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# Reactions of lithiated 2,5-dimethylazaferrocene with selected electrophiles

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**Abstract**

Lithiation of 2,5-dimethylazaferrocene **1** with *sec*-BuLi/TMEDA in THF at −78 °C proceeds (as shown by quenching with $D_2O$) to comparable extent on the methyl groups and the Cp ring. However, the outcome of the reaction of the lithiated **1** with an electrophile depends on the nature of this electrophile. In the reaction with 4-methoxybenzaldehyde only the product originated from the lateral lithiation is formed, whereas the reaction with 4-methoxyacetophenone and 4,4′-dimethoxybenzophenone afforded mixtures of the products resulting from lateral and ring-lithiation. Similar results were also obtained in the reaction of lithiated **1** with chlorodiphenylphosphine and diphenyl diselenide. On the other hand, the exclusive formation of the Cp-substituted product was observed in the reaction of lithiated **1** with *N*,*N*-dimethylformamide. The structures of selected products (oily compounds were transformed into the corresponding crystalline $W(CO)_5$-complexes) were confirmed by X-ray diffraction. The presented reactions open a novel entry to specifically substituted azaferrocenes (especially those containing heteroatom substituents) with potential applications as ligands for the homogenous catalysis.


*Keywords:* Azaferrocene; Lithiation; Selectivity; X-ray diffraction

## 1. Introduction

Synthesized forty years ago [1,2], the simplest heteroferrocene, azaferrocene, has recently attracted attention as the backbone of planar chiral nucleophilic catalysts [3], ligands for asymmetric catalysis [4] and a redox active nitrogen ligand enabling novel photoinduced redox processes of metalloporphyrins and metallophthalocyanines [5]. It also undergoes interesting photochemical transformations [6]. Unfortunately, in contrast to the very rich synthetic chemistry of its carbocyclic counterpart, ferrocene, chemistry of azaferrocene is still underdeveloped. This is mainly due to the intrinsic instability of azaferrocene and to the presence of the nucleophilic nitrogen atom, hampering electrophilic substitution reactions [1,7]. Up to now the most promising synthetic strategy for introduction to azaferrocene of desired carbon chains and/or functional groups is based on its lithiation. It has been found that azaferrocene is lithiated by *n*-BuLi to comparable extent on the Cp ring and at the α-position of the pyrrolyl ring [8]. Moreover, reactions of lithiated azaferrocene with electrophiles show unexpected (and yet inexplicable) selectivities, giving (depending on the nature of the electrophile) either Cp- or pyrrolyl-substituted products [9,10]. In the case of 1′,2′,3′,4′,5′-pentamethylazaferrocene the only lithiation site is the α position of the pyrrolyl ligand and a method of generation of enantiomerically pure planary chiral 2-lithio derivatives of this metallocene has recently been elaborated [11,12]. Another interesting problem is the possibility to achieve lateral lithiation of the alkyl groups in 2-position. It has been reported that

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1′,2,2′,3′,4′,5,5′-heptamethylazaferrocene undergoes selective lithiation at the methyl group in the position 2 [13]. In the presence of chiral ligands an enantioselective lateral lithiation was accomplished.

We have previously reported [14] that reaction of 2,5-dimethylazaferrocene **1** with *sec*-BuLi and TMEDA in THF at −78 °C followed by quenching with $D_2O$ furnishes starting metallocene having the deuterium label in the Cp ring (54%), methyl groups (38%) and in the β-positions of the pyrrolyl ligand (8%). However, interestingly, the reaction of lithiated metallocene with benzyl chloride or 4-methoxybenzaldehyde afforded exclusively products resulting from the lateral lithiation.

Herein we report an extension of our preliminary study on a broader range of carbon- and hetero-electrophiles. We found that depending on the nature of the electrophile reacting with lithiated 2,5-dimethylazaferrocene it is possible to obtain products substituted either at the Cp ring or at the lateral methyl group. This opens a novel entry to specifically substituted azaferrocenes (especially those containing heteroatom substituents) with potential applications as ligands for homogenous catalysis.

## 2. Results and discussion

### 2.1. Quenching of the lithiated *1* with $D_2O$

It has been reported [14] that treatment of **1** with *sec*-BuLi and TMEDA in THF at −78 °C for 1.5 h, followed by quenching with $D_2O$ brought about the introduction of deuterium into the Cp ring (54%), methyl groups (38%) and in the β-positions of the pyrrolyl ligand (8%). Now we report that practically the same distribution of the deuterium label was obtained in the absence of TMEDA, and when the reaction time with *sec*-BuLi and TMEDA was limited to 6 min ($^2$H NMR data). This means that there is no equilibration between lithio derivatives having metal in the Cp ring and in the methyl group.

### 2.2. Reaction of the lithiated *1* with selected carbonyl compounds

The above data clearly indicate that reaction of **1** with *sec*-BuLi in THF leads to comparable amounts of laterally and Cp-lithiated products. However, it has been found that treatment of a mixture of these compounds with 4-methoxybenzaldehyde gave **2** as the sole isolable product (obtained in 30% yield along with 50% of recovered **1**). This compound is planar chiral and contains a stereogenic centre in the lateral chain. Thus four stereoisomers are possible (two racemic diastereomers). However, $^1$H NMR data suggested that only one diastereomer was formed. Its stereochemistry will be discussed below (Scheme 1).

In contrast to the above reaction, treatment of lithiated **1** with 4-methoxyacetophenone afforded a mixture of products originating from both ring- and laterally lithiated **1** (**3** and **4**, respectively). These products were isolated by column chromatography in 24% and 13% yield along with recovered **1** (35%). Their structures were confirmed by spectroscopic methods and elemental analyses. The $^1$H NMR spectrum of **3** exhibits four separate signals of protons of the $C_5H_4$ ring (due to the presence of the stereogenic center in the lateral chain one can expect two pairs of diastereotopic protons in this ring), two signals of β-pyrrolyl protons as well as two three-proton signals of the diastereotopic methyl groups. On the other hand, the $^1$H NMR spectrum of **4** shows the five-proton singlet of the unsubstituted Cp ligand and the AB pattern for the diastereotopic protons of the $CH_2$ group. Two sets of signals are observed, which may indicate the formation of two diastereomers in the ∼10:3 ratio.

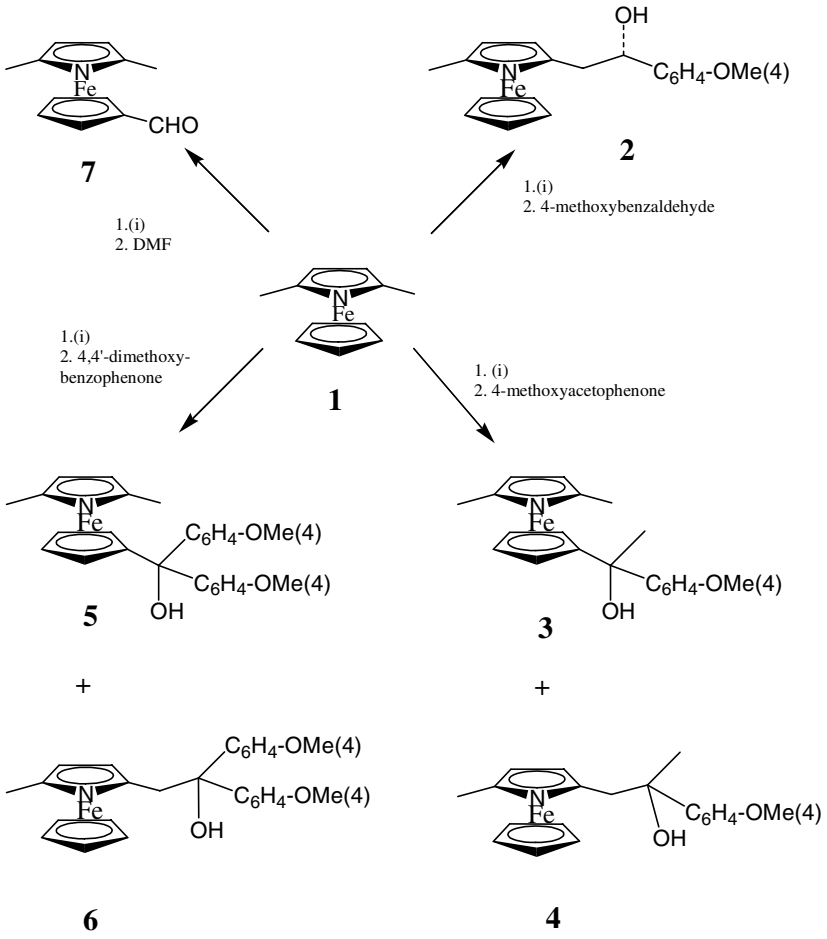
Under the same conditions, lithiated **1** reacted with 4,4′-dimethoxybenzophenone to afford a mixture of regioisomeric products **5** and **6**. These compounds were separated by column chromatography and isolated in 25% and 21% yield, respectively (along with 12% of recovered **1**). Their structures were established by spectroscopic methods as well as by X-ray diffraction (vide infra).

Finally, it has been found that treatment of lithiated **1** with *N*,*N*-dimethylformamide in THF at −78 °C affords exclusively fairly unstable aldehyde **7** isolated as an orange–red oil in 22% yield along with the recovered **1** (40%). The substitution at the Cp-ring was deduced from the $^1$H NMR spectrum of **7** showing in the region of $\delta$ 4–5 ppm three two-proton signals (β-pyrrolyl and two pairs of the $C_5H_4$ protons), as well as a singlet at 2.22 ppm corresponding to six methyl protons and a singlet of the formyl proton at 9.99 ppm.

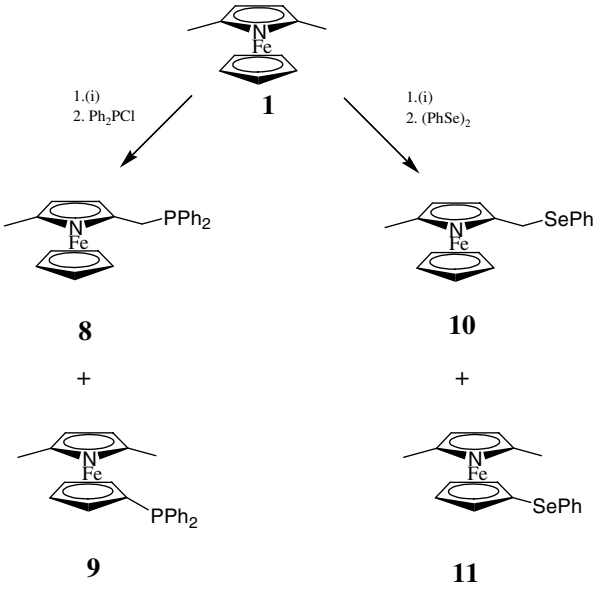
### 2.3. Reaction of lithiated *1* with chlorodiphenylphosphine and diphenyldiselenide

It seemed to us interesting to find out how the lithiated **1** reacts with heteroelectrophiles because such reactions would lead to azaferrocenes containing heteroatoms in lateral chains, potential chelating ligands for homogenous catalysis (Scheme 2).

It has been found that quenching of lithiated **1** with chlorodiphenylphosphine leads a mixture of isomeric products **8** and **9,** having the diphenylphosphino group bound to the lateral carbon and to the Cp ring, respectively. These products were separated by column chromatography and their structures confirmed unequivocally by spectroscopic methods. The $^1$H NMR spectrum of **8** displays two signals of the pyrrolyl β-protons (4.32 and 4.10, each corresponding to one proton) and a singlet of five Cp protons at 4.16 ppm.




Scheme 1. Reaction of lithiated **1** with carbonyl compunds. (i) *sec*-BuLi–TMEDA, THF, −78 °C.



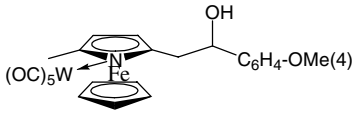

Scheme 2. Reaction of lithiated **1** with heteroelectrophiles: (i) *sec*-BuLi–TMEDA, THF, −78 °C.

Furthermore, two doublets of diastereotopic $CH_2$ protons (3.58 and 3.40 ppm) were observed along with a singlet corresponding to the methyl group (2.26 ppm). The spectrum of **9** shows in the region of 4–4.5 ppm three two-protons signals: the singlet at 4.25 ppm (pyrrolyl β-protons), and two triplets (4.39 and 4.10 ppm) assignable to the protons of the monosubstituted Cp ligand. The protons of the methyl groups give rise to a singlet (6H) at 2.13 ppm. Compounds **8** and **9** are fairly unstable in the air and undergo oxidation to the corresponding P-oxides. Formation of such compounds was evidenced by appearance of signals at ∼28 ppm in the $^{31}P$ NMR spectra ($FcCH_2P(O)Ph_2$ shows signal at 29 ppm [15]) and peaks corresponding to M + 16 (M + O) in the mass spectra of partly oxidized samples.

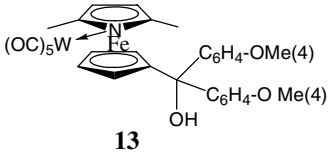
Similarly, the reaction of lithiated **1** with diphenyl diselenide afforded a mixture of the laterally- and Cp-substituted azaferrocenes (**10** and **11**, respectively). These compounds were easily separated by column chromatography and isolated in 26% and 10%, respectively, along with recovered **1** (12%).Their structures were unambiguously confirmed by spectral and analytical data.

### 2.4. X-ray diffraction study of compounds 6, 12 and 13

Most of the synthesized compounds are oils and only **6** afforded crystals suitable for X-ray analysis. However, we have found that reaction of **2** and **5** with photochemically generated $W(CO)_5(THF)$ affords crystalline complexes **12** and **13**, for which X-ray quality crystals were obtained. Crystal data and structure refinement details are given in Table 1.




**12**

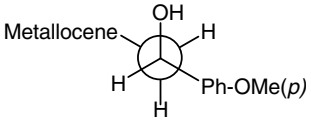



**13**

The molecular structures of compounds **6**, **12** and **13** are shown in Figs. 1–3.

Compound **6** forms in the crystal centrosymmetric dimers via OH–N hydrogen bonds, linking together two enantiomers of this compound (Fig. 1).

Compound **12** is a single, racemic diastereomer. Enantiomers are intercalated and linked by hydrogen bonds between OH groups and CO ligands (Fig. 2(b)). The structure shows the absolute configuration of these enantiomers ($S,R_p$) and ($R,S_p$). The lateral chain adopts an *anti*-periplanar conformation **A**, which minimalizes steric interactions between bulky aryl- and metallocenyl moieties.




**A**

Conformation **A**

Table 1
Crystal data and structure refinement for **6**, **12** and **13**

| Compound | **6** | **12** | **13** |
|---|---|---|---|
| Chemical formula | $2(C_{26}H_{27}NO_3Fe)$ | $C_{24}H_{21}FeNO_7W$ | $C_{31}H_{27}FeNO_8W$ |
| Formula weight | 914.68 | 675.12 | 781.24 |
| $\Lambda$ (Å) | 0.71073 | 0.71073 | 0.71073 |
| $T$ (K) | 100(1) | 100(1) | 100(1) |
| Space group | $P\bar{1}$ | $P2_1/c$ | $P2_1/c$ |
| Crystal system | Triclinic | Monoclinic | Monoclinic |
| Unit cell dimensions | | | |
| $a$ (Å) | 10.702(1) | 9.080(1) | 11.904(1) |
| $b$ (Å) | 11.400(2) | 22.166(2) | 18.361(2) |
| $c$ (Å) | 20.684(2) | 11.677(1) | 13.967(2) |
| $\alpha$ (°) | 94.99(1) | 90 | 90 |
| $\beta$ (°) | 94.30(1) | 95.76(1) | 109.51(1) |
| $\gamma$ (°) | 116.76(1) | 90 | 90 |
| $V$ (Å$^3$) | 2226.1(5) | 2338.3(4) | 2877.5(6) |
| $Z$ | 2 | 4 | 4 |
| $D_c$ (mg/m$^3$) | 1.365 | 1.918 | 1.803 |
| $F(000)$ | 960 | 1312 | 1536 |
| Habit | Plate | Block | Block |
| Crystal size (mm) | $0.4 \times 0.3 \times 0.03$ | $0.4 \times 0.3 \times 0.3$ | $0.3 \times 0.3 \times 0.2$ |
| $\mu$ (mm$^{-1}$) | 0.705 | 5.581 | 4.552 |
| Absorption correction | Analytical | Analytical | Analytical |
| Maximum and minimum transmission | 0.870 and 0.573 | 0.712 and 0.257 | 0.8360 and 0.4885 |
| Type of diffractometer | Kuma KM4CCD $\kappa$-axis diffractometer | | |
| Diffraction geometry | $\omega$ | $\Omega$ | $\omega$ |
| $\theta$ Range (°) | 2.95–28.37 | 3.27–28.41 | 3.02–28.43 |
| Number of reflections measured | 18011 | 14453 | 18891 |
| Number of unique reflections | 9928 | 5443 | 6720 |
| $R_{int}$ | 0.0412 | 0.0267 | 0.0184 |
| Number of observed reflections | 8022[$I > 2\sigma(I)$] | 4892[$I > 2\sigma(I)$] | 6089[$I > 2\sigma(I)$] |
| Refinement method | Least-squares on $F^2$ | | |
| Number of parameters | 613 | 311 | 383 |
| Final $R$ indices[a] [$I > 2\sigma(I)$] | $R_1 = 0.0490$, $wR_2 = 0.1143$ | $R_1 = 0.0207$, $wR_2 = 0481$ | $R_1 = 0.0180$, $wR_2 = 0.0391$ |
| Final $R$ indices[a] (all data) | $R_1 = 0.0666$, $wR_2 = 0.1214$ | $R_1 = 0.0255$, $wR_2 = 0.0494$ | $R_1 = 0.0221$, $wR_2 = 0.0400$ |
| Goodness-of-fit (S) | 1.050 | 1.058 | 1.078 |
| Largest diff. peak and hole e Å$^{-3}$ | 0.835 and −0.438 | 0.647 and −1.330 | 1.207 and −0.623 |

[a] $R1 = \sum\|F^o - |F^c|\| / \sum|F^o|$; $wR_2 = \left\{\sum[w(F_o^2 - F_c^2)^2] \Big/ \sum[w(F_o^2)^2]\right\}^{1/2}$.

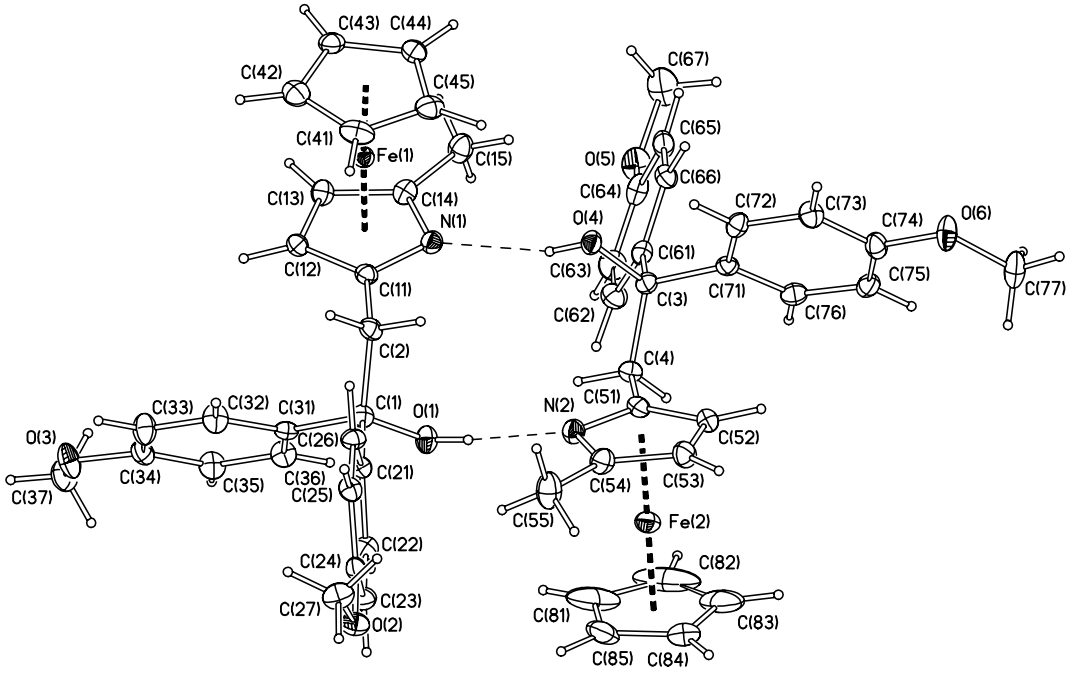



Fig. 1. ORTEP drawing showing dimers of **6**. Selected bond lengths and angles: O(1)–H(1)···N(2) 2.923(3) Å; O(1)–H(1)···N(2) 176°; O(4)–H(4)···N(1) 2.843(3) Å; O(4)–H(4)···N(1) 161°.

This conformation also dominates in solution as indicated by the vicinal coupling constants in the –CH–$CH_2$– system (9.2 and 4.0 Hz) [14].

The molecular packing of compound **12** (Fig. 2(b)) and **13** (not shown) display a network of hydrogen bonds between OH groups and CO ligands.

## 3. Discussion and concluding remarks

The results obtained in this work clearly show that the outcome of the reaction of lithiated **1** with an electrophile depends critically on the nature of this electrophile. It is possible to obtain selectively products coming from either laterally- or Cp-lithiated **1**, or mixtures of them. Unfortunately, at this stage it is not clear which structural features of electrophile determine the regioselectivity of its reaction with lithiated **1**. It is worthy noting that similar behaviour was reported for lithiated parent azaferrocene. The treatment of this compound with *n*-BuLi in THF at −50 °C, followed by quenching with iodomethane afforded a mixture of 2- and 1′-methylazaferrocene and 1′,2-dimethylazaferrocene, suggesting that 2- and 1′-lithioazaferrocenes are formed in comparable amounts along with some amount of 1′,2-dilithioazaferrocene [8]. However, when benzophenone, benzaldehyde, dibenzyl ketone or diisopropyl ketone were used as quenchers the exclusive formation of 2-substituted azaferrocenes was observed [9,10]. On the other hand, reaction of lithiated azaferrocene with cyclohexanone afforded exclusively 1′-substituted product [10].

The observed regioselectivity does not seem to be due to the lack of the reactivity of one of the regioisomeric lithio derivatives of **1** toward a given electrophile. In fact, when reaction mixture after treatment with the electrophile was treated with $D_2O$, the recovered **1** did not contain deuterium (checked by MS spectrum). Another, yet inexplicable feature of the above reactions is the recovery in all cases of considerable amounts of starting **1**. The use of a larger excess of *sec*-BuLi did not bring about decrease of the amount of recovered **1**, but resulted in a sharp decrease of the yields of the reaction products.

The yields of the above-mentioned reactions are rather modest, but the products are easily separated and purified by column chromatography. The lithiation of **1**, followed by reaction with an electrophile constitutes therefore a novel and efficient way to specifically substituted azaferrocenes, that were so far synthetically inaccessible.

## 4. Experimental

### 4.1. General remarks

All reactions were carried out under an atmosphere of argon. Solvents were dried by using standard procedures. Chromatographic purifications were carried out on Silica gel 60 (Merck, 230–400 mesh ASTM). The NMR spectra were determined on Varian Gemini 200 BB (200 MHz for $^1$H) and Bruker DRX500 (500 MHz for $^1$H) in $CDCl_3$ solutions. They were calibrated by

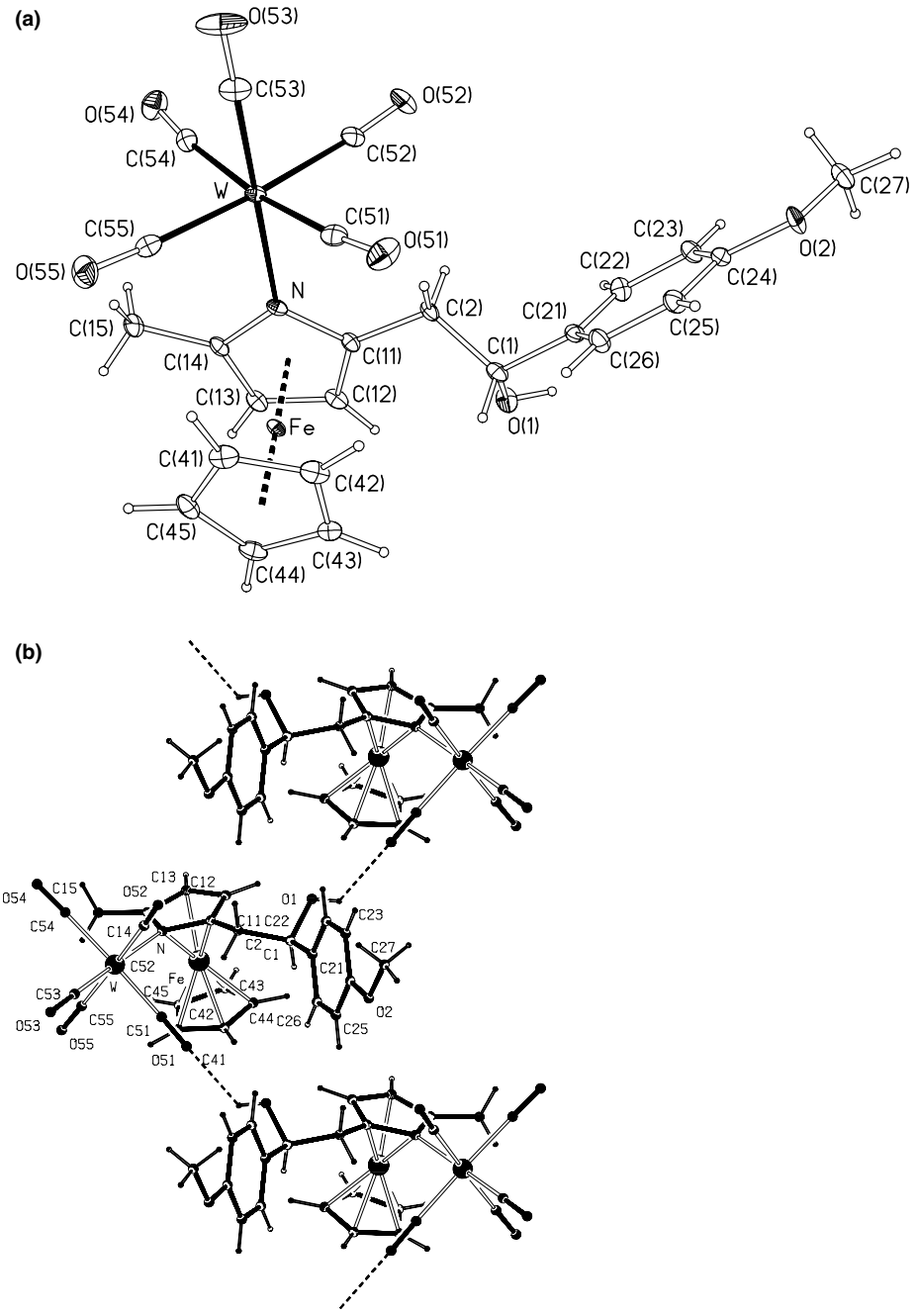



Fig. 2. ORTEP drawing (a) and intermolecular hydrogen bonds in crystals of **12** (b). The distance O(1)–H(1)···O(51) is 2.99(4) Å and the angle O(1)–H(1)···O(51) is 129(4)°.

using internal $Me_4Si$, chloroform ($^1H$) signal or external 85% $H_3PO_4$ ($^{31}P$) references. IR spectra were recorded on a FT-IR Nexus Nicolet apparatus. Mass spectra were run on a Finnigan MAT 95 spectrometer. The combustion analyses were determined by Analytical Services of the Center of Molecular and Macromolecular Studies of the Polish Academy of the Sciences (Łódź).

2,5-Dimethylazaferrocene and compound **2** were prepared according to the literature procedures ([16] and [14], respectively).

### 4.2. Reaction of lithiated *1* with 4-methoxyacetophenone

*sec*-BuLi (1.4 M in cyclohexane, 2.0 ml, 2.8 mmol) was added to an argon-saturated solution of 2,5-dimethylazaferrocene (508 mg, 2.3 mmol) and TMEDA (150 μl, 0.98 mmol) in THF (15 ml) at −78 °C. The orange coloration of the solution rapidly turned brown. After the mixture was stirred for 1.5 h at −78 °C, 4-methoxyacetophenone (771 mg, 5.1 mmol) in 6 ml THF was added and the stirring was continued for

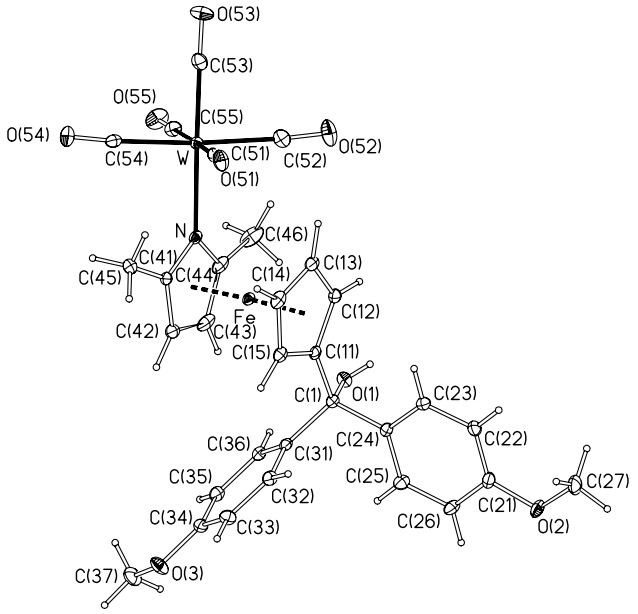



Fig. 3. ORTEP drawing of **13**.

1.5 h. The reaction mixture was allowed to warm to room temperature and poured onto water. Extraction with dichloromethane, drying over $MgSO_4$ and solvent evaporation gave brown oil which was subjected to column chromatography (ethyl acetate–hexane (5:1) as eluent). The following fractions were collected:

First, containining **3** (orange oil). Yield: 210 mg (24%). $^1$H NMR $\delta$ ($CDCl_3$): 7.38 (AB d, 2H, $J$ = 8.8 Hz, $C_6H_4$), 6.83 (AB d, 2H, $J$ = 8.8 Hz, $C_6H_4$), ~5.3 (bs, 1H, OH), 4.38 (m, 2H, β-pyrrolyl, $C_5H_4$), 4.31 (d, 1H, $J$ = 2.2 Hz, β-pyrrolyl), 4.09 (m, 1H, $C_5H_4$), 4.02 (m, 1H, $C_5H_4$), 3.90 (m, 1H, $C_5H_4$), 3.79 (s, 3H, $OCH_3$), 2.36 (s, 3H, $CH_3$–pyrrolyl), 2.11 (s, 3H, $CH_3$–pyrrolyl), 1.77 (s, 3H, $CH_3$). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3311 (OH); 3007, 2931 (C–H). EIMS (70 eV): $m/e$ = 365 $[M]^+$. Anal. Calc. for $C_{20}H_{23}O_2NFe_*1/2H_2O$: C, 64.18; H, 6.46. Found: C, 64.21; H, 6.52%.

Second (orange oil). This fraction was subjected to a second chromatography (chloroform as eluent). The two fractions were collected:

First, containing recovered **1** (orange oil). Yield: 177 mg, (35%). Second, containing **4** as a mixture of diastereomers (10:3 according to $^1$H NMR) (orange oil). Yield: 108 mg (13%).

$^1$H NMR $\delta$ ($CDCl_3$): 7.41 (AB d, $J$ = 8.7 Hz, $C_6H_4$), 7.19 (AB d, $J$ = 8.7 Hz, $C_6H_4$), 6.86 (AB d, $J$ = 8.7 Hz, $C_6H_4$), 6.74 (AB d, $J$ = 8.7 Hz, $C_6H_4$), 4.39 (d, $J$ = 1.9 Hz, β-pyrrolyl), 4.28 (d, $J$ = 1.9 Hz, β-pyrrolyl), 4.23 (d, $J$ = 1.9 Hz, β-pyrrolyl), 4.11 (s, $C_5H_5$), 4.04 (s, $C_5H_5$), 3.78 (s, $OCH_3$), 3.72 (s, $OCH_3$), 3.18 (AB, $J$ = 14.0 Hz, $CH_2$), 3.09 (AB, $J$ = 14.0 Hz, $CH_2$), 2.28 (s, 3H, $CH_3$–pyrrolyl), 2.22 (s, 3H, $CH_3$–pyrrolyl), 1.49 (s, 3H, $CH_3$), 1.27 (s, 3H, $CH_3$). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3377 (OH); 3014, 2972, 2931 (C–H). MS (EI, 70 eV) $m/e$ = 365 $[M]^+$. HRMS: $m/e$ = 365.1066 (Calc. for $C_{20}H_{23}NO_2Fe$: 365.1078). Anal. Calc. for $C_{20}H_{23}NO_2Fe \cdot 2H_2O$: C, 59.86; H, 6.78. Found: C, 60.00; H, 6.27%.

### 4.3. Reaction of lithiated *1* with 4,4′-dimethoxybenzophenone

*sec*-BuLi (1.4 M in cyclohexane, 1.4 ml, 1.9 mmol) was added to an argon-saturated solution of **1** (310 mg, 1.44 mmol) and TMEDA (80 μl, 0.53 mmol) at −78 °C in THF (10 ml). The orange coloration of the solution rapidly turned brown. After the mixture was stirred for 1.5 h at −78 °C, 4,4′-dimethoxybenzophenone (387 mg, 1.6 mmol) in THF (7 ml) was added and the stirring was continued for 1.5 h. The reaction mixture was allowed to warm to room temperature and poured onto water. Extraction with dichloromethane, drying over $MgSO_4$ and solvent evaporation gave brown oil which was subjected to column chromatography (ethyl acetate–hexane (5:1) as eluent). The following fractions were collected:

First, containing **5** (orange foam). Yield: 162 mg (25%). $^1$H NMR $\delta$ ($CDCl_3$): 7.32 (AB d, 4H, $J$ = 8.6 Hz, $C_6H_4$), 6.79 (AB d, 4H, $J$ = 8.6 Hz, $C_6H_4$), 4.32 (s, 2H, β-pyrrolyl), 4.12 (bs, 2H, $C_5H_4$), 4.09 (bs, 2H, $C_5H_4$), 3.77 (s, 6H, $OCH_3$), 2.09 (s, 6H, $CH_3$–pyrrolyl). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3296 (OH), 3007, 2960, 2935, 2839 (C–H). MS (EI, 70 eV) $m/e$ = 457 $[M]^+$. Anal. Calc. for $C_{26}H_{27}O_3NFe$: C, 68.28; H, 5.95. Found: C, 68.19; H, 6.16%.

Second, containing **6** (orange crystals). Yield: 137 mg (21%).$^1$H NMR: $\delta$ ($CDCl_3$): 7.39 (AB d, 2H, $J$ = 8.5 Hz, $C_6H_4$), 7.21 (AB d, 2H, $J$ = 8.5 Hz, $C_6H_4$), 6.82 (AB d, 2H, $J$ = 8.5 Hz, $C_6H_4$), 6.69 (AB d, 2H, $J$ = 8.5 Hz, $C_6H_4$), 4.92 (s, 1H, OH), 4.25 (s, 1H, β-pyrrolyl), 4.16 (s, 5H, $C_5H_5$), 4.14 (s, 1H, β-pyrrolyl), 3.77 (s, 3H, $OCH_3$), 3.72 (s, 3H, $OCH_3$), 3.68 (d, 1H, $J$ = 14.5 Hz, $CH_2$), 3.58 (d, 1H, $J$ = 14.5 Hz, $CH_2$), 2.23 (s, 3H, $CH_3$–pyrrolyl). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3334 (OH); 3007, 296, 2935 (C–H). MS (EI, 70 eV) $m/e$ = 457 $[M]^+$, 439 $[M - H_2O]^+$. Anal. Calc. for $C_{26}H_{27}O_3NFe$: C, 68.28; H, 5.95. Found: C, 68.01; H, 6.16%.

Third, containing recovered **1** (orange oil). Yield: 38 mg, (12%).

### 4.4. Reaction of lithiated *1* with N,N-dimethylformamide

*sec*-BuLi (1.4 M in cyclohexane, 1.0 ml, 1.4 mmol) was added to an argon-saturated solution of 2,5-dimethylazaferrocene (215 mg, 1.0 mmol) and TMEDA (76 μl, 0.50 mmol) in THF (12 ml) at −78 °C. The orange coloration of the solution rapidly turned brown. After the mixture was stirred for 1.5 h at −78 °C, fresh distilled DMF (116 μl, 1.5 mmol) was added and the stirring was continued for 1 h. The reaction mixture was allowed to warm to room temperature and poured onto

water. Extraction with dichloromethane, drying over $MgSO_4$ and solvent evaporation gave brown oil which was subjected to column chromatography (chloroform as eluent). The following fractions were collected:

First, recovered **1** (orange oil). Yield: 86 mg (40%).

Second, containing **7** (orange–red, unstable oil) Yield: 54 mg (22%).$^1$H NMR: $\delta$ ($CDCl_3$): 9.99 (s, 1H, CHO), 4.77 (s, 2H,$C_5H_4$), 4.60 (s, 2H, $C_5H_4$), 4.46 (s, 2H, β-pyrrolyl), 2.22 (s, 6H, $CH_3$–pyrrolyl). IR ($CHCl_3$, $\nu$ [$cm^{-1}$]): 1684 (CHO); 2958, 2924 (C–H). MS (CI, isobutane): $m/e$ = 244 $(M + H)^+$.

### 4.5. Reaction of lithiated *1* with $(Ph)_2PCl$

*sec*-BuLi (1.4 M in cyclohexane, 1.0 ml, 1.4 mmol) was added to an argon-saturated solution of **1** (275 mg, 1.4 mmol) and TMEDA (90 μl, 0.59 mmol) in THF (12 ml) at −78 °C. The orange coloration of the solution rapidly turned brown. After the mixture was stirred for 1.5 h at −78 °C, chlorodiphenylphosphine (270 μl, 1.5 mmol) in THF (5 ml) was added and the stirring was continued for 2 h. The reaction mixture was allowed to warm to room temperature and poured onto water. Extraction with dichloromethane, drying over $MgSO_4$ and solvent evaporation gave brown oil which was subjected to column chromatography (ethyl acetate–hexane (5:1) as eluent). The following fractions were collected:

First (40 mg), exhibiting complex $^1$H and $^{31}$P NMR spectra, which has not been identified.

Second, containing **8** (orange oil). Yield: 60 mg (13%). 1H NMR: $\delta$ ($CDCl_3$): 7.34–7.8 (m, 10H, $C_6H_5$), 4.32 (s, 1H, β-pyrrolyl), 4.16 (s, 5H, $C_5H_5$), 4.10 (s, 1H, β-pyrrolyl), 3.58 (d, $J$ = 11.0 Hz, 1H, 1/2$CH_2$), 3.40 (d, $J$ = 11.0 Hz, 1H, 1/2$CH_2$), 2.26 (s, 3H, $CH_3$). $^{31}$P NMR ($CDCl_3$): −13.0. HRMS: $m/e$ = 399.0822 (Calc. for $C_{23}H_{22}NPFe$: 399.0839).

Third, containing **9** (orange oil). Yield: 120 mg, (25%). $^1$H NMR: $\delta$ ($CDCl_3$): 7.78–7.22 (m, 10H, $C_6H_5$), 4.39 (t, $J$ = 1.4 Hz, 2H, $C_5H_4$), 4.25 (s, 2H, β-pyrrolyl), 4.10 (t, $J$ = 1.4 Hz, 2H, $C_5H_4$), 2.13 (s, 6H, $CH_3$–pyrrolyl). $^{31}$P NMR (81 MHz, $CDCl_3$): −18.24. HRMS: $m/e$ = 399.0821 (Calc. for $C_{23}H_{22}NPFe$: 399.0839). Anal. Calc. for $C_{23}H_{22}NPFe$: C, 69.19; H, 5.55. Found: C, 69.11; H, 5.65%.

Second, containing recovered **1** (orange oil). Yield: 37 mg (13%).

### 4.6. Reaction of lithiated *1* with diphenyl diselenide

*sec*-BuLi (1.4 M in cyclohexane, 1.4 ml, 1.9 mmol) was added to an argon-saturated solution of 2,5-dimethylazaferrocene (387 mg, 1.8 mmol) and TMEDA (135 μl, 0.89 mmol) in THF (12 ml) at −78 °C. The orange coloration of the solution rapidly turned brown. After the mixture was stirred for 1.5 h at −78 °C, $(PhSe)_2$ (624 mg, 2.0 mmol) in THF (5 ml) was added and the stirring was continued for 2 h. The reaction mixture was allowed to warm to room temperature and poured onto water. Extraction with dichloromethane, drying over $MgSO_4$ and solvent evaporation gave brown oil which was subjected to column chromatography (ethyl acetate–hexane (5:1) as eluent). The following fractions were collected:

First (yellow) containing recovered $(PhSe)_2$.

Second, containing **11** (orange oil). Yield: 66 mg (10%). $^1$H NMR $\delta$ ($CDCl_3$): 7.20–7.14 (m, 5H,$C_6H_5$), 4.42 (s, 2H, β-pyrrolyl), 4.35 (t, 2H, $J$ = 1.4 Hz, $C_5H_4$), 4.33 (t, 2H, $J$ = 1.4 Hz, $C_5H_4$), 2.31 (s, 6H, $CH_3$-pyrrolyl).HRMS $m/e$ = 370.9859 (Calc. for $C_{17}H_{17}NSeFe$: 370.9876) Anal. Calc. for $C_{17}H_{17}NSeFe$: C, 55.17; H, 4.63. Found: C, 54.89; H, 4.59%.

Third, containing **10** (orange oil). Yield: 174 mg (26%).$^1$H NMR $\delta$ ($CDCl_3$): 7.52–7.22 (m, 5H, $C_6H_5$), 4.42 (d, 1H, $J$ = 1.92 Hz, β-pyrrolyl), 4.32 (d, 1H, $J$ = 1.92 Hz, β-pyrrolyl), 4.25 (d, 1H, $J$ = 12.4 Hz, $CH_2$), 4.18 (s, 5H, $C_5H_5$), 4.09 (d, 1H, $J$ = 12.4 Hz, $CH_2$), 2.28 (s, 3H, $CH_3$–pyrrolyl). HRMS $m/e$ = 370.9892 (Calc. for $C_{17}H_{17}NSeFe$: 370.9876). Anal. Calcd. for $C_{17}H_{17}NSeFe$: C, 55.17; H, 4.63. Found: C, 55.02; H, 4.73%.

Fourth, containing recovered **1**. Yield: 45 mg, (12%).

### 4.7. Synthesis of *12*

$W(CO)_6$ (105 mg, 0.3 mmol) dissolved in THF (25 ml) was photolysed with a 200 W high-pressure mercury lamp for 2 h. The photolyte was treated with **2** (51 mg, 0.14 mmol) and the resulting solution was stirred at room temperature for 2 h. Removal of solvent, column chromatography (eluent: chloroform), and crystallization from chloroform–hexane afforded **12**. Yield: 54 mg (57%).$^1$H NMR: $\delta$ ($CDCl_3$): 7.41 (AB d, 2H, $J$ = 8.8 Hz, $C_6H_4$), 6.96 (AB d, 2H, $J$ = 8.8 Hz, $C_6H_4$), 4.71 (m, 1H, CH), 4.71 (d, 1H, $J$ = 2.4 Hz, β-pyrrolyl), 4.63 (d, 1H, $J$ = 2.4 Hz, β-pyrrolyl), 4.26 (s, 5H, $C_5H_5$), 3.84 (s, 3H, $OCH_3$), 3.51 (dd, 1H, $J$ = 15.6 Hz, $J$ = 4.7 Hz, $CH_2$), 3.23 (dd, 1H, $J$ = 15.6 Hz, $J$ = 8.3 Hz, $CH_2$), 2.63 (s, 3H, $CH_3$–pyrrolyl). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3330 (OH); 1923 (W–CO). MS (EI, 70 eV) $m/e$ = 591 $[M - 3CO]^+$, 535 $[M - 5CO]^+$, 351 $[M - W(CO)_5]^+$. Anal. Calc. for $C_{24}H_{21}O_7NFeW$: C, 42.67; H, 3.14. Found: C, 42.57; H, 3.45%.

### 4.8. Synthesis of *13*

$W(CO)_6$ (140 mg, 0.4 mmol) dissolved in THF (25 ml) was photolysed with a 200 W high-pressure mercury lamp for 2 h. The photolyte was treated with **5** (89 mg, 0.19 mmol) and the resulting solution was stirred at room temperature for 2 h. Removal of solvent, column chromatography (eluent: chloroform), and crystalliza-

tion from chloroform–hexane afforded **13**. Yield: 86 mg (58%).

$^1$H NMR $\delta$ ($CDCl_3$): 7.07 (AB d, 4H, $J$ = 6.4 Hz, $C_6H_4$), 6.79 (AB d, 4H, $J$ = 6.4 Hz, $C_6H_4$), 4.51 (s, 2H, β-pyrrolyl), 4.37 (s, 2H, $C_5H_4$), 4.24 (s, 2H, $C_5H_4$), 3.78 (s, 6H, $OCH_3$), 2.40 (s, 6H, $CH_3$–pyrrolyl). IR ($CHCl_3$ $\nu$ [$cm^{-1}$]): 3300 (OH); 1923 (W–CO). MS (EI,70eV) $m/e$ = 638 $[M - 4CO - OCH_3]^+$. Anal. Calc. for $C_{31}H_{27}O_8NFeW$: C, 47.66; H, 3.48. Found: C, 47.62; H, 3.64%.

## 5. Crystal structure determinations

Crystals of **6**, **12** and **13** suitable for X-ray analysis were obtained from layered chloroform–pentane.

Preliminary examination and intensities data collections were carried out on a KUMA KM4 $\kappa$-axis diffractometer with graphite-monochromated Mo Kα and with a CCD camera. All data were corrected for Lorentz, polarization and absorption effects. Data reduction and analysis were carried out with the Oxford Diffraction programs [17]. The structures were solved by direct methods and refined by the full-matrix least-squares method on all $F^2$ data using the SHELXTL [18]. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode. Hydrogen atoms bound to oxygen atoms were located from difference maps and refined as riding. Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 236706–236708, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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