Chemistry of metallacyclic alkenylcarbene complexes V. [1]
Synthesis, structure and S_N2'-type reactions of a chelated iron (η^2-olefin)dioxocarbene complex

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Abstract

The novel ferracyclic (η^2-alkene)carbene complexes of type 3 and 9 are easily accessible either from the corresponding (ω-alkenyl)carbene complexes 1 or from the chelated (η^2-olefin)acyl complex 8, depending on the central metal fragment and the heteroatom substituent X at the carbene carbon atom. X-ray structural data of 9 are provided and compared with those of 3 and similar metallacycles of the 'earlier' transition metals W and Mn. With nucleophiles, 9 yields new (η^2-olefin) complexes bearing a substituted rearranged alkene ligand in an S_N2'-type reaction, thus offering a new method for the α-allylation of carbon nucleophiles like enoxyborates.

Keywords: Metallacycle; Carbene; Iron; Cyclopentadienyl; Alkene; Crystal structure

1. Introduction

In the course of our investigation of unsaturated metallacyclic carbene complexes of late transition metals, we developed an efficient method for the α-dienylation of various carbon nucleophiles by means of reaction with (ω-alkenyl) ironcarbene complexes 1 [2]. This reaction proceeds via initial attack of the nucleophile on the allyl terminus of 1 with formation of an (η^2-olefin)carbene intermediate 2, subsequent Claisen–Ireland-type rearrangement of 2 to the allyl complex 4, and ends with deprotonation, loss of carbon monoxide and η^4-coordination of the organic (3E)-1,3-diene ligand giving 5 (Scheme 1).

Similar S_N2'-type reactions at η^3-allyl complexes of iron are long known, since the investigations of Shvo and coworkers [3] and Aumann et al. [4]. More untypical though is the carbene functionality operating as a leaving group rather than an electrophilic centre for the direct attack of the nucleophile. We could never isolate intermediates 2, but only their aza analogues 3, which

obviously do not rearrange to (3E)-1,3-diene complexes due to the formation of isonitrile ligands at zero-valent central metals being less favourable. So we decided to prepare (η^2-olefin)dioxocarbene complexes of iron more stable than 2 under basic conditions, and to take a closer look at their structural features, their reactivity towards
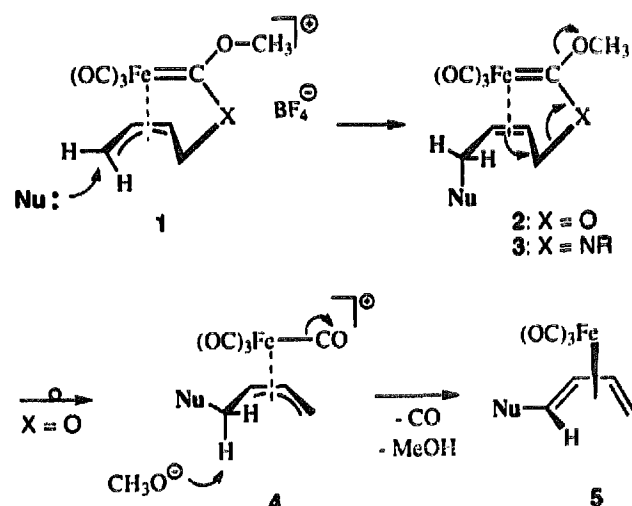
Scheme 1. S_N2'-type rearrangement at (ω-alkenyl-1-ylidene) complexes of iron 1 leading to α-dienylation of nucleophiles.

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[1] Part IV: Ref. [1].

various nucleophiles and their aptitude to similar S_N2'-type rearrangements.

2. Results and discussion

2.1. Synthesis and structure

Only a couple of stable metallacyclic (η^2-olefin)carbene complexes featuring the central metal fragment (η^5-C_5H_5)(OC)Fe^{II} are known, unfortunately none of them with dioxosubstituted carbene carbon atoms [5]. Rosenblum and coworker [6], who were the first to report the synthesis and structural properties of a non-chelated iron (η^2-olefin)dioxocarbene complex bearing this central metal fragment, also described a useful two-step synthesis of the chelated iron (η^2-olefin)acyl complex 8, a suitable precursor to our target system. Reaction of Fp(L)$^+$BF$_4^-$ 6 (L = displaceable donor ligand like THF or isobutene) and allyl alcohol gives first the 'untethered' (η^2-olefin) complex 7 which can be deprotonated and subsequently cyclized to 8 with NEt$_3$ in nitromethane [7]. As in the case of our synthesis of (ω-alkenyl)carbene complexes 1 [8] from the corresponding ferralactones and -lactams (for syntheses and chemistry of ferralactones and -lactams see Ref. [9]), we were able to convert 8 into the cationic (η^2-olefin)carbene complex 9 by Meerwein alkylation with Me$_3$O$^+$BF$_4^-$ in almost quantitative yield (Scheme 2).

Fig. 1 shows the molecular structure of the cation of 9 which forms fairly air-stable, bright yellow crystals of space group $P2(1)/c$. The coordination geometry about the iron centre is roughly octahedral (or pseudo-tetrahedral), most bond distances and angles are in the normal range and as expected. Besides the inherent planar chirality due to the metallacycle, 9 has an additional asymmetric central metal atom. Only isomers
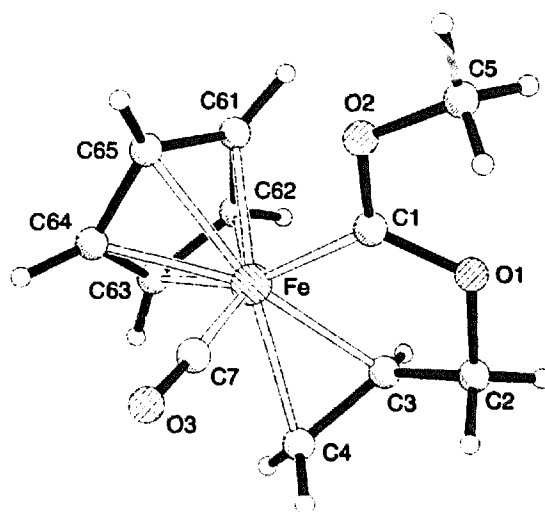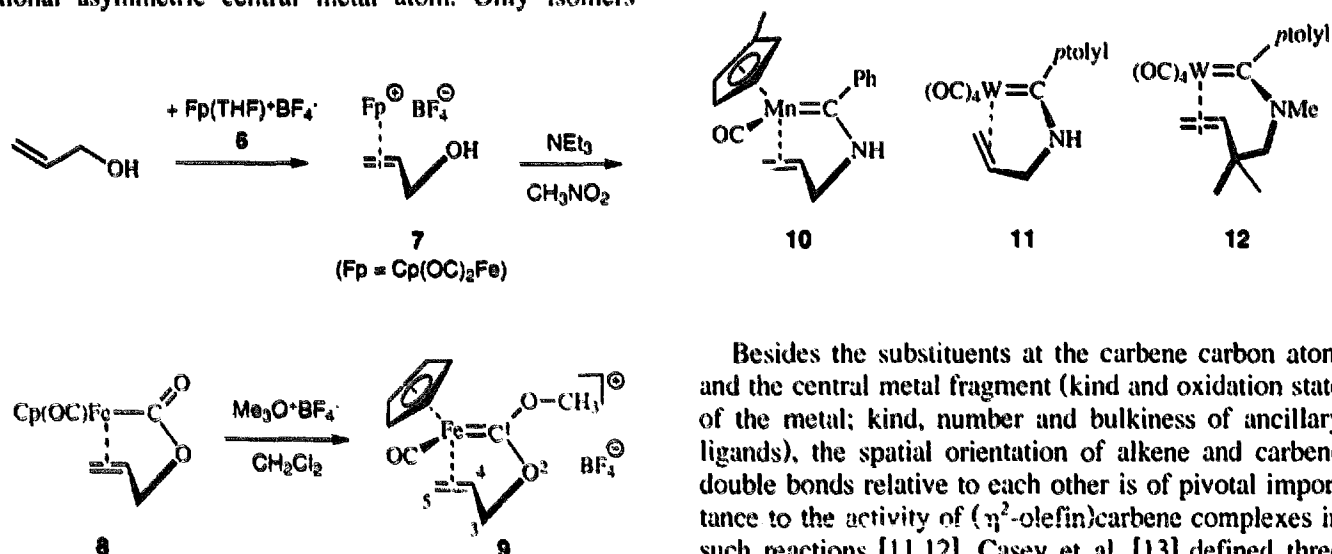

Fig. 1. Molecular structure of the cation of 9. Selected bond lengths (Å) and angles (°): Fe-C1 1.88(9), Fe-C3 2.108(9), Fe-C4 2.143(9), Fe-C7 1.762(11), Fe-C61 2.093(9), C1-O1 1.316(9), C1-O2 1.288(9), C5-O2 1.471(10), C3-C4 1.401(12); C2-C3-C4 118.6(9), C1-Fe-C4 106.3(4), C1-Fe-C3 78.3(4), C1-Fe-C7 88.6(4), C3-Fe-C4 38.5(3).

with E configuration of the C1-O2 bond and with the alkene moiety lying close to and 'underneath' the cyclopentadienyl ligand are formed. [A 3D structure of 9 is downloadable in pdb-format from http://www.organik.uni-erlangen.de/schobert/Fe01.pdb.] Up to now several types of chelated (η^2-olefin)carbene complexes 10–12 of 'earlier' transition metals have been prepared and investigated, especially as model systems for studying prominent transition-metal-mediated alkene reactions like cyclopropanation, metathesis and Ziegler–Natta polymerization [10].

10   11   12

Besides the substituents at the carbene carbon atom and the central metal fragment (kind and oxidation state of the metal; kind, number and bulkiness of ancillary ligands), the spatial orientation of alkene and carbene double bonds relative to each other is of pivotal importance to the activity of (η^2-olefin)carbene complexes in such reactions [11,12]. Casey et al. [13] defined three angles, α, β and γ, to unambiguously describe this orientation. The angle α between the midpoint of the
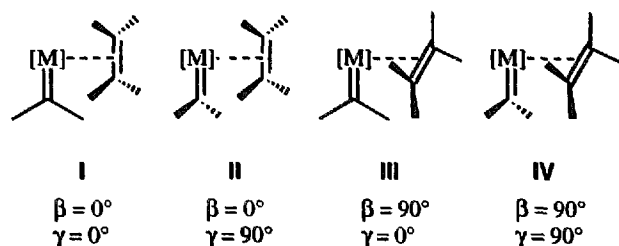

7
(Fp = Cp(OC)$_2$Fe)

8   9

Scheme 2. Rosenblum's synthesis of 8 and Meerwein alkylation to (η^2-olefin)dioxocarbene complex 9.

I   II   III   IV

$\beta = 0°$ $\beta = 0°$ $\beta = 90°$ $\beta = 90°$
$\gamma = 0°$ $\gamma = 90°$ $\gamma = 0°$ $\gamma = 90°$

Fig. 2. Idealized spatial orientations of alkene and carbene moieties in cis metal (η^2-olefin)carbene complexes described according to Casey et al. [13].

olefin, the metal centre and the carbene carbon atom is 180° for trans- and 90° for cis-constellations of these moieties. Only cis complexes bear relevance to the interesting reactions mentioned above. β is defined by the dihedral angle between the plane containing the carbene carbon, the metal and the olefin midpoint and the plane defined by the [MC_2] metal alkene moiety. β is 0° for parallel [M=C] and [C=C] units and 90° for perpendicular arrangements of these groups. The angle γ is independent of olefin rotation and defines the twist between the plane of the carbene carbon, the metal and the alkene midpoint and the mean plane of the carbene group [M=CRR']. Fig. 2 shows four extreme geometries and their description by Casey's angles and Table 1 summarizes the geometrical features and chemical properties of the main types of metallaoxa- and metal-laazacyclic (η^2-olefin)carbene complexes.

Interestingly, 9 and 10 have very small angles γ due to merely restricted rotation about the $M-C_{carbene}$ bond in complexes of the type $CpL_2M=CR_2$ (M = Fe, Mn) for electronic reasons [12,14], and thus possible optimization of the conformational requirements of the chelate ring. By and large complex 9 is geometrically best described as a hybrid of conformations I and III in Fig. 2, suitable for S_N2'-type rearrangements but highly unfavourable for cyclopropanation or metathesis reactions which require β to be close to 0° and γ to be not, as demonstrated by complex 12. The structure and reactivity of 3a resemble those of the tungsten complex 11, as is quite reasonable. Low-valent central metals bearing ancillary carbonyl ligands in combination with a tether length of two atoms between the carbene carbon

and the olefin function are responsible for the observed geometries, and the endocyclic nitrogen substituent at the carbene atom together with an overall complex charge of zero renders both complexes rather inert towards attack of nucleophiles on the olefin terminus. Templeton's manganese complex 10, although having very similar structural features, is far less stable than 9 and 3, presumably due to an uncommon oxidation state of the central metal. Whereas 10 is extremely air sensitive, 3a, being a neutral metallaazacyclic complex as well, is oxidized only by a mixture of H_2O_2 and KOH to give the corresponding urethane in high yield. A last remarkable fact, which can be drawn from Table 1, is that both iron carbene complexes (regardless of their particular charge and central metal fragment) bear an olefin ligand with a comparably long C=C bond distance (1.40 and 1.41 Å respectively). This is distinctly longer than in the cases of all other complexes quoted in Table 1, and might be interpreted as a somewhat stronger bonding interaction between iron and the η^2-alkene ligand and thus more effective activation of the olefin.

2.2. Reactions

9 reacts selectively with certain carbon and heteroatom nucleophiles at the terminal carbon atom C-5 of the η^2-alkene ligand. As in the case of allyl terminated ferracyclic carbene complexes 1, potassium enoxyborates are the carbon nucleophiles of choice. They can easily be prepared in situ by standard procedures [15] and react with 9 straight away at −78 °C. The sole product isolated upon aqueous work-up and subsequent purification is the η^2-olefin complex 13, which has already been prepared by Rosenblum and coworker [16] from 6 and 5-hexene-2-one. 13 is the starting material for Rosenblum's shortcut synthesis of carbopenam systems via iron-mediated annulation reactions [16,17]. Scheme 3 depicts a plausible mechanism for the formation of 13 through initial S_N2'-type attack of the enoxyborate on the alkene terminus C-5 and subsequent recomplexation of the newly generated and shifted olefin moiety. The formation of a cationic ironolefin complex from an enolate and a cationic starting complex is somewhat surprising, but the expulsion

Table 1
Geometric features and reactivities of metallaoxa- and metallaazacyclic (η^2-olefin)carbene complexes

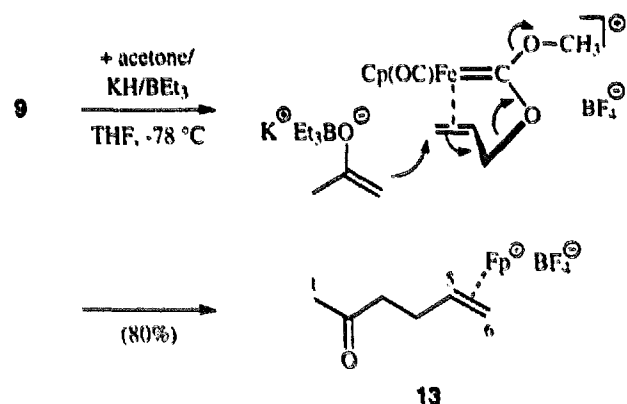| Complex	α (°)	β (°)	γ (°)	$d(M=C)$ (Å)	$d(C=C)$ (Å)	Reactivity
3a [a]	85.5	74.6	31.9	1.96	1.41	stable
9	91.0	45.0	4.5	1.88	1.40	S_N2'-reaction
10	95.9	30.6	7.0	1.89	1.37	very air sensitive
11	76.8	77.0	25.7	2.21	1.38	stable
12	90.7	3.5	42.0	2.18	1.36	cyclopropanation

[a] R = Me, Nu = EtCO(Me)CH; for structural data see Ref. [2].

of the methoxy residue is likely to be furthered by a loose interaction of the methoxy oxygen atom with the Lewis acidic triethylborane, being always present in the mixture in excess. Similar reactions of borontrihalogenides with methoxycarbene complexes have long been known [18].
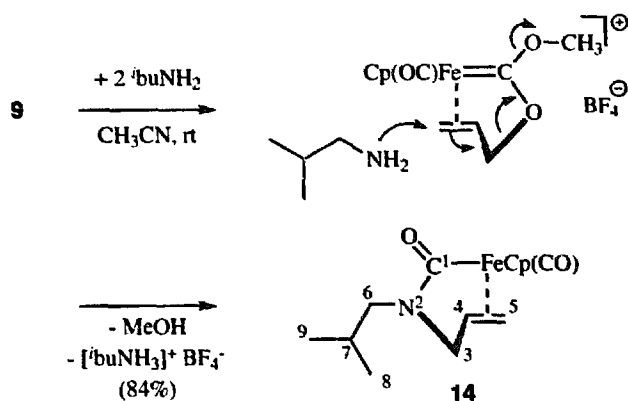
Primary amines as heteroatom nucleophiles react likewise. Once treated with two equivalents of isobutylamine for instance, 9 gives the corresponding ferralactam 14. Initial $S_N 2'$ attack of the amine on the terminal alkene carbon atom C-5 with relocation of the double bond, loss of the methoxy group and recyclization is a plausible mechanistic sequence for this reaction (Scheme 4). The second equivalent of the amine is needed to deprotonate the intermediate ammonium species formed by the initial N–C coupling reaction. The secondary amine thus obtained then undergoes recyclization to 14. When just one equivalent of the amine is used the reaction stops halfway, yielding 14 also but leaving 50% of the starting complex 9 unreacted. This behaviour is quite reminiscent of the reaction of the (ω-alkenyl)carbene complexes 1 with primary amines to give the corresponding rearranged (ω-alkenyl) ferralactam complexes [8].

2.3. Conclusions

Chelated dioxocarbene complexes with a 'two atom' tether between the carbene carbon and the π-donor (η^2-alkene in the case of 9 and η^1-allyl in the case of 1) react with certain carbon and heteroatom nucleophiles in a similar way: attack of the nucleophile on the terminus of the π-donor ligand, rearrangement of the π-system with concomitant loss of a leaving group (either the entire carbene moiety [C(OR)O−] or only the methoxy residue), and recomplexation in one of several ways as the last step. Whereas 1 gives rise to substituted diene complexes 5 on reaction with carbon nucleophiles and to ferralactam complexes on reaction with primary amines, the olefin complex 9 forms a new unchelated

Scheme 4. $S_N 2'$-type reaction of 9 with heteroatom nucleophiles. Formation of a ferralactam.

olefin complex 13 on reaction with enolates but a similar ferralactam on reaction with isobutylamine. Besides the carbene substituents, it is the ring size or tether length respectively that governs not only the structure of complexes like 1 and 9 but also their reactivity towards nucleophiles.

As the novel complex 9 is rather stable, the analogous chelated (η^2-alkene)dioxocarbene complexes 2 featuring a tricarbonyliron(0) central fragment are likely to be isolable as well, once the preparation conditions are carefully chosen and any excess of bases or nucleophiles, leading to deprotonation furnishing 5, is avoided. Pertinent investigations are currently underway.

3. Experimental

3.1. (η^5-Cyclopentadienyl)carbonyl[(4-5-η^2)-1-methoxy-2-oxa-4-pentene-1-ylidene]iron(II)-tetrafluoroborate (9)

A solution of 1.17 g (5.00 mmol) 8 in 10 ml of dry dichloromethane was chilled to 0 °C and then treated with 0.88 g (6.00 mmol; 1.2 equiv.) of Meerwein salt $Me_3O^+BF_4^-$ in one portion. The resulting mixture was stirred at room temperature for 3 h and subsequently evaporated to dryness by means of an oil pump. The crude product thus obtained was purified by column chromatography in ambient atmosphere (silica;

Scheme 3. $S_N 2'$-type reaction of 9 with carbon nucleophiles. α-Alkylation of a potassium enoxyborate.

CH_2Cl_2/CH_3CN, 1:1). Evaporation of the eluate left bright yellow crystals which could be recrystallized from CH_2Cl_2. Yield 1.60 g (4.75 mmol; 95%) of 9, m.p. 96 °C. ^1H NMR (400 MHz, CD_3CN, TMS): $\delta = 3.45$ (d, $^3J(4,5^{en}) = 12.45$ Hz, 1H; 5-H^{en}), 3.64 (dd, $^3J(3^{en},4) = 9.05$, $^2J(3^{en},3^{ex}) = 10.50$ Hz, 1H; 3-H^{en}), 3.73 (d, $^3J(4,5^{ex}) = 7.57$ Hz, 1H; 5-H^{ex}), 4.10 (s, 3H; OCH_3), 5.17 (dd, $^3J(3^{ex},4) = 5.50$, $^2J(3^{en},3^{ex}) = 10.50$ Hz, 1H; 3-H^{ex}), 5.19 (s, 5H; Cp–H), 5.55–5.62 (m, 1H; 4-H). ^{13}C NMR (100.5 MHz, CD_3CN, TMS): $\delta = 56.29$ (OCH_3), 62.03 (OCH_2), 74.21 (C-4), 78.87 (C-5), 89.29 (Cp–C), 215.71 (CO), 255.49 (C=Fe). IR (neat): $\tilde{v} = 2960$ cm^{-1} (s), 2920, 2870 (s), 2050 and 1980 (vs), 1720 (w), 1260 (s), 1100–1020 (s, br.), 810 (s). MS (70 eV): m/z (%): 186 (72) [Cp_2Fe^+], 121 (21) [$CpFe^+$], 100 (36), 69 (20), 59 (67), 41 (100). Anal. Found: C, 39.41; H, 3.91. $C_{11}H_{13}BF_4FeO_3$ (335.87) Calc.: C, 39.34; H, 3.90.

3.2. X-ray structure determination of 9

Clear, bright yellow single crystals were obtained by slowly cooling a solution of 9 in CH_2Cl_2 to -10 °C; formula $C_{11}H_{13}BF_4FeO_3$, molar mass 335.876 g mol^{-1}, crystal size $0.30 \times 0.30 \times 0.20$ mm^3, $a = 7.532(2)$, $b = 10.202(2)$, $c = 17.733(4)$ Å, $\alpha = 90°$, $\beta = 101.56(3)°$, $\gamma = 90°$, $V = 1335.0(5)$ Å^3, $T = 293$ K, $d_{calc} = 1.671$ g cm^{-3}, $\mu = 1.179$ mm^{-1}, $Z = 4$, monoclinic, space group $P2(1)/c$, CAD4-MACH3 diffractometer, $\lambda = 0.71073$ Å, Θ-range 2.32° to 26.33°; ω–Θ scans, index ranges $0 \le h \le 9$, $0 \le k \le 12$, $-22 \le l \le 21$, 2774 collected reflections, 2713 independent reflections [$I >$ $2\sigma(I)$], 181 refined parameters, absorption correction. Structure solution: direct methods (SHELXS86), structure refinement: full-matrix least-squares on F^2 (SHELXL93), $R_1 = 0.0707$ [$w = 1/\sigma^2(F_o)$], $wR_2 = 0.1491$ ([$I >$ $2\sigma(I)$]), largest difference peak and hole 0.588 and -0.527 e Å^{-3}. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405379, the names of the authors and the journal citation. Atomic coordinates and isotropic displacement parameters are given in Table 2.

3.3. (η^5-Cyclopentadienyl)[(5-6-η^2)-5-hexene-2-one]dicarbonyliron(II)-tetrafluoroborate (13) [16]

To a slurry of 123 mg (3.00 mmol) of KH in ca. 5 ml of THF, kept at room temperature, was slowly added 175 ml (2.56 mmol) of acetone with vigorous stirring. After 5 min the unreacted hydride was removed by filtration and the resulting clear, yellowish solution treated with 1.25 equiv. of triethylborane [15]. After a further 5 min the solution thus obtained was transferred with a cannula to a slurry of 572 mg (2.00 mmol) of 9 in 5 ml of dry THF at -78 °C. The reaction was stopped by the addition of one equivalent of a saturated aqueous solution of NH_4Cl after another hour at -78 °C. The mixture was then repeatedly extracted with CH_2Cl_2 and the combined organic extracts dried. The solvent was evaporated and the crude residue purified by recrystallization from CH_2Cl_2–ether. Yield 580 mg (1.60 mmol;

Table 2
Atomic coordinates [$\times 10^4$] and isotropic equivalent displacement parameters [Å$^2 \times 10^3$] for 9

Atom	x	y	z	U_{eq}
Fe(1)	3506(2)	6163(1)	1446(1)	44(1)
C(1)	4561(11)	7578(9)	1008(4)	46(2)
O(1)	3813(7)	8743(6)	872(3)	50(1)
C(2)	2003(12)	8789(9)	1058(5)	62(2)
C(3)	1811(12)	7731(10)	1619(5)	57(2)
C(4)	706(13)	6652(10)	1360(6)	75(3)
O(2)	6089(8)	7487(6)	791(4)	63(2)
C(5)	6742(13)	8583(10)	382(7)	88(4)
C(61)	5859(13)	5983(11)	2298(5)	65(3)
C(62)	4355(14)	5909(11)	2653(5)	66(3)
C(63)	3293(15)	4852(11)	2345(6)	72(3)
C(64)	4157(18)	4231(10)	1804(6)	79(4)
C(65)	5748(15)	4955(10)	1754(6)	70(3)
C(7)	2763(13)	5526(10)	513(6)	62(3)
O(3)	2314(12)	5052(8)	-77(4)	96(3)
B(1)	-716(18)	12146(16)	1216(8)	76(4)
F(1)	-449(11)	13200(9)	1722(4)	131(3)
F(2)	-2447(9)	12184(9)	882(4)	132(3)
F(3)	424(10)	12239(9)	758(4)	137(3)
F(4)	-402(11)	11056(8)	1679(5)	133(3)

U_{eq} is defined as 1/3 of the trace of the orthogonal U_{ij} tensor.

80%) of **13** as a yellow powder. ^{1}H NMR (400 MHz, CD$_3$NO$_2$, TMS): $\delta = 2.15$ (s, 3H; 1-H), 2.70–2.75 (m, 4H; 3-H, 4-H), 3.55 (d, $^3J(5,6^{trans}) = 15$ Hz, 1H; 6-H^{trans}), 3.95 (d, $^3J(5,6^{cis}) = 7.5$ Hz, 1H; 6-H^{cis}), 5.15 (mc, 1H; 5-H). IR (KBr): $\tilde{v} = 2085$ cm^{-1} (s), 2045 (s), 1710 (m), 810 (s).

3.4. (η^5-Cyclopentadienyl)[(4-5-η^2)-2-isobutyl-1-oxo-2-aza-4-pentene-1-yl]carbonyliron(II) (14)

A solution of 672 mg (2.00 mmol) of **9** in 10 ml of dry acetonitrile was treated with 292 mg (400 μl, 4.00 mmol; 2.00 equiv.) of isobutylamine, the resulting solution was subsequently stirred at room temperature for 2 h and then evaporated to dryness by means of an oil pump. The crude product thus obtained was purified by column chromatography in ambient atmosphere (silica; diethylether). Evaporation of the eluate left 485 mg (1.68 mmol; 84%) of **14** as a ropy yellowish oil. ^{1}H NMR (400 MHz, CD$_3$CN, TMS): $\delta = 0.77$ (d, $^3J = 6.7$ Hz, 3H; 8-H), 0.80 (d, $^3J = 6.7$ Hz, 3H; 9-H), 1.85 (m, 1H; 7-H), 2.05 (t, $^3J(3^{cn},4) = {}^2J(3^{cn},3^{cx}) = 10.0$ Hz, 1H; 3-H^{cn}), 2.55 (d, $^3J(4,5^{cn}) = 12.0$ Hz, 1H; 5-H^{cn}), 3.05 (dd, $^3J(6^a,7) = 7.0$, $^2J(6^a,6^b) = 13.5$ Hz, 1H; 6-H^a), 3.20 (dd, $^3J(6^b,7) = 8.5$, $^2J(6^a,6^b) = 13.5$ Hz, 1H; 6-H^b), 3.30 (d, $^3J(4,5^{cx}) = 8.0$ Hz, 1H; 5-H^{cx}), 3.70 (dd, $^2J(3^{cn},3^{cx}) = 10.0$, $^3J(3^{cx},4) = 6.0$ Hz, 1H; 3-H^{cx}), 4.75 (m, 1H; 4-H), 4.80 (s, 5H; Cp–H). IR (neat): $\tilde{v} = 2085$ cm^{-1} (vs), 1585 (s), 1260, 810 (s). MS (70 eV): m/z (%): 289 (33) [M$^+$], 261 (14) [M$^+$ – CO], 233 (88) [M$^+$ – 2CO], 190 (91) [Cp$_2$Fe$^+$], 177 (33), 162 (26), 148 (39), 121 (100) [CpFe$^+$], 56 (28). Anal. Found: C, 58.06; H, 6.65; N, 4.76. C$_{14}$H$_{19}$FeNO$_2$ (289.16) Calc.: C, 58.15; H, 6.62; N, 4.84.

Acknowledgements

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