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An expedient approach to ferrocenyl thioamides via Fischer carbenes

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ABSTRACT

Oxidative demetalation of Fischer ferrocenyl ethoxy carbene complexes (**1a–c**, M = Cr, Mo, W) and new Fischer ferrocenyl R-amino carbene complexes [**2–5** (**a–c**), **11–15** (**a–c**), and **21–22** (**a–c**); M = Cr, Mo, W; R = H, CH_3, C_2H_5, C_3H_7, $(CH_2)_2OH$, $(CH_2)_3OH$, $(CH_2)_2(OMe)_2$, $(CH_2)_3N(Me)_2$, $CH_2CH{=}CH_2$, $(CH_2)_2OSi(CH_3)_3$, $(CH_2)_3OSi(CH_3)_3$] with elemental sulfur–$NaBH_4$ were carried out under mild conditions, obtaining *O*-ethyl ferrocenecarbothioate (**6**) and novel ferrocenyl thioamides (**7–10** and **16–20**) in excellent yields.

1. Introduction

Since their discovery in 1815 by Gay-Lussac [1], thioamides have made a significant impact in the development of chemistry. These compounds have been used as convenient building blocks in organic synthesis [2]. Their use in the synthesis of aliphatic, aromatic, and heterocyclic compounds with pharmacological interest has been widely reported in the literature [3]. Also, in recent years they have attracted considerable interest in peptide chemistry [4].

There are various synthetic methods of thioamides such as the thiolysis of nitriles, imidoyl halogenides, amidines and imidic esters, addition of nucleophiles to isothiocyanates, and thionation of amides [5]. In general the thionation of amides is the most useful method for replacing the oxygen of amides by sulfur. In this sense, several methods have been reported through direct treatment of the amide with thionating reagents such as P_4S_{10} [6], Lawesson's reagent [7], R_3OBF_4/NaSH [8], P_4S_{10}/Na_2CO_3 [9], P_4S_{10}/Al_2O_3 [10]; or by prior activation of the amide with an electrophilic reagent, for example, a combination of oxalyl chloride or phosphorus oxychloride with benzyltriethylammonium tetrathiomolybdate [11], phosphorus oxychloride with hexamethyldisilathiane [12], and triflic anhydride with aqueous ammonium sulfide [13].

Although, the synthesis of alkyl thioamides is well-known, scarce synthesis of ferrocenyl analogous is informed, which may be due to the difficulty of obtaining a thiocarbonyl moiety bonded to the ferrocene. The general methods for the synthesis of ferrocenyl thioamides involve several steps and low overall yields (Scheme 1). Usually, the presence of the ferrocenylamide is necessary, and P_4S_{10} [14] or Lawesson's reagent [15], as thionating agents, are used in the final step (Method A). Nevertheless, the practical use of these methods is limited by the availability of the starting amide. Kato and co-workers [16] reported a multisteps procedure with overall yields around 8–15% (Method B), which involves as key intermediate the bis-(ferrocenecarbothioyl) sulfide. One-pot alternatives for the preparation of these compounds include the Willgerodt-Kindler reaction (Method C) [17], the use of ferrocenyl lithium prepared *in situ*, and the subsequent reaction with an appropriate *N,N*-dialkylthiocarbamoyl chloride (Method D) [18], or by a Friedel-Crafts type reaction between ferrocene and KSCN in a strongly acidic medium (Method E) [19].

Fischer carbene complexes are attractive synthetic intermediates which have demonstrated versatile applications in organic synthesis [20]. Nowadays, their use has been extended to other fields like materials chemistry [21], or bioorganometallics [22]. Different procedures have been developed to remove the metal moiety and transform Fischer carbene complexes into organic products. The oxidation appears to be a convenient method to convert Fischer alkoxy carbene complexes into the corresponding ester products [23]. Thus, different protocols are available to carry out this transformation [24–26]. However, when Fischer amine carbene complexes are used as starting material, harsh reaction conditions are usually required. In some cases, only activated aminocarbene complexes can be oxidatively demetalated, leading to low yields of corresponding amide and side-products [27]. As part of a project directed to the synthesis and modifications of

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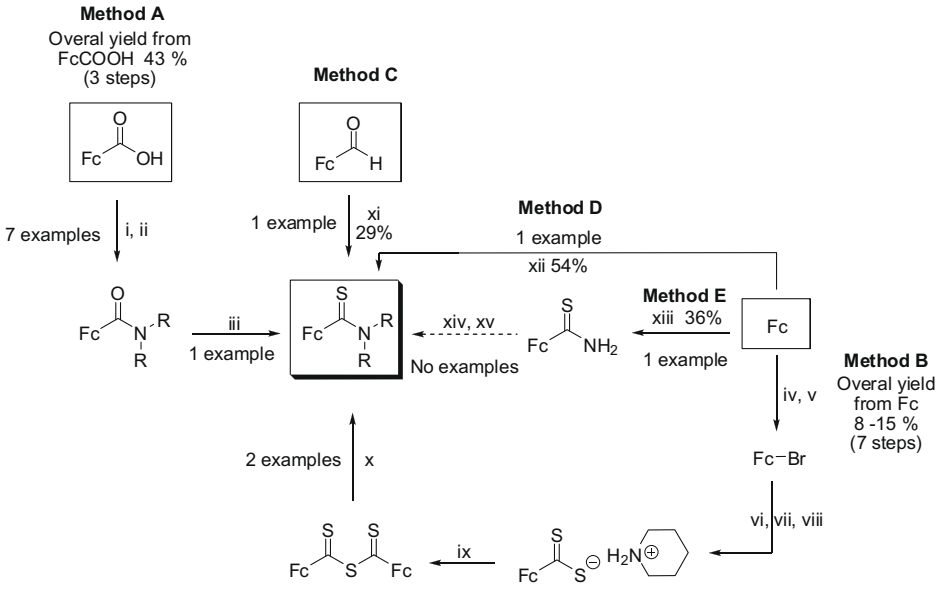


Scheme 1. Method A: (i) $(COCl)_2$, DMF or Py, 0 °C, petroleum ether, 1.5–2 h, 79%; (ii) RNH_2, NEt_3, RT, CH_2Cl_2, 20 h 81%; (iii) Lawesson's reagent, toluene reflux, 4 h 66%. Method B: (iv) MeOH, RT, $Hg(AcO)_2$, 10 h, 73%, (v) DMF, 0 °C, NBS, 3 h, 57%; (vi) Mg, 1,2-dibromoethane, ether, 25 °C, 3 h; (vii) CS_2, THF, 0 °C, then 15 h at RT, (viii) piperidine, 54%; (ix) 2-chloro-1-methylpyridinium iodide, −20 °C, MeOH, 1 h, 76%; (x) R_2NH, ether, RT, 5 h, 45% or 85%. Method C: (xi) Me_2NH_2Cl, S_8, NaAcO, DMF, 100 °C, 3 h 29%. Method D: (xii) n-BuLi, TMEDA, ether, RT, then $ClC(=S)NMe_2$, −78 to RT, 2 h, 54%. Method E: (xiii) KSCN excess, MSA excess, CH_2Cl_2, RT, 2 h, 36%; (xiv) phthaloyl dichloride, K_2CO_3, THF, 0 °C, 2 h, 65–94%; (xv) RNH_2, Et_3N, $CHCl_3$, 0 °C, 10 min, 50–100%.

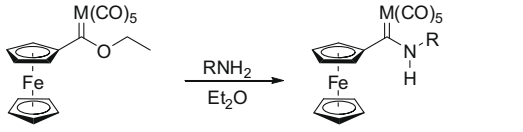
ferrocenyl carbene complexes developed in our laboratories [28,29], we report a systematic study of $NaBH_4$-promoted demetalation of ferrocenyl aminocarbene complexes with elemental sulfur as an alternative to easily obtain ferrocenyl thioester and ferrocenyl thioamides in excellent yields.

2. Results and discussion

The starting ferrocenylalkoxycarbene complexes **1a–c** (M = Cr, Mo, W) were prepared in good yield by the use of improved methods [28] related to those already described in the literature [30,31]. The synthesis of the corresponding amino ferrocenyl carbene complexes **2**, **3**, **4** and **5** were carried out by aminolysis of **1a–c** with ammonium hydroxide and three different amines leading **2a–c** and **3–5(a–c)**, respectively (Scheme 2). These reactions are nearly quantitative and proceed in short reaction times.

Since, to our knowledge **2a** has not been structurally characterized by X-ray diffraction analyses and only some examples about the synthesis of stable analogous Fischer carbene complexes exist [32]. The X-ray diffraction determination of **2a** was undertaken. The ORTEP view appears in Fig. 1.

According to the gathered data, the bond distances of Cr1–C6 [2.118(2)] and N1–C6 [1.307(3)] show a clear contribution of a delocalized system, where the major contributor is the imine form, additionally stabilized by the presence of a weak intermolecular hydrogen bond N1–H(1A)···O1 [2.31(2)] [33]. The geometry around chromium atom is octahedral, slightly distorted.



1a) M=Cr
1b) M=Mo
1c) M=W

2a M=Cr, 2b M=Mo, 2c M=W R = H
3a M=Cr, 3b M=Mo, 3c M=W R = Me
4a M=Cr, 4b M=Mo, 4c M=W R = Et
5a M=Cr, 5b M=Mo, 5c M=W R = Pr

Scheme 2. Synthesis of Fischer ferrocenyl alkylamino carbene complexes **2–5**(**a–c**).

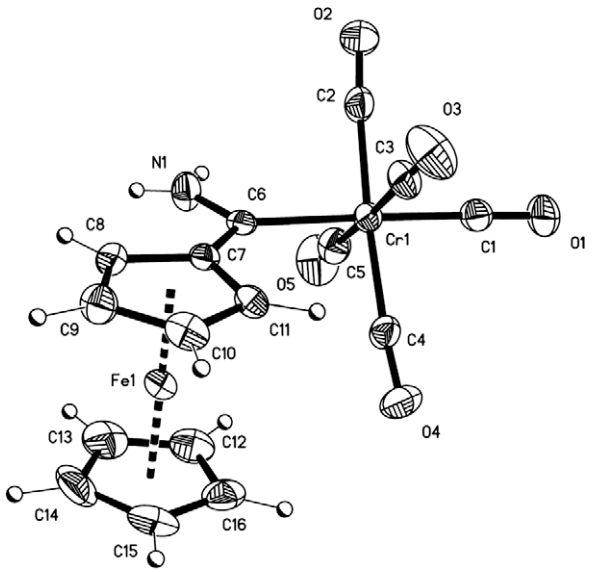
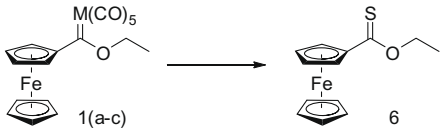
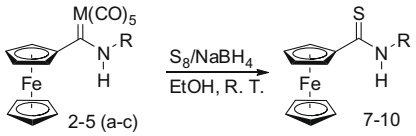


Fig. 1. X-ray crystal structure of complex **2a**. Ellipsoids are shown at the 30% probability level. Selected bond length (Å) and angles (deg): Cr1–C1 1.847(3), Cr1–C6 2.118(2), N1–C6 1.307(3), C6–C7 1.460(3), Cg1–Fe1 1.6406(11), Cg2–Fe1 1.6510(16), C1–Cr1–C6 177.68(10), C7–C6–Cr1 127.16(15), C3–Cr1–C5 177.29(12), N1–C6–C7 112.8(2), N1–C6–Cr1 119.93(17), Cg1–Fe1–Cg2 178.13(7). Cg(1) and Cg(2) are the centroids of the (C7, C8, C9, C10, C11) Cp ring and the (C12, C13, C14, C15, C16) Cp ring, respectively.

With the aim of knowing the demetalation reaction condition of Fischer ferrocenyl carbene complexes, we have initially explored the reactivity of **1a** with the traditional thionating reagents. We applied the method firstly reported by Fischer [23] but no product was obtained. Then, Lawesson or Davies's agents were used affording the ferrocenyl thioester in acceptable yield (Scheme 3, Table 1). However, the isolation of the desired product in some cases can be difficult and the use of aromatic solvents as benzene or toluene is necessary. Recently, a new demetalation protocol appears to be an



Scheme 3. Oxidation of Ethoxy ferrocenyl carbene complexes **1**(**a**–**c**).



Scheme 4. Oxidation of amino ferrocenyl carbene complexes **2**–**5**(**a**–**c**) by the mixture $S_8/NaBH_4$.

Table 1
Optimization condition for the synthesis of *O*-ethyl ferrocenecarbothioate **6**.

Entry	Reaction condition	Time	% Yield (**6**)[a]	
1	S_8/Benzene	24 h	(**1a**)	–
2	LR/Benzene reflux	2.5 h	(**1a**)	80
3	DR/Benzene reflux	2 h	(**1a**)	75
4	P_4S_{10}/Benzene reflux	2 h	(**1a**)	55
5	$S_8/NaBH_4$, EtOH, RT	1 h	(**1a**)	88
6	$S_8/NaBH_4$, EtOH, RT	5 min	(**1b**)	87
7	$S_8/NaBH_4$, EtOH, RT	5 h	(**1c**)	90

[a] Yields are for isolated pure material.

Table 2
Yields of *N*-alkyl ferrocenyl thioamides **7**–**10**.

Entry	Starting material	R	Product[a]	Yield (%)[b]	Time
1	**2a**, M = Cr	H	**7**	87	25 min
2	**2b**, M = Mo	H	**7**	60	5 min
3	**2c**, M = W	H	**7**	85	24 h
4	**3a**, M = Cr	Me	**8**	95	25 min
5	**3b**, M = Mo	Me	**8**	65	5 min
6	**3c**, M = W	Me	**8**	85	24 h
7	**4a**, M = Cr	Et	**9**	95	25 min
8	**4b**, M = Mo	Et	**9**	65	5 min
9	**4c**, M = W	Et	**9**	85	24 h
10	**5a**, M = Cr	Pr	**10**	95	25 min
11	**5b**, M = Mo	Pr	**10**	65	5 min
12	**5c**, M = W	Pr	**10**	85	24 h

[a] See Scheme 4 and the Section 4 for details.
[b] Yields are for isolated pure materials.

efficient method to obtain thioureas, selenoureas [34], thioamides and selenoamides [35], by the use of a combination of elemental sulfur or selenium and metallic hydrides ($LiAlH_4$, $NaBH_4$). Taking in account this strategy, we used the mixture $S_8/NaBH_4$ as the demetalating agent, thus the *O*-ethyl ferrocenecarbothioate **6** was obtained in similar yield from **1a–c** (Table 1, entries 5, 6 and 7), but only few minutes and room temperature were required to carry out this transformation. Comparing this result with those related to traditional thionating agents [23], the mixture $S_8/NaBH_4$ is the must clean and efficient method to accomplish this reaction.

The *O*-ethyl ferrocenecarbothioate **6** was obtained as a red solid. The mass spectrum of **6** is agreed with the molecular formula of the expected ferrocenyl thioester and confirms the loss of the fragment [$M(CO)_5$]. The ^{13}C NMR spectrum exhibits a signal at 216.5 ppm assigned to thioester group. The X-ray crystal structure of ferrocenyl thioester **6** shows the thiocarbonyl group directly bonded to ferrocene, the bond angles of O(1)–C(11)–S(1), 124.62° and C(1)–C(11)–S(1), 124.25° and O1–C11–C1, 111.12° confirm that this group has a trigonal geometry (Fig. 2).

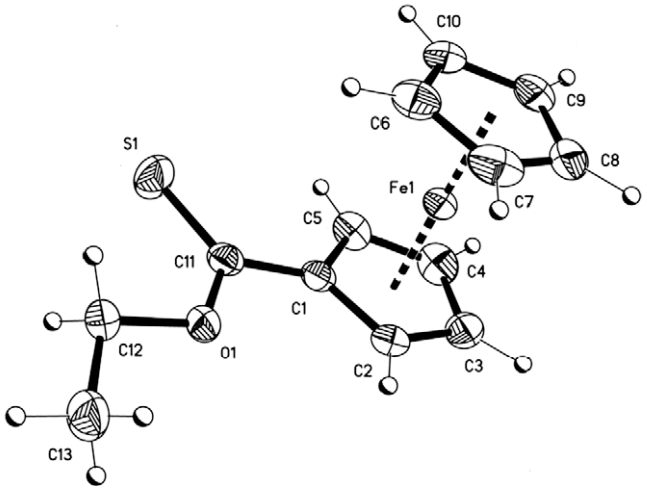


Fig. 2. X-ray crystal structure of compound **6**. Ellipsoids are shown at the 30% probability level. Selected bond length (Å) and angles (deg): S1–C11 1.643(2), O1–C11 1.327(3), C1–C11 1.453(3), O1–C12 1.455(3), Fe1–Cg1 1.645(1), Fe1–Cg2 1.644(2), C1–C11–S1 124.25(18), O1–C11–C1 111.12(19), O1–C11–S1 124.62(18), Cg(1)–Fe(1)–Cg(2) 179.0(1). Cg(1) and Cg(2) are the centroids of the (C1, C2, C3, C4, C5) Cp ring and the (C6, C7, C8, C9, C10) Cp ring, respectively.

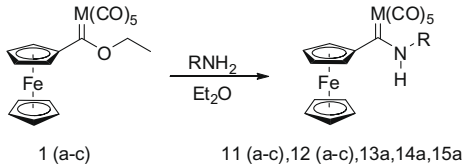
We applied $S_8/NaBH_4$ demetalation protocol to alkyl amino ferrocenyl carbenes synthesised (Scheme 4, Table 2). The reaction proceeds quickly for amino ferrocenyl carbenes of chromium (**2a–5a**) and molybdenum (**2b–5b**) (25 and 5 min, respectively) although; molybdenum carbenes lead to the formation of side-products if the reaction time is elongated. When, the carbene precursor contains tungsten, the reaction was completed on 24 h. Early approaches to obtain similar ferrocenyl carbothioamides were described by Plazuk et al. [19a] using a Friedel-Crafts type reaction of ferrocene with potassium thiocyanate in a strongly acid medium, obtaining a low yield for **7**.

Subsequently, demetalation reaction was systematized by screening the compatibility of different functional groups on lateral chain. With this aim, we have synthesised several ferrocenyl carbene complexes (Scheme 5) following the aminolysis procedure above described. In all cases, the reaction proceeds in good yield.

The new carbene complexes **11–15 (a–c)** exhibit on their infrared spectra bands around 2000 cm^{-1} characteristic of M–CO. In all cases, the molecular ion is observed in the mass spectra. In the ^{13}C NMR spectra, a signal for carbenic carbon around 270, 260 and 250 ppm of chromium, molybdenum and tungsten complexes, respectively is observed, as well as signals around 200–225 ppm for M–CO.

For complex **14a**, the structural arrangement was fully established by X-ray diffraction analysis (Fig. 3). Comparing the bond distances and bond angles of **2a** and **14a**, we can observe some slight differences in the geometry of aminocarbene function. The bond angle C3–Cr1–C5 is decreased in **14a** [2a:177.29(12); 14a:173.90(12)] as result of the presence of voluminous substituent bonded to nitrogen of aminocarbene. Like **2a**, the bond distances of Cr1–C6 [2.128(2)] and N1–C6 [1.308(3)] show a clear contribution of a delocalized system, where the major contributor is the imine form, additionally stabilized by the presence of a weak intramolecular hydrogen bond N1–H1···N2 [2.312(19)] [33]. The geometry around chromium atom is octahedral, slightly distorted.

Table 3 summarizes the evaluation of the scope in demetalation reaction of amino ferrocenyl carbene complexes **11–15(a–c)** to afford the novel ferrocenyl thioamides **16–20** (Scheme 6). In contrast with the results obtained by Yu and co-workers [35] with



Scheme 5. Synthesis of amino ferrocenyl carbene complexes.

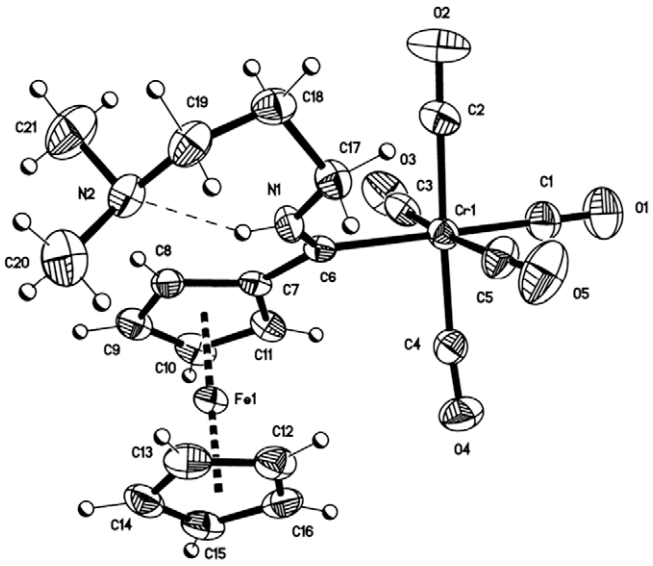
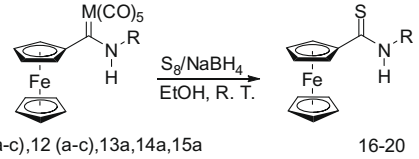


Fig. 3. X-ray crystal structure of complex **14a**. Ellipsoids are shown at the 30% probability level. Selected bond length (Å) and angles (deg): Cr1–C1 1.838(3), Cr1–C6 2.128(2), C6–C7 1.488(3), N1–C6 1.308(3), Cg1–Fe1 1.6405(11), Cg2–Fe1 1.6464(12), C1–Cr1–C6 176.41(11), C7–C6–Cr1 123.21(16), C3–Cr1–C5 173.90(12), N1–C6–C7 111.5(2), N1–C6–Cr1 125.24(17), Cg1–Fe1–Cg2 179.27(8). Cg(1) and Cg(2) are the centroids of the (C7, C8, C9, C10, C11) Cp ring and the (C12, C13, C14, C15, C16) Cp ring, respectively.

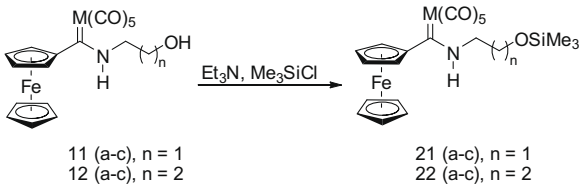
Table 3
Yields of N-alkyl ferrocenyl thioamides **16**–**20**.

Entry	Compound	R	Product	Yield (%)	Time
1	M = Cr, **11a**	CH_2CH_2OH	**16**	**90**	10 min
2	M = Mo, **11b**	CH_2CH_2OH	**16**	50	5 min
3	M = W, **11c**	CH_2CH_2OH	**16**	70	12 h
4	M = Cr, **12a**	$CH_2CH_2CH_2OH$	**17**	**90**	15 min
5	M = Mo, **12b**	$CH_2CH_2CH_2OH$	**17**	50	5 min
6	M = W, **12c**	$CH_2CH_2CH_2OH$	**17**	85	10 min
7	M = Cr, **13a**	$CH_2CH(OMe)_2$	**18**	**92**	2 h
8	M = Cr, **14a**	$CH_2CH_2CH_2N(Me)_2$	**19**	**89**	2 h
9	M = Cr, **15a**	$CH_2CH{=}CH_2$	**20**	**89**	10 h



Scheme 6. Oxidation of amino ferrocenyl carbene complexes by the mixture $S_8/NaBH_4$.

Fischer imine carbenes, we obtain the un-coordinated ferrocenyl thioamides and apparently the presence of the ferrocenyl moiety increases the reactivity of carbene toward demetalation. Additionally, we observe that carbene precursors which contain chromium as metal are the most accessible, even though molybdenum precursors react in a short time, they conduce to side-products and tungsten carbene complexes need long reaction times. These experimental data are agreed with the reactivity observed for Fischer carbene complexes.



Scheme 7. Synthesis of ω-(trimethylsiloxy)alkylamino ferrocenyl carbene complexes **21**(**a**–**c**) and **22**(**a**–**c**).

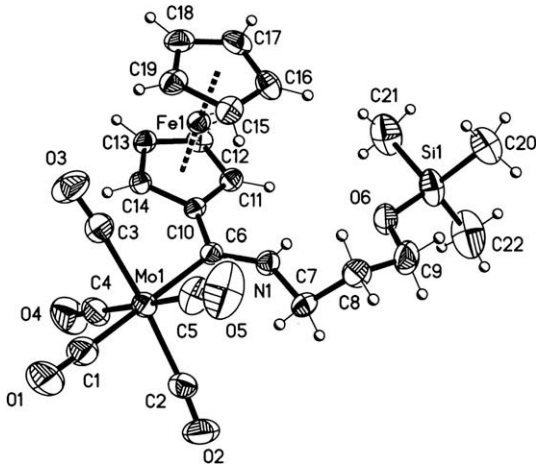


Fig. 4. X-ray crystal structure of complex **22b**. Ellipsoids are shown at the 30% probability level. Selected bond length (Å) and angles (deg): Mo1–C6 2.278(3), N1–C6 1.301(4), N1–C7 1.466(4), C6–C10 1.483(4), Si1–O6 1.643(3), Cg1–Fe1 1.6439(14), Cg2–Fe1 1.662(3), Cg2–Fe1 1.647(10), N1–C6–C10 111.1(3), N1–C6–Mo1 125.5(2), C1–Mo1–C6 179.62(16), Cg1–Fe1–Cg2 178.60(15), Cg1–Fe1–Cg2 177.4(4). Cg1 and Cg2 are the centroids of the (C10–C14) Cp ring and the (C15–C19) Cp ring, respectively for molecule A.

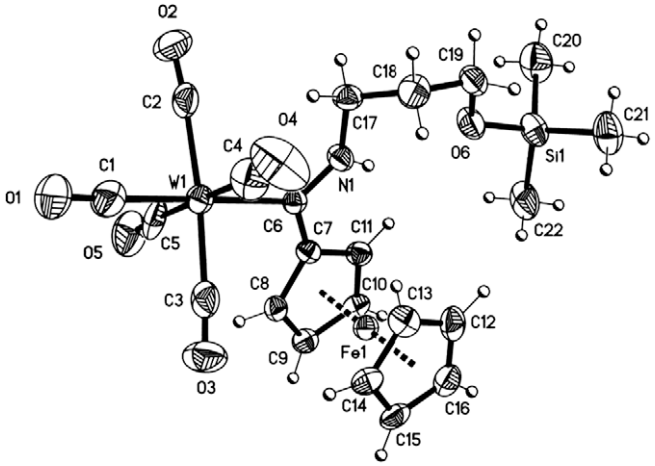


Fig. 5. X-ray crystal structure of complex **22c**. Ellipsoids are shown at the 30% probability level. Selected bond length (Å) and angles (deg): W1–C6 2.256(6), N1–C6 1.315(7), N1–C17 1.457(7), C6–C7 1.476(7), Si1–O6 1.669(9), Cg1–Fe1 1.640(2) Cg2–Fe1 1.661(7), Cg2–Fe1 1.644(17), C1–W1–C6 179.4(3), N1–C6–C7 110.5(5), N1–C6–W1 126.1(4), Cg1–Fe1–Cg2 179.0(3), Cg1–Fe1–Cg2 176.7(6). Cg1 and Cg2 are the centroids of the (C7–C11) Cp ring and the (C12–C16) Cp ring, respectively for molecule C.

The new thioamides **7–10** and **16–20** were characterized by conventional spectroscopic techniques. They exhibit in infrared spectra a characteristic band between 1600–1550 and ≈1275 cm^{-1} assigned to fragment N–C=S. In their ^{13}C NMR spectra, a typical signal ≈200 ppm is indicative of the carbon in thioamide function. Additionally, the molecular ion for each new thioamide confirms the demetalation of starting carbene complex.

In the case of ω-hydroxialkylamino carbenes **11(a–c)** and **12(a–c)**, when the metal in carbene moiety is Mo or W, we observe a slight diminution in yield (Table 3: entries 2, 3, 5 and 6), which can be result of a possible side reaction in demetalation process. For avoiding it, we carried out a protecting reaction of alcohol group with chlorotrimethylsilane to afford the corresponding Fischer ω-(trimethylsiloxy)alkylamino ferrocenylcarbene complexes **21a–c** and **22a–c**, in good yields (Scheme 7).

The structural arrangement for **22b** (Fig. 4) and **22c** (Fig. 5) was fully established by a single-crystal X-ray diffraction analysis. The compound **22b** crystallized as two independent molecules showing the same structural arrangement. We confirm the presence of trimethylsilil group directly bonded to oxygen atom and the carbene moiety intact. The geometry around molybdenum atom is octahedral, slightly distorted. Additionally, we observe a weak intramolecular hydrogen bond between N1–H1···O6 for molecule A and, N2–H2···O12 for molecule B. Both conformers present disorder in non substituted Cp ring of ferrocenyl group, as well as in CH_2–$OSi(CH_3)_3$ moiety. The analogous tungsten complex **22c** exhibits similar data, confirming the structure proposed.

With the ferrocenyl carbene complexes **21a–c** and **22a–c**, we perform the demetalating procedure but, in all reactions a complicated mixture of products were obtained. These results confirm that the presence of siloxane groups on lateral chain does not improve the demetalation reaction. In order to understand this behavior, further studies using other ω-(trialkylsiloxy)alkylamino ferrocenylcarbene complexes are now being carried out in our laboratories.

3. Conclusions

A new route to easily access a diversity of new potential ferrocenyl thioamides in good yields, using amino ferrocenyl carbene complexes as key substrates has been developed. This approach involves 2 steps with overall yields of 81–94% (from ferrocene, 3 steps, 69–83%). The scope of method was evidenced by the tolerance to different functional groups on side chain of amino ferrocenyl carbene. In general, the carbene precursors must accessible to achieve the demetalation procedure are those contain chromium as metal. Synthetic applications of these ferrocenyl thioamides are on development.

4. Experimental

4.1. Materials and instruments

THF and ether were distilled from benzophenone, under a nitrogen atmosphere. All reagents and solvents were obtained from commercial suppliers and used without further purification. All compounds were characterized by IR spectra, recorded on a Perkin–Elmer 283B or 1420 spectrophotometer, by KBr technique, and all data are expressed in wave numbers (cm^{-1}). Melting points were obtained on a Melt-Temp II apparatus and are uncorrected. NMR spectra were measured with a Jeol Eclipse +300 and a Varian Gemini (200 MHz), using $CDCl_3$ as solvent. Chemical shifts are in ppm (δ), relative to TMS. The MS-FAB and MS-EI spectra were obtained on a JEOL SX 102A. Elemental analyses were performed by the Analysis Service at the Faculty of Chemistry (UNAM).

4.2. Syntheses

4.2.1. Synthesis of Fischer ethoxyferrocenylcarbenes (*1a–c*)

The preparation of ferrocenylated group 6 metals Fischer-type carbenes was carried out using the methodology previously described elsewhere [28].

4.2.2. Synthesis of Fischer alkylaminoferrocenylcarbenes *2–5(a–c)*

4.2.2.1. General methodology. To a solution of **1a** (1 g, 2.29 mmol) in anhydrous diethyl ether was added at room temperature 0.4 ml of NH_4OH, then the reaction was stirred by 2 h. The solvent was evaporated under vacuum. The product was purified by chromatography on alumina using hexane–CH_2Cl_2 (9:1) as eluent.

*4.2.2.2. Complex **2a**.* $C_{16}H_{11}CrFeNO_5$, m. p. 139 °C (153–154 °C [36]), ^1H NMR (300 MHz, $CDCl_3$), δ: 4.25 (s, 5H), 4.68 (s, 2H), 4.75 (s, 2H), δ 8.25 (s, 2H), ^{13}C NMR (75 MHz, $CDCl_3$), δ: 69.8, 70.5, 73.2, 87.8, 217.8, 222.5, 278.1. IR υ_{max}(KBr), cm^{-1}: 3442, 3334, 3266, 2052, 1970, 1910, and 1866. MS (FAB^+), *m/z*: 405 (M^+), 349 [M^+–2(CO)], 321 [M^+–3(CO)], 293 [M^+–4(CO)], 265 [M^+–5(CO)], 211 [M^+–$Cr(CO)_5$].

*4.2.2.3. Complex **2b**.* $C_{16}H_{11}FeMoNO_5$, m. p. 140 °C, ^1H NMR (300 MHz, $CDCl_3$), δ: 4.26 (s, 5H), 4.70 (t, 2H *J* = 1.2 Hz), 4.75 (t, 2H, *J* = 1.2 Hz). 7.98 (s, 1H), 8.26 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 70.4, 70.5, 73.5, 87.4, 207.0, 212.7, 268.2. IR υ_{max}(KBr), cm^{-1}. 3438, 2060, 1977, 1919, 1882. MS (EI^+) *m/z*: 449 (M^+), 393 [M^+–2CO], 365 [M^+–3(CO)], 309 [M^+–5(CO)], 213 [M^+–$Mo(CO)_5$].

*4.2.2.4. Complex **2c**.* $C_{16}H_{11}FeNO_5W$, m. p. 158 °C, ^1H NMR (200 MHz, $CDCl_3$), δ: 4.27 (s, 5H), 4.73 (s, 4H), 7.95(s, 1H), 8.52(s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 70.6, 70.9, 73.6, 198.8, 202.5, 254.6. IR υ_{max}(KBr)/cm^{-1}: 3438, 3337, 2060, 1972, 1900, 1876, 1885. MS (FAB^+), *m/z*: 537 (M^+), 481 [M^+–2(CO)], 453 [M^+–3(CO)], 397 [M^+–5(CO)], 213 [M^+–$W(CO)_5$].

*4.2.2.5. Complex **3a**.* $C_{17}H_{13}CrFeNO_5$, m. p. 122–124 °C, ^1H NMR (300 MHz, $CDCl_3$), δ: 3.68 (s, 3H), 4.20, (s, 5H), 4.46 (s, 4H), 9.52 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$), δ 39.8, 68.5, 69.5, 70.4, 98.1, 217.9, 223.7, 273.3. IR υ_{max}(KBr)/cm^{-1}: 3337, 2052, 1903, 1866. MS (FAB^+), *m/z*: 419 (M^+), 363 [M^+–2(CO)], 335 [M^+–3(CO)], 307 [M^+–4(CO)], 279 [M^+–5(CO)], 227 [M^+–$Cr(CO)_5$]. Elemental Analysis, Exp: %C 48.71, %H 3.54, %N 3.54; Calc: %C 48.72, %H 3.10, %N 3.34.

*4.2.2.6. Complex **3b**.* $C_{17}H_{13}FeMoNO_5$, m. p. 128 °C, ^1H NMR (200 MHz, $CDCl_3$) δ: 3.64 (d, 3H), 4.21 (s, 2H), 4.51 (d, 2H, *J* = 1.8 Hz), 4.56 (d, 2H, *J* = 1.8 Hz), 9.13 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 41.2, 69.2, 69.5, 71.0, 95.0, 206.8, 213.4, 264.8. IR υ_{max}(KBr)/cm^{-1} 3311, 2059, 1903, 1862. MS (EI^+) *m/z*: 463 (M^+), 407 [M^+–2(CO)], 379 [M^+–3(CO)], 323 [M^+–5(CO)], 227 [M^+–$Mo(CO)_5$].

*4.2.2.7. Complex **3c**.* $C_{17}H_{13}FeNO_5W$, m. p. 137–138 °C, ^1H NMR (200 MHz, $CDCl_3$), δ: 3.58 (s, 3H), 4.22 (s, 5H), 4.53 (s, 2H), 4.58 (s, 2H), 9.11 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 42.2, 69.7, 71.1, 76.4, 96.3, 198.5, 203.1, 252.9. IR υ_{max}(KBr)/cm^{-1}: 3338., 2061, 1900, 1860. MS (EI^+), *m/z*: 551 (M^+), 495 [M^+–2(CO)], 467 [M^+–3(CO)], 411 [M^+–5(CO)], 227 [M^+–$W(CO)_5$]. Elemental Analysis, Exp: %C 40.80, %H 3.42, %N 2.34; Calc: %C 37.02, %H 2.36, %N 2.54.

*4.2.2.8. Complex **4a**.* $C_{18}H_{15}CrFeNO_5$, m. p. 106–108 °C, ^1H NMR (300 MHz, $CDCl_3$), δ: 1.53 (s, 3H), 4.10 (s, 2H), 4.18 (s, 5H), 4.45 (s, 4H), 9.45 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 15.1, 47.7, 68.4, 69.5, 70.1, 99.4, 217.9, 223.6 and 270.6. IR υ_{max}(KBr)/cm^{-1}, 3430,

3316, 2051, 1883. MS (EI^+), *m/z*: 433 (M^+), 377 [M^+–2(CO)], 349 [M^+–3(CO)], 321 [M^+–4(CO)], 293 [M^+–5(CO)], 241 [M^+–$Cr(CO)_5$].

4.2.2.9. Complex ***4b***. $C_{18}H_{15}FeMoNO_5$, m. p. 98 °C, ^1H NMR (200 MHz, $CDCl_3$), δ: 1.485 (t, 3H), 4.02 (m, 2H), 4.19 (s, 5H), 4.50 (s, 2H), 4.53 (s, 2H), 9.02 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 15.0, 49.2, 69.2, 69.6, 70.8, 95.6, 206.7, 213.5, 261.0. IR υ_{max}(KBr)/cm^{-1}. 3314, 2060, 1915, 1870. MS (IE^+) *m/z*: 477 (M^+), 421 [M^+–2(CO)], 393 [M^+–3(CO)], 337 [M^+–5(CO)], 241 [M^+–$Mo(CO)_5$].

4.2.2.10. Complex ***4c***. $C_{18}H_{15}FeNO_5W$, m. p. 131 °C. ^1H NMR (200 MHz, $CDCl_3$). δ: 1.49 (t, 3H), 3.98 (m, 2H), 4.20, (s, 5H), 4.50 (t, 2H, *J* = 1.8 Hz), 4.56 (t, 2H, *J* = 1.8 Hz), 9.0 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ: 15.0, 50.0, 69.6, 69.7, 70.8, 97.2, 198.5, 203.1, 249.6. IR ν_{max}(KBr) cm^{-1}: 3319, 2059, 1881. MS (EI^+) *m/z*: 565 (M^+), 509 [M^+–2(CO)], 481 [M^+–3(CO)], 425 [M^+–5(CO)], 241 [M^+–$W(CO)_5$].

4.2.2.11. Complex ***5a***. $C_{19}H_{17}CrFeNO_5$, m. p. 84 °C. ^1H NMR (300 MHz, $CDCl_3$), δ: 1.17 (s, 3H), 1.89 (s, 2H), 4.02, (s, 2H), 4.19 (s, 5H), 4.47 (s, 4H), 9.5 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 11.2, 23.2, 54.4, 68.3, 69.4, 70.0, 99.4, 217.8, 223.6, 270.6. IR υ_{max}(KBr)/cm^{-1}: 3222, 2051, 1895. MS (EI^+), *m/z*: 447 (M^+), 391 [M^+–2(CO)], 363 [M^+–3(CO)], 335 [M^+–4(CO)], 307 [M^+–5(CO)], 255 [M^+–$Cr(CO)_5$].

4.2.2.12. Complex ***5b***. $C_{19}H_{17}FeMoNO_5$, m. p. 88 °C. ^1H NMR (300 MHz, $CDCl_3$), δ: 1.15, (t, 3H), 1.87 (m, 2H), 3.94 (m, 2H), 4.20 (s, 5H), 4.49 (s, 2H), 4.53 (s, 2H), 9.08 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 11.2, 23.2, 55.9, 69.1, 69.5, 70.7, 96.0, 206.9, 213.6, 261.8. IR υ_{max}(KBr)/cm^{-1}: 3311, 2988, 2060, 1900, 1881. MS (IE^+), *m/z*: 491 (M^+), 435 [M^+–2(CO)], 407 [M^+–3(CO)], 351 [M^+–5(CO)], 255 [M^+–$Mo(CO)_5$].

4.2.2.13. Complex ***5c***. $C_{19}H_{17}FeNO_5W$. m. p. 108 °C. ^1H NMR (300 MHz, $CDCl_3$), δ: 1.16 (t, 3H), 1.87 (m, 2H), 3.90 (m, 2H), 4.2 (s, 2H), 4.54 (s, 2H), 4.70 (s, 5H), 9.05 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 11.2, 23.1, 56.6, 69.5, 69.6, 70.8, 97.4, 198.6, 203.3, 250.0. IR υ_{max}(KBr)/cm^{-1}. 3311, 2927, 2060, 1967, 1902, 1886. MS (FAB^+) *m/z*: 579 (M^+), 523 [M^+–2(CO)], 495 [M^+–3(CO)], 439 [M^+–5(CO)], 255 [M^+–$W(CO)_5$].

4.2.3. Synthesis of ethoxy ferrocenyl thioester ***6***

4.2.3.1. Preparation of thionating agent. To a solution of 0.01 mol of $NaBH_4$ in 10 mL of ethanol was added 0.01 mol of powdered sulfur, and the mixture was vigorously stirred at room temperature for 30 min under nitrogen atmosphere.

The thionating agent was then added to a solution of **1a–c** (0.001 mol) in 5 mL of ethanol under nitrogen atmosphere; the reaction was monitored by TLC on silica-gel. After the reaction was completed, the crude was filtered off through celite and the solvent was evaporated under vacuum. The resultant mixture was purified by silica-gel column using hexane as eluent, afforded **6** ($C_{13}H_{14}FeOS$) as a dark red crystalline solid with m. p. 45 °C. [(from **1a**, M = Cr, yield: 88%, *t* = 1 h), (from **1b**, M = Mo, yield: 87%, *t* = 5 min) (from **1c**, M = W, yield: 90%, *t* = 5 h)]. ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.45 [t, 3H, CH_3]; 4.15 [s, 5H, Cp]; 4.49 [t, 2H, Cp]; 4.64 [q, 2H, CH_2O]; 5.00 [t, 2H, Cp]. ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.1 [CH_3]; 67.2 [CH_2O]; 70.7 [Cp]; 71.0 [Cp]; 72.3 [Cp]; 82.6 [C_{ipso} Cp]; 216.5 [C(S)OEt]. IR ($CHCl_3$) ν_{max}, cm^{-1}: 3005, 2978 and 2923 (C–H), 1453 (C=S). MS-EI *m/z* (%): 274 [M+] (10), 256 (70), 64 (100). Elemental Analysis, Exp: %C 57.37, %H 5.44, %S 11.60; Calc: %C 56.93, %H 5.11, %S 11.7.

4.2.4. General synthesis of ferrocenyl thioamides

The alkylamino ferrocenyl carbene was dissolved in 5 mL of ethanol, then the thionating agent was added and the reaction was monitored by TLC. After the total conversion of corresponding carbene complex, the solvent was removed under vacuum and the resultant residue was purified by flash alumina column chromatography.

4.2.4.1. Complex ***7***. Orange solid, $C_{11}H_{11}FeNS$; m. p. 158 °C (160 °C [17a]). ^1H NMR (300 MHz, $CDCl_3$) δ: 4.22 (s, 5H, Cp), 4.51 (t, 2H, *J* = 1.9 Hz, Cp), 4.86 (t, 2H, *J* = 1.9 Hz, Cp), 7.27 (s, 2H, NH_2). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 69.6, 71.2, 72.2, 80.9, 204. 6. IR υ_{max}(KBr) cm^{-1}: 3359, 3155 (NH_2), 1624 (N–C=S). MS-EI^+ (*m/z*): 245 (M^+), 213 (M^+–S). Elemental Analysis, Exp: %C 54.4, %H 4.1, %N 5.21, %S 12.9, Calc: %C 54.5, %H 4.5, %N 5.7, %S 13.1.

4.2.4.2. Complex ***8***. Orange solid, $C_{12}H_{13}FeNS$. m. p 120 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.27 (s, 3H), 4.18 (s, 5H), 4.42 (t, 2H, Cp), 4.86 (t, 2H, Cp), 7.15 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 33.0, 68.7, 70.8, 71.2, 84.0, 200.7. IR υ_{max}(KBr) cm^{-1}: 3253 (NH), 1275 (C=S), 1534 (N–C=S). MS-EI^+ (*m/z*): 259 (M^+). Elemental Analysis, Exp: %C 56.4, %H 5.47, %N 5.29, %S 11.8; Calc: %C 55.6, %H 5.1, %N 5.4, %S 12.4.

4.2.4.3. Complex ***9***. Orange solid, $C_{13}H_{15}FeNS$. m. p.: 102 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.35 (t, 3H, CH_3), 3.82 (q, 2H, CH_2), 4.18 (s, 5H, Cp), 4.42 (t, 2H, Cp), 4.84 (t, 2H, Cp)]. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 13.9, 40.2, 68.7, 70.8, 71.8, 99.7, 199.4. IR υ_{max}(KBr) cm^{-1}: 3222(NH), 1534 (N–C=S). MS-EI^+ (*m/z*): 273 (M^+), 240 (M^+–HS). Elemental Analysis, Exp: %C 57.8, %H 5.98, %N 4.91, %S 11.9; Calc: %C 57.1, %H 5.5, %N 5.1, %S 11.7.

4.2.4.4. Complex ***10***. Orange solid, $C_{14}H_{17}FeNS$. m. p. 97 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.14 (t, 3H, CH_3), 1.91 (m, 2H, CH_3CH_2), 4.02 (t, 2H, Cp), 4.19 (s, 5H, Cp), 4.44 (br s, 4H, Cp and CH_2), 9.49 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.6, 21.8, 47.4, 70.4, 70.8, 71.1, 83.9, 199.4. IR υ_{max}(KBr) cm^{-1}: 1261 (C=S), 1530 (N–C=S). MS-EI^+ (*m/z*): 287 (M^+), 254 (M^+–HS). Elemental Analysis, Exp: %C 57.8, %H 6.2, %N 4.6, %S 12.9; Calc: %C 58.5, %H 6.1, %N 4.9, %S 11.1.

4.2.5. Synthesis of Fischer -hydroxy alkylamino ferrocenyl carbene complexes ***11–12(a–c)***

To a solution of **1a–c** (23 mmol, 1 g) in 20 mL of anhydrous diethyl ether under nitrogen atmosphere was added ethanolamine (49 mmol). The reaction mixture was stirred at room temperature for 3 h and then diluted with 20 mL of water. The organic phase was separated and dried with anhydrous Na_2SO_4, after the solvent was evaporated in vacuum. The crude product was purified by flash column chromatography using alumina and Hexane–CH_2Cl_2, 9:1 as eluent. The products **11a–c** were obtained as red solids. A similar procedure conduces to complexes **12a–c**.

4.2.5.1. Complex ***11a***. $C_{18}H_{15}CrFeNO_6$, red solid (91%), m. p. 84–85 °C, ^1H NMR (300 MHz, $CDCl_3$) δ: 1.99 (s, 1H), 4.12 (s, 2H), 4.24, (s, 7H), 4.44 (s, 2H), 4.47 (S, 2H), 10.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 54.0, 61.4, 68.5, 69.5, 70.1, 99.3, 217.9, 223.5, 272.0. IR υ_{max}(KBr)/cm^{-1}: 1925, 2053 (C=O), MS-EI^+ (*m/z*). 449 (M^+), 421 (M^+–CO), 393 [M^+–3(CO)], 309 [M^+–5(CO)], 257 [M^+–$Cr(CO)_5$].

4.2.5.2. Complex ***11b***. $C_{18}H_{15}FeMoNO_6$, red solid (85%), m. p. 93–94 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 1.96 (s, 1H, OH), 4.07 (d, 4H), 4.27 (s, 5H), 4.54 (d, 2H), 4.63 (s, 2H), 9.62 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.6, 61.4, 69.4, 69.7, 70. 8, 96.3, 206.9, 213.6, 263.3. IR υ_{max}(KBr) cm^{-1}: 2060, 1897 (CO), 1652 (C=C). MS (FAB^+) *m/z*: 465 (M^+–CO), 437[M^+–2(CO)], 409 [M^+–3(CO)],

381[M^+–4(CO)] 353 [M^+–5(CO)], 257 [M^+–$Mo(CO)_5$]. Elemental Analysis, Exp: %C 44. 51, %N 2.83, %H 3.27, Calc: %C 43.81, %N 2.84, %H 3.04.

4.2.5.3. Complex ***11c***. $C_{18}H_{15}FeNO_6W$, red solid (90%), m. p. 118–119 °C: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.06 (s, 1H), 4.06 (s, 2H), 4.28 (s, 5H), 4.49 (s, 2H), 4.57 (s, 2H), 9.61 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 56.1, 61.2, 69.7, 70.1, 71.0, 97.4, 198.7, 203.4, 251.1. IR υ_{max}(KBr)cm^{-1}: 2061, 1924 (CO). MS-FAB$^+$ (*m/z*): 581 (M^++1), 525 [(M^++1)–2(CO)], 254 [M^+–$W(CO)_5$]. Elemental Analysis, Exp: %C 37.02, %H 2.30, %N, 2.27; Calc: %C 37.18, %H 2.58, %N 2.41.

4.2.5.4. Complex ***12a***. $C_{19}H_{17}CrFeNO_6$, red solid (90%), m. p. 116–117 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.86 (s, 1H), 2.06 (s, 2H), 4.18 (br s, 9H), 4.45 (s, 2H), 4.58 (s, 2H), 9.99 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.01, 53.18, 62.90, 69.42, 69.79, 70.86, 95.03, 218.24, 223.72, 267.25. IR υ_{max}(KBr),cm^{-1}. 1923, 2051 (C═O). MS-FAB$^+$ (*m/z*): 463 (M^++1), 323 [M^++1–$(CO)_5$]. Elemental Analysis, Exp: %C 49.37, %H 3.93, %N 3.01; Calc: %C 49.5, %H 3.67, %N 3.02.

4.2.5.5. Complex ***12b***. $C_{19}H_{17}FeMoNO_6$, red solid (80%), m. p. 110 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.96 (s, 1H, OH), 4.07 (d, 4H, H_a, H_b), 4.27 (s, 5H, H_i), 4.54 (d, 4H, H_g, H_h), 9.62 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 55.6 (C_b), 61.4 (C_a), 69.4 (C_i), 69.7 (C_h), 70. 8 (C_g), 96.3 (C_f), 206.9 (C_d), 213.6 (C_e), 263.3 (C_j). IR υ_{max}(KBr) cm^{-1}: 2060, 1897 (CO), 1652 (C═C). MS (FAB$^+$) *m/z:* 507 (M^+), 479(M^+–CO), 451 (M^+–2CO), 423 (M^+–3CO), 395 (M^+–4CO), 367(M^+–5CO), 271 [M^+–$Mo(CO)_5$]. Elemental Analysis, Exp: %C 44.98, %H 3.34, %N, 2.74; Calc: %C 44.97, %H 3.35, %N 2.76.

4.2.5.6. Complex ***12c***. $C_{19}H_{17}FeNO_6W$, red solid (90%), m. p. 101–102 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.92 (s, 1H), 2.07 (s, 2H), 4.07 (s, 4H), 4.20 (s, 5H), 4.51 (s, 2H), 4.65 (s, 2H), 9.80 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.8, 55.7, 63.1, 70.0, 70.5, 71.4, 94.2, 199.0, 203.4, 247.4. IR υ_{max}(KBr)/cm^{-1}. 2057, 1890 (CO). MS-EI$^+$ (*m/z*): 595 (M^+), 539 [M^+–2(CO)], 271 [M^+–$W(CO)_5$]. Elemental Analysis, Exp: %C 38.23, %H 3.18, %N 2.44; Calc: %C 38.32, %H 2.85, %N 2.35.

4.2.6. Synthesis of Fischer R-amino ferrocenyl carbene complexes ***13a****, 14a and* ***15a***

4.2.6.1. Complex ***13a***. To solution of **1a** (2.3 mmol, 1 g) in anhydrous diethyl ether was added at room temperature, amino acetaldehyde dimethyl acetal (0.7 ml, 6.4 mmol), the mixture was monitored by TLC, then the solvent was evaporated and the crude of reaction was purified by flash column chromatography using alumina and Hexane–CH_2Cl_2 as eluent. The product is obtained as an orange solid (1.05 g) 92%, $C_{20}H_{19}CrFeNO_7$, m. p. 102–104 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: δ 3.59 (s, 6H), δ 4.19 (s, 7H), δ 4.43 (s, 4H), δ 4.69 (s, 1H), δ 9.74 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 53.9, 55.4, 68.5, 99.6, 102.6, 217.8, 223.5, 273.0. IR υ_{max}(KBr), cm^{-1}: 3222, 2050, 1896. MS-FAB$^+$ (*m/z*): 493 (M^+), 465 (M^+–CO), 437 [M^+–2(CO)], 409 [M^+–3(CO)], 381 [M^+–4(CO)], 353 [M^+–5(CO)], 301 [M^+–$Cr(CO)_5$].

4.2.6.2. Complex ***14a***. $C_{21}H_{22}CrFeN_2O_5$, orange solid (93%), m. p. 108–109 °C, ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.93 (s, 2H), 2.40 (s, 6H), 2.64 (s, 2H), 4.13 (s, 2H), 4.19 (s, 5H), 4.52 (s, 2H), 4.69 (s, 2H), 10.75 (s, 1H). NMR ^{13}C (75 MHz, $CDCl_3$) δ: 25.5, 45.9, 55.12, 59.9, 69.8, 71.9, 74.1, 92.1, 218.6, 223.4, 264.2. IR υ_{max}(KBr), cm^{-1}: 3427, 2046, 1901.MS-FAB$^+$(*m/z*): 490 (M^+), 434 [M^+–2(CO)], 406 [M^+–3(CO)], 378 [M^+–4(CO)], 350 [M^+–5(CO)].

4.2.6.3. Complex 15a. This compound was synthesised by our methodologies [28] $C_{19}H_{15}CrFeNO_5$, ^{1}H NMR (300 MHz, $CDCl_3$), δ: 4.21 (s, 5H), δ 4.49 (br s, 4H), 4.71 (br s, 1H), 5.51 (br s, 2H), 6.14 (br s, 1H), 9.47 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 55.3, 68.6, 69.6, 70.4, 98.9, 120.4, 217.7, 223.5, and 272.6. MS (FAB$^+$) *m/z*: 445(M^+), 417 (M^+–CO), 361 [M^+–3(CO)], 333 [M^+–4(CO)], 305 [M^+–5(CO)], 267 (FcCCrNH). HR-MS (FAB$^+$) $C_{19}H_{15}CrFeNO_5$: Calc. 444.9705%. Found: 444.9721%.

4.2.7. Synthesis of ferrocenyl thioamides ***16–20***

4.2.7.1. Complex ***16***. $C_{13}H_{15}FeNOS$, orange solid, m. p. 148–149 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.60 (t, 2H, C*H*$_2$N), 3.74 (t, 2H, C*H*$_2$O), 4.14 (s, 5H, Cp), 4.44 (t, 2H, *J* = 1.65 Hz, Cp), 4.89 (s, 1H, O*H*), 5.03 (t, 2H, *J* = 1.65, Cp), 9.47 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 48.1, 58.7, 69.7, 70.9, 71.3, 83.8, 198.4. IR υ_{max}(KBr) cm^{-1}: 1544 (N–C═S). MS-EI$^+$ (*m/z*): 289 (M^+), 255 (M^+–H_2S). Elemental Analysis, Exp: %C 53.7, %H 5.36, %N 4.80, %S 10.8, Calc: %C 53.97, %H 5.19, %N 4.84, %S 11.07.

4.2.7.2. Complex ***17***. $C_{14}H_{17}FeNOS$, orange solid, m. p. 113–115 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.92 (m, 2H,C*H*$_2$), 3.85 (t, 2H, C*H*$_2$N), 3.97 (t, 2H, C*H*$_2$O), 4.19 (s, 5H, Cp), 4.42 (t, 2H, *J* = 1.92 Hz, Cp), 4.85 (t, 2H, *J* = 1.92 Hz, Cp). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.9, 44.2, 61.2, 68.9, 70.8, 71.2, 83.8, 199.9. IR υ_{max}(KBr) cm^{-1}. 3309, 3255 (N–H), 1540 (N–C═S). MS-EI$^+$ (*m/z*): 303 (M^+), 269 (M^+–H_2S).

4.2.7.3. Complex ***18***. $C_{15}H_{19}FeNO_2S$, orange solid, m. p. 117–118 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.47 (s, 6H, C*H*$_3$O). 3.96 (d, 2H, *J* = 5.22 Hz, C*H*$_2$N), 4.19 (s, 5H, Cp), 4.43 (t, 2H, *J* = 1.8 Hz, Cp), 4.64 (t, 1H, *J* = 4.95 Hz, C*H*), 4.84 (t, 2H, *J* = 1.8 Hz, Cp). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 46.9, 54.9, 68.9, 70.7, 71.2, 83.6, 101.8, 200.4. IR υ_{max}(KBr) cm^{-1}: 3325, 2883, 1532. MS-EI$^+$ (*m/z*): 333 (M^+), 299 (M^+–H_2S). Elemental Analysis. Exp: %C 54. 58, %H 5.97, %N 4.05, %S 8.79. Calc: %C 54.05, %H 5.70, %N 4.20, %S 9.61.

4.2.7.4. Complex ***19***. $C_{16}H_{22}FeN_2S$, orange solid, m. p. 128–130 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.84 (m, 2H, C*H*$_2$), 2.39 (s, 6H, (C*H*$_3$)$_2$N), 2.59 (m, 2H, C*H*$_2$N), 3.84 (m, 2H, C*H*$_2$N), 4.17 (s, 5H, Cp), 4.40 (m, 2H, Cp), 4.81 (t, 2H, Cp), 10.3 (s, 1H, N*H*). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 23.5, 45.5, 47.5, 59.8, 68.7, 70.5, 71.0, 83.70, 198.3. IR υ_{max}(KBr) cm^{-1}: 3145, 1530. MS. EI$^+$, *m/z*: 330 (M^+), 296 (M^+–H_2S). Elemental Analysis, Exp: %C 58.3, %H 6.78, %N 8.54, %S 9.28; Calc: %C 58.18, %H 6.67, %N 8.48, %S 9.69.

4.2.7.5. Complex ***20***. $C_{14}H_{15}FeNS$, orange solid, m. p. 68–70 °C. ^{1}H NMR (300 MHz, $CDCl_3$,) δ: 4.19 (s, 5H), 4.35 (s, 4H), 4.86 (s, 2H), 5.30 (m, 2H), 5.98 (m, 1H), 7.31 (s, 1H), ^{13}C NMR (75 MHz, $CDCl_3$) δ: 47.9, 68.7, 70.7, 71.1, 83.6, 118.0, 132.6, 199.9. IR υ_{max}(KBr), cm^{-1}: 3313, 3250, 2004, 1907, 1522. MS-IE$^+$ (*m/z*): 285 (M^+), 270 (M^+–CH_3), 252 (M^+–HS).

4.2.8. Synthesis of Fischer -siloxyalkylaminoferrocenylcarbene complexes ***21****(****a****–****c****) and* ***22****(****a****–****c****)*

To a solution of **6a** (0.2 g, 0.3 mmol) in 15 mL of anhydrous toluene was added drop wise at room temperature 0.1 mL of triethylamine. The mixture was stirred until complete homogenization. Then 0.1 mL of chlorotrimethylsilane (0.79 mmol) was added. The reaction was stirred by 15 h. Finally, the reaction mixture was filtered on celite, the filtrated is recovered and the solvent was eliminated on vacuum. The product was purified on column chromatography of neutral alumina, using hexane as eluent.

4.2.8.1. Complex ***21a***. $C_{21}H_{23}CrFeNO_6Si$, orange solid (89%), m. p. 79 °C, ^{1}H NMR (200 MHz, $CDCl_3$) δ: 0.243 (s, 9H, C*H*$_3$), 4.02 (br s, 2H, C*H*$_2$O), 4.15 (br s, 2H, C*H*$_2$N), 4.23 (s, 5H, Cp), 4.42 (s, 4H, Cp), 10. 05 (s, 1H, N*H*). ^{13}C NMR (50 MHz, $CDCl_3$), δ: −0.4 (*C*H$_3$), 54.5

(CH_2N), 60.9 (CH_2O), 68.3 (C_p), 69.4 (C_p), 69.8 (C_p), 100.0 ($C_{ipso}Cp$), 217.6, 223.2 (CO), 271.2 (C=Mo). NMR ^{29}Si ($CDCl_3$) δ: 22.1 (CH_3–Si–O). IR υ_{max}(KBr) cm^{-1}: 3234 (NH), 2051, 1901 (CO), 1253 (C–Si), MS-EI$^+$ (*m/z*) 521 (M^+), 493 (M^+–CO), 465 [M^+–2(CO)], 409 [M^+–4(CO)], 381 [M^+–5(CO)].

4.2.8.2. Complex ***21b***. $C_{21}H_{23}FeMoNO_6Si$, orange solid (73%) m. p. 77 °C, ^1H NMR (300 MHz, $CDCl_3$) δ: 0.28 (s, 9H, CH_3), 3.96 (s, 2H, CH_2O), 4.06 (s, 2H, CH_2N), 4.26 (s, 5H, Cp), 4.47 (s, 4H, Cp), 9.68 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −0.47, (CH_3), 56.0 (CH_2N), 61.0 (CH_2O), 69.0 (C_p), 69.5 (C_p), 70.4 (C_p), 97.3($C_{ipso}Cp$), 206.9 and 213.9 (CO), 263.5 (C=Mo). NMR ^{29}Si ($CDCl_3$) δ: 21.89 (CH_3–Si–O)). IR υ_{max}(KBr) cm^{-1}: 3241 (NH), 1903, 2058 (CO), 1254, (C–Si). MS-FAB$^+$ (*m/z*): 565(M^+), 509 [M^+–2(CO)], 425 [M^+–5(CO)], 329 [M^+–$Mo(CO)_5$].

4.2.8.3. Complex ***21c***. $C_{21}H_{23}FeNO_6SiW$, orange solid (78%), m. p. 77 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.32 (s, 9H, CH_3), 3.99 (m, 4H, CH_2O and), 4.02 (s, 5H, Cp), 4.49 (m, 4H, Cp), 9.66 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −0.47, (CH_3), 56.5 (CH_2N), 60.8 (CH_2O), 69.5 (C_p), 69.7 (C_p), 70.53 (C_p), 98.7($C_{ipso}Cp$), 198.7 and 203.6 (CO), 251.1 (C=W). NMR ^{29}Si ($CDCl_3$) δ: 22.04 (CH_3–Si–O). IR υ_{max}(KBr) cm^{-1}: 3248(N–H), 2055, 1896 (CO), 1251 (C–Si). MS-EI$^+$ (*m/z*): 653 (M^+), 597 (M^+-56), 569 [M^+–3(CO)], 513 [M^+–5(CO)], 329 [M^+–$W(CO)_5$]. Elemental Analysis, Exp: %C 40.85, %H, %N, Calc: %C 38.59, %H 3.93, %N 2.14.

4.2.8.4. Complex ***22a***. $C_{22}H_{25}CrFeNO_6Si$, orange solid (83%), m. p. 74 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.03 (s, 2H, CH_2), 3.90 (s, 2H, CH_2O), 4.19 (s, 2H, CH_2N), 4.31 (s, 5H, Cp), 4.48 (s, 2H, Cp), 4.62 (s, 2H, Cp), 9.79 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −0.47 (CH_3), 29.75 (CH_2), 52.97 (CH_2N), 62.36 (CH_2O), 69.64 (C_p), 69.79 (C_p), 70.95 (C_p), 94.0 ($C_{ipso}Cp$), 218.31 and 223.45 (CO), 266.82 (C=Cr). NMR ^{29}Si ($CDCl_3$) δ: 21.36 (CH_3–Si–O). IR υ_{max}(KBr) cm^{-1}: 3286 (NH), 2048, 1906 (CO). MS-FAB$^+$ (*m/z*) 536 (M^++1), 479 [M^+–2(CO)], 423 [M^+–4(CO)], 395 [M^+–5(CO)].

4.2.8.5. Complex 22b. $C_{22}H_{25}FeMoNO_6Si$, orange solid (72%), m. p. 115 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.25 (s, 9H, CH_3), 2.01 (s, 2H, CH_2), 3.89 (s, 2H, CH_2O), 4.18 (s, 2H, CH_2N), 4.32 (s, 5H, Cp), 4.51 (s, 2H, Cp), 4.64 (s, 2H, Cp), 9.64 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −0.5 (CH_3), 31.5 (CH_2), 54.8 (CH_2N), 62.6 (CH_2O), 69.8 (C_p), 70.3 (C_p), 71.4 (C_p), 91.8 ($C_{ipso}Cp$), 207.2 and 213.4 (CO), 257.9 (C=Mo). NMR ^{29}Si ($CDCl_3$) δ: 21.42 (CH_3–Si–O). IR υ_{max}(KBr)/cm^{-1}: 3277 (NH), 1925, 2052 (CO), 1256 (C–Si). MS-EI$^+$ (*m/z*): 579 (M^+), 523 [M–2(CO)], 495 [M^+–3(CO)], 467 [M^+–4(CO)], 439 [M^+–5(CO)], 343 [M^+–$Mo(CO)_5$].

4.2.8.6. Complex ***22c***. $C_{22}H_{25}FeNO_6SiW$, orange solid (79%), m. p. 89 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.27 (s, 9H, CH_3), 2.02 (m, 2H, CH_2), 3.91 (m, 2H, CH_2O), 4.04 (t, 2H, CH_2N), 4.20 (s, 5H, Cp), 4.54 (s, 2H, Cp), 4.67 (s, 2H, Cp), 9.62 (s, 1H, NH). ^{13}C NMR (75 MHz, $CDCl_3$), δ: −0.4 (CH_3), 31.4 (CH_2), 55.8 (CH_2N), 62.8 (CH_2O), 70.0 (C_p), 70.8 (C_p), 71.5 (C_p), 93.0 ($C_{ipso}Cp$), 199 and 205 (CO), 246.5 (C=W)). NMR ^{29}Si ($CDCl_3$) δ: 21.54 (CH_3–Si–O). IR υ_{max}(KBr) cm^{-1}: 3295 (NH), 1903, 2055 (CO), 1256 (C–Si). MS-EI$^+$ (*m/z*): 667 (M^+), 611, [M^+–2(CO)], 555 [M^+–4(CO)], 527 [M^+–5(CO)], 343 [M^+–$W(CO)_5$].

4.3. X-ray crystallography

Suitable X-ray quality crystals of **2a**, **6**, **14a**, **22b** and **22c** were grown by slow evaporation of a dichloromethane/n-hexane solvent mixture at −5 °C. Single red crystals of compounds **2a**, **6**, **14a**, **22b** and **22c** were mounted on a glass fiber at room temperature. The crystals were then placed on a Bruker Smart Apex CCD diffractometer, equipped with Mo KR radiation; decay was negligible in both cases. Details of crystallographic data collected on compounds **2a**, **6**, **14a**, **22b** and **22c** are provided in Table 4. Systematic absences and intensity statistics were used in space group determination. The structure was solved using direct methods [37]. Anisotropic structure refinements were achieved using full-matrix, least-squares techniques on all non-hydrogen atoms. All hydrogen atoms were placed in idealized positions, based on hybridization,

Table 4
Crystal data and structure refinement for **2a**, **6**, **14a**, **22b** and **22c**.

	2a	6	14a	22b	22c
Empirical Formula	$C_{16}H_{11}CrFeNO_5$	$C_{13}H_{14}FeOS$	$C_{21}H_{22}CrFeN_2O_5$	$C_{22}H_{25}FeMoNO_6Si$	$C_{22}H_{25}FeNO_6SiW$
Formula Weight (g mol^{-1})	405.11	274.15	490.26	579.31	667.22
Crystal size (mm)	0.324 × 0.012 × 0.138	0.242 × 0.232 × 0.158	0.244 × 0.204 × 0.082	0.342 × 0.232 × 0.068	0.422 × 0.076 × 0.074
Color	Red	Red	Red	Orange	Red
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{2}_1/n$	$P\bar{2}_1/n$
a (Å)	11.353(2)	7.486(1)	9.831(1)	14.175(1)	14.150(3)
b (Å)	10.936(2)	8.002(1)	10.548(1)	13.368(1)	13.318(3)
c (Å)	13.816(2)	10.719(1)	12.284(1)	27.280(2)	27.298(5)
α (°)	90	81.221(2)	78.996(1)	90	90
β (°)	106.273(2)	75.448(2)	79.270(1)	94.657(1)	94.69(2)
γ (°)	90	77.711(2)	63.141(1)	90	90
V (Å^3)	1646.6(4)	604.0(1)	1108.2(2)	5152.3(7)	5127.1(8)
Z	4	2	2	8	8
$D_{calc.}$ (g cm^3)	1.634	1.508	1.469	1.494	1.729
Number of collected reflections	13 108	5834	21 769	42 615	42 311
Number of independent reflections (R_{int})	3007, R_{int} = 0.0527	62 213 unique, R_{int} = 0.010	7881, R_{int} = 0.0527	9431, R_{int} = 0.0464	9382, R_{int} = 0.0626
Absorption correction method	Analytical	Semi-empirical from equivalent	Analytical	Semi-empirical from equivalent	Semi-empirical from equivalent
Maximum and minimum transmission	0.8191 and 06 421	0.8048 and 0.7062	0.9154 and 0.7538	0.925 and 0.723	0.6841 and 0.2644
Data/parameters	3007/225	2213/146	7881/277	9431/713	9382/803
Final *R* indices [$I>2\sigma(I)$]	R_1 = 0.0303, wR_2 = 0.0675	R_1 = 0.0357, wR_2 = 0.0874	R_1 = 0.0590, wR_2 = 0.0760	R_1 = 0.0408, wR_2 = 0.0901	R_1 = 0.0422, wR_2 = 0.0806
R indices (all data)	R_1 = 0.0384, wR_2 = 0.0701	R_1 = 0.0405, wR_2 = 0.0898	R_1 = 0.1314, wR_2 = 0.0870	R_1 = 0.0619, wR_2 = 0.0992	R_1 = 0.0687, wR_2 = 0.0891
Goodness-of-fit on F^2	0.952	1.059	1.006	1.013	1.006

with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. Structure solutions and refinements were performed using SHELXTL V 6.10 [38].

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Appendix A. Supplementary data

CCDC 729446, 729447, 729448, 729449 and 729450 contains 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.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2009.07.044.

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