.E. Watts, J. Chem. Soc., Chem. Commun. (1974) 857.
[5] T.S. Abram, W.E. Watts, J. Chem. Soc., Perkin Trans. 1 (1977) 1527.
[6] R.E. Connor, K.M. Nicholas, J. Organomet. Chem. 125 (1977) C45.
[7] K.M. Nicholas, Acc. Chem. Res. 20 (1987) 207.
[8] (a) I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, J. Chem. Soc., Perkin Trans. 1 (1973) 97;
(b) N.E. Schore, Chem. Rev. 88 (1988) 1081;
(c) Y.K. Chung, Coord. Chem. Rev. 188 (1999) 297.
[9] A.J. Fletcher, S.D.R. Christie, J. Chem. Soc., Perkin Trans. 1 (2000) 1657.
[10] M.L.N. Rao, M. Periasamy, Organometallics 15 (1996) 442.
[11] C. Moise, J. Tirouflet, H. Singer, Bull. Soc. Chim. Fr. (1969) 1182.
[12] N. Duffy, J. McAdam, C. Nervi, D. Osella, M. Ravera, B. Robinson, J. Simpson, Inorg. Chim. Acta 247 (1996) 99.
[13] E. Champeil, S.M. Draper, J. Chem. Soc., Dalton Trans. (2001) 1440.
[14] (a) J. Lukasser, Ph.D. Thesis, University of Innsbruck, Austria, 1994;
(b) H. Schottenberger, J. Lukasser, B. Bildstein, P. Brüggeller, L. Zsolnai, in: 1st JOM Conference, Munich, Germany, 1993.
[15] M.I. Bruce, B.W. Skelton, M.E. Smith, A.H. White, Aust. J. Chem. 52 (1999) 431.
[16] I.D. Campbell, G. Eglinton, Org. Synth. Coll. 5 (1973) 517.