Journal of Organometallic Chemistry 695 (2010) 446–452

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Formation of multifunctional ligands by nucleophilic addition of alcohols and thiols to the alkyne groups in compound $C_5H_5FeC_5H_4C{\equiv}CSC{\equiv}CH$: Reactivity studies

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ARTICLE INFO

Article history:
Received 3 September 2009
Received in revised form 16 October 2009
Accepted 22 October 2009
Available online 28 October 2009

Keywords:
Multifunctional ligands
Metal carbonyls
Hydrothiolation
Hydroalkoxylation

ABSTRACT

The multifunctional ligands [(*Z*)–FcC≡CSC(H)=C(H)XR] [X = O, R = Me (**2a**); X = O, R = Et (**2b**); X = S, R = Ph (**3**); X = S, R = C_6F_5 (**5**)] and [(*Z,Z*)–Fc(SR)C=C(H)SC(H)=C(H)SR] [R = Ph (**4**), C_6F_5 (**6**)] have been prepared through hydroalkoxylation and hydrothiolation processes of the alkyne groups in the compound FcC≡CSC≡CH **1.** Reactions between compound **3** and the carbonyl metals $Co_2(CO)_8$, $Os_3(CO)_{10}(NCMe)_2$ and $Fe_2(CO)_9$ have allowed the synthesis of the polynuclear compounds [(*Z*)-{$Co_2(CO)_6$}(μ-η²-FcCCSC(H)=C(H)SPh)] **9**, [(*Z*)-$Os_3(CO)_9$(μ-CO){μ_3-η²-FcCCSC(H)=C(H)(SPh)}] **10** and [(*Z*)-{$Fe_3(CO)_9$}-[μ_3,η³-(*CCS*)-FcCCSC(H)=C(H)(SPh)] **11**. All the compounds have been characterized by elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy, mass spectrometry and the crystal structure of compounds [(*Z*)-FcC≡CSC(H)=C(H)OMe] **2a** and [{$Co_2(CO)_6$}$_2$(μ-η²:η²-FcCCSCCSiMe$_3$)] **7** have been solved by X ray diffraction analysis.

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1. Introduction

Multifunctional ligands play an important role in stabilizing metal centres [1]. Additionally, compounds containing ferrocenyl groups are interesting due to the redox properties of this group [2].

On the other hand, addition of thiols or alcohols to alkyne groups, hydrothiolation and hydroalkoxylation processes, respectively, using transition metal as catalysts or promoted by bases, is a useful method for the preparation of vinyl-sulfides and ethers [3]. Depending on the conditions, *E* or *Z* isomers, as well as a mixture of both, formed by either Markovnikov or anti-Markovnikov addition, are observed. These compounds are important intermediates in organic synthesis [4].

Taking into account the above mentioned, our main goal has been to prepare multifunctional ligands bearing a ferrocenyl group by addition of thiols and alcohols to the carbon–carbon triple bonds in the compound FcC≡CSC≡CH **1**.

Herein, we report the synthesis of a series of unsymmetrical vinyl-sulfides and ethers that might act as multifunctional ligands and some preliminary studies on the reactivity of compound [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** in the presence of transition carbonyl metals. All the new compounds have been characterized by elemental analysis and spectroscopic methods. The crystal structures of the vinyl ether [(*Z*)-FcC≡CSC(H)=C(H)(OMe)] **2a** and the cobalt carbonyl complex [{$Co_2(CO)_6$}$_2$(μ-η²:η²-FcCCSCCSiMe$_3$)] **8** have been solved by X ray diffraction studies.

2. Results and discussion

Compound FcC≡CSC≡CSiMe$_3$ was treated with KF in THF and the mixture kept at room temperature for 1 h to afford the desilylated compound FcC≡CSC≡CH **1**. Its formation is evidenced by the presence of a signal at 3.00 ppm corresponding to the proton of the terminal alkyne, as well as the absence of the resonance corresponding to the SiMe$_3$ group in the ^{1}H NMR spectrum. However, when the desilylation reaction was carried out using K_2CO_3 in MeOH, an equimolecular mixture of the compound **1** together to the new compound [(*Z*)-FcC≡CSC(H)=C(H)(OMe)] **2a** were obtained. Analogous reaction using EtOH instead of MeOH, yields to the similar compound [(*Z*)-FcC≡CSC(H)=C(H)(OEt)] **2b** (Scheme 1).

Compound **2** is obtained in quantitative amount when a methanol (**2a**) or ethanol (**2b**) solution of compound FcC≡CSC≡CH **1** is treated with a saturated solution of K_2CO_3 in the corresponding alcohol and heating the mixture at 60 °C for 48 h. This reaction is regioselective yielding only to the *Z* isomer. Both compounds have been characterized by ^{1}H and ^{13}C NMR spectroscopy as well as by elemental analysis and FAB mass spectrometry (see Section 4) and the crystal structure of [(*Z*)-FcC≡CSC(H)=C(H)(OMe)] **2a** solved by an X ray diffraction study.

Their formation implies a *trans* anti-Markovnikov addition of the alcohol, as is evidenced by the presence in their ^{1}H NMR

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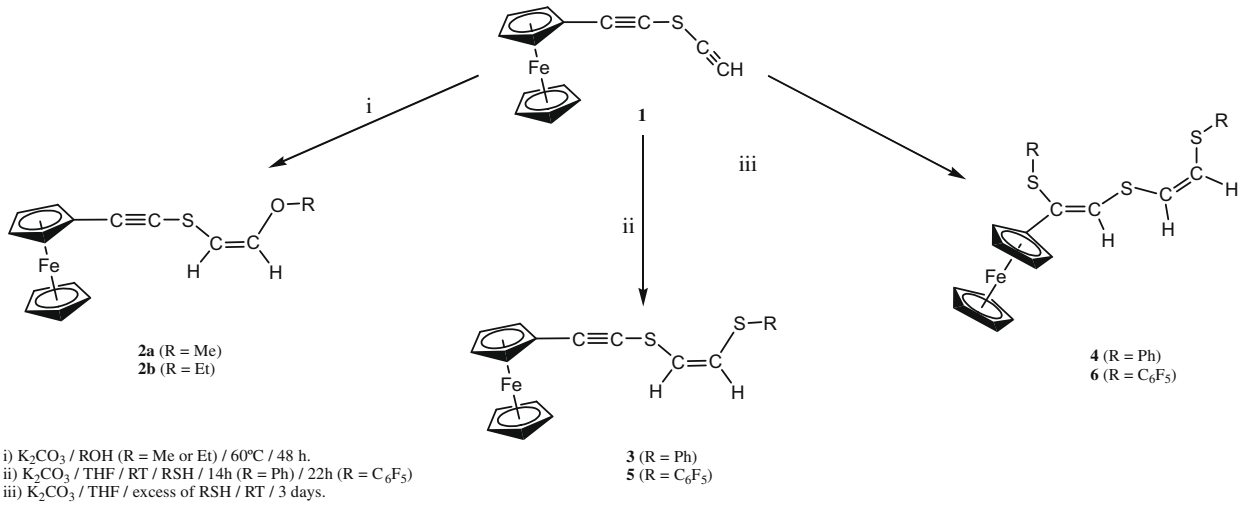
doi:10.1016/j.jorganchem.2009.10.026



Scheme 1.

spectra of two doublet resonances [6.24 (d, 1H, =C(H)OMe, J = 5.2 Hz) and 5.09 (d, 1H, C(H)=C, J = 5.2 Hz)] **2a** and [6.30 (d, 1H, =C(H)(OEt), J = 5.2 Hz] and 5.07 [d, 1H, C(H)=C, J = 5.2 Hz)] **2b**, whose proton coupling constant value corresponds to a *cis* position. The reports on hydroalkoxylation reactions of alkynes are less abundant as compared with those regarding to hydrothiolation. Nucleophilic addition to terminal alkynes are expected to follow the anti-Markovnikov's rule while the transition-metal-catalyzed reactions may give either Markovnikov or anti-Markovnikov adducts. Thus, recently it has been reported that the addition of MeOH to different non-functionalized terminal alkynes RC≡CH (R = H, ^{n}Pr, ^{n}Bu, Ph, HC≡C(CH$_2$)$_4$) yields to Markovnikov derivatives and only in the case of hex-1-yne and hept-1-yne anti-Markovnikov products are observed [5]. It is noteworthy that although the presence of two C–C triple bonds in compound FcC≡CCSC≡CH **1** would allow the addition of one alcohol molecule to each alkyne group or a double addition to the same C≡C bond, only the formation of compounds **2** has been observed even using a big excess of alcohol or base and variations in the temperature and reaction time. This fact is in contrast with the reports on double hydroalkoxylation [5,6].

Compound [(*Z*)-FcC≡CSC(H)=C(H)(OMe)] **2a** crystallises in the *P21/a* space group. An ORTEP drawing of it is shown in Fig. 1. The C(1)–C(2) [1.215(7) Å] and C(3)–C(4) [1.328(7) Å] distances are comparable to those exhibited by compounds [Ru$_3$(CO)$_9$(μ$_3$-η^2:η^4:η^3-Me$_3$SiCC(C$_2$Fc)SC(Fc)CSC≡CSiMe$_3$)] [1.208(6) and 1.344(5) Å] [7], FcC≡CSC≡CSiMe$_3$ [1.185(4) and 1.189(4) Å] [7], FcC(CH$_3$)$_2$Fc′–C≡C–C≡C–Ph [1.193(4) and 1.200(4) Å] [8], (H$_3$CCOS)(H)C=C(OCOCH$_3$)(COOH) [1.336(5) Å] [9], (C$_5$H$_5$FeC$_5$H$_4$)-(H)C=C(H)(S^{t}Bu) [1.351(8) Å] [10].

Additionally, distances of 1.683(5), 1.774(5) and 1.356(7) Å found for the S(2)–C(2), S(2)–C(3) and C(4)–O(1) bonds, respectively, are shorter than those corresponding to a single bond. This fact seems to be as a result of the contribution of the electron lone pairs on the sulfur and oxygen atoms. Similar values are found in compound *trans*-[Pt{(*E*)-C(SMe)=CHPh}Cl(PEt$_3$)$_2$]·CHCl$_3$ [1.766(6) Å] [11] and [HOs$_3$(CO)$_{10}$(μ-η^1:η^2-PhCH$_2$C=CH–C=CH–O)] [1.400 (12) Å] [12]. The C(2)–S(2)–C(3) angle [101.1(2)] is comparable to those found for the compounds FcC≡CSC≡CSiMe$_3$ [99.10(16)] [7], *trans*-[Ph(Et$_3$P)$_2$PtC≡CSC≡CPt–(Et$_3$P)$_2$Ph] [105.0(3)] and *cis*-[Pt(Me$_2$bipy){C≡CSC≡CSi^{i}Pr$_3$}$_2$] [105.4(9)] [13]. The ferrocenyl group shows an almost-perfect eclipsed geometry with its rings. Similar features have been observed in related structures of [C$_5$H$_5$FeC$_5$H$_4$(C≡CC$_6$H$_4$)$_2$SMe] [14] and [C$_5$H$_5$FeC$_5$H$_4$C≡C(C$_4$-H$_2$S)$_3$C≡CC$_5$H$_4$FeC$_5$H$_5$] [15].

In contrast with the above mentioned on the hydroalkoxylation reactions, a mono or double hydrothiolation takes place in compound FcC≡CCSC≡CH **1** depending on the amount of thiol present in the reaction. Thus, when compound **1** reacts with HSR (R = Ph, C$_6$F$_5$) in 1:5 stoichiometry, using K$_2$CO$_3$ as base, an anti-Markovnikov addition occurs to generate the *Z* isomers [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** and [(*Z*)-FcC≡CSC(H)=C(H)SC$_6$F$_5$] **5** (Scheme 1).

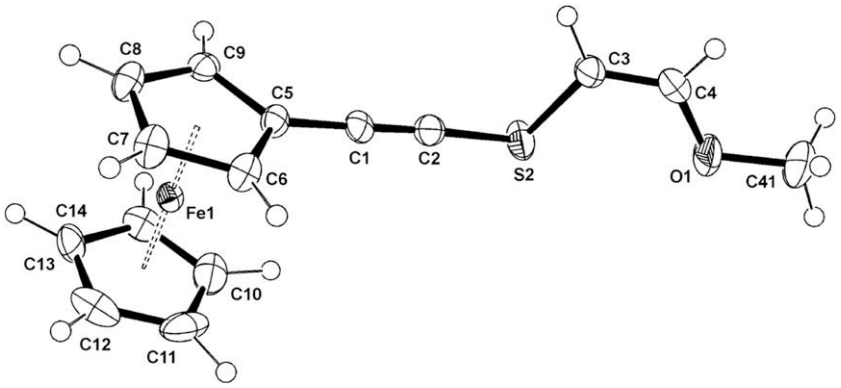


Fig. 1. Molecular structure of **2a**. Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.215(7), C(3)–C(4) 1.328(7), C(2)–S(2) 1.683(5), C(3)–S(2) 1.774(5), C(4)–O(1) 1.356(7), C(4)–O(1)–C(41) 115.8(5), C(2)–S(2)–C(3) 101.1(2). Ellipsoids are drawn at the 50% probability level.

Although the Cs_2CO_3 is a base widely used in the catalytic additions, the K_2CO_3 is the most convenient base in reactions carried out in a large scale due to its low cost.

The resonances corresponding to the olephinic protons in the ^1H NMR spectrum of compound **3** appear overlapped at 6.46 ppm, however, two doublet signals at 6.61 and 6.27 ppm are exhibited for compound **5**. In both cases a coupling constant of 8.0 Hz suggests a *cis* geometry. In order to make an accurate assignment of the ^{13}C resonances due to the presence of different olephinic protons in the molecule, a HMQC NMR experiments were carried out. Similar resonances (^1H and $^{13}C\{^1H\}$ NMR) are observed for compounds [(*Z*)-$PPh_2CH{=}CHSC_{12}H_{25}$] [3e], [(*Z*)-PhSCH=CHPh] [16] and [(*Z,Z*)-$(MeO_2CCH{=}CHS)_2C_2B_{10}H_{10}$] [17]. Additionally, NMR data of compound **5** (see Section 4) are in accordance with a mixture of two positional isomers in a 2:1 ratio. Complexes [(*Z,Z*)-Fc(SR)C=C(H)SC(H)=C(H)SR] [R = Ph (**4**), C_6F_5 (**6**)] are obtained from analogous reactions by using a big excess of the HSR instead (Scheme 1). The ^1H and $^{13}C\{^1H\}$ NMR data are indicative of the presence in the molecule of two olephinic groups as a consequence of a double hydrothiolation (see Section 4) and they are in the range expected for comparable derivatives [17]. 1D-NOE experiments suggested a *Z,Z* stereochemistry at the two double carbon–carbon bonds. Similar behaviour has been reported for compound PhC≡CP(Ph)C≡CPh, structurally analogous to FcC≡CCSC≡CH **1**, which suffers an *anti* double hydrothiolation to yield the compound [$Ph(C_{12}H_{25}S)$C=(H)CP(Ph)C(H)=$C(SC_{12}H_{25})$Ph] [3e]. Additionally, the parent ion in the mass spectrum [*m*/*z*: 486 (**4**) and *m*/*z*: 666 (**6**)] agree with this formula.

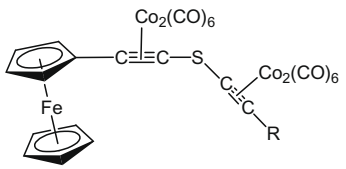
It is well known that the alkyne cobaltcarbonyl complexes may promote the addition of protic substances HXR (X = O, S, Se) to the carbon–carbon triple bond by demetallation [18]. In order to search if this method allows the formation of different isomers to those observed before and their role as metalloligands, our initial goal was to prepare the new alkyne cobaltcarbonyl complex [{$Co_2(CO)_6$}$_2$(μ-η^2-FcCCSCCH)] **8** (Fig. 2) and study its behaviour in the addition of thiols.

Reaction of FcC≡CSC≡CH **1** with $Co_2(CO)_8$ in dichloromethane at room temperature during 0.5 h afforded the trimerization benzene derivative [{$Co_2(CO)_6$}$_3$(μ-η^2-FcCCS)$_2$(μ-η^2-HCCS)]C_6H_2Fc as the main compound together to small amount of compound **8**. Although the role of cobalt carbonyls in trimerization processes is well known to give substituted benzenes [19], reports on trimerization of ferrocenyl alkynes are not abundant. Using FcC≡CH, either 1,3,5- and 1,2,4-triferrocenyl benzenes or a mixture of both of them have been prepared [20]. According to the mechanisms described for these authors, we agree that once the complex [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCH)] is formed, it can react with a molecule of the alkyne [{$Co_2(CO)_6$}(μ-η^2-FcCCSC≡CH)] followed by another molecule of the ferrocenyl alkyne [{$Co_2(CO)_6$}(μ-η^2-FcC≡CSCCH)] to give the trimerization product [{$Co_2(CO)_6$}$_3$-(μ-η^2-FcCCS)$_2$(μ-η^2-HCCS)]C_6H_2Fc after demetallation. Its spectroscopic and spectrometric data are the following: IR (ν_{CO} 2092m, 2061 s, 2030 vs), ^1H NMR {7.19 (s, 2H, C_6H_2), 6.77 (s, 1H, HC≡C), 4.54–4.36 (m, 12H, C_5H_4), 4.34 (s, 5H, C_5H_5), 4.31 (s, 5H, C_5H_5), 4.20 (s, 5H, C_5H_5)}, MS(ESI$^+$) *m*/*z*: 1488–1152 (M^+–*n*CO, *n* = 6–18).

This result revealed the difficulty to obtain compound [{Co_2-$(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCH)] **8** in good yield using FcC≡CSC≡CH as precursor, probably due to the presence of a terminal alkyne group that seems to favour the trimerization. Therefore, we decided to investigate if the synthesis of compound [{Co_2-$(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCSiMe$_3$)] **7** followed by its desilylation, was a better method to prepare it. $Co_2(CO)_8$ was added to a hexane solution of FcC≡CSC≡$CSiMe_3$ in 2:1 stoichiometry and stirred at room temperature for 1.5 h, then the residue was purified by column chromatographic affording to the green compound [{Co_2-$(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCSiMe$_3$)] **7** in high yield (Fig. 2). This compound has been characterized by IR, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and mass spectrometry (see Section 4). In addition, X-ray diffraction studies have been carried out on it. Single crystals of compound **7** were grown from hexane at −20 °C. An ORTEP view is shown in Fig. 3 and selected bond and angles are collected as figure captions. The structure consists of an angular thioether in which each alkynic group is perpendicularly bound to a dicobalt hexacarbonyl unit. The Co_2C_2 cores adopt the expected tetrahedral arrangement. The Co–Co [2.500(2) and 2.491(2) Å] and C(alkyne)–C(alkyne) [1.377(10) and 1.378(10) Å] bond distances falling within the normal range [21]. The CCS and CSC angles [127.7(6), 128.0(6) and 109.1(4)] are comparable with those found in compounds [{$Co_2(CO)_6$}(μ-η^2-RCCSMe)] (R = Me [136.9(2); 101.3(1)]; R = ^{t}Bu [137.1(1); 102.3(1)]; R = Ph [135.9(3); 102.0(2)] R = $EtCO_2$ [136.7(1); 100.86(9)]) [22]. All carbonyl ligands around the cobalt are terminal.

Once the compound [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCH)] **8** was prepared, we studied its reactivity in the presence of thiols. However, all attempts to prepare vinyl-sulfides by demetallation failed, leading to very unsoluble compounds.

In order to know the ability of compound [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** to act as multifunctional ligand, we have carried out some preliminary studies. Reactions between **3** and the metal carbonyls $Co_2(CO)_8$, $Os_3(CO)_{10}(NCMe)_2$ and $Fe_2(CO)_9$ have revealed that the vinyl-sulfide ligand acts as a 6-electron donor towards a sulfur atom and the alkyne group in compound [(*Z*)-{Fe_3-$(CO)_9$}[μ_3,η^3-(*CCS*)-FcCCSC(H)=C(H)(SPh)] **11** while it is donating four electrons through the C≡C bond in compounds



7 (R = $SiMe_3$)
8 (R = H)

Fig. 2. Structure of compounds **7** and **8**.

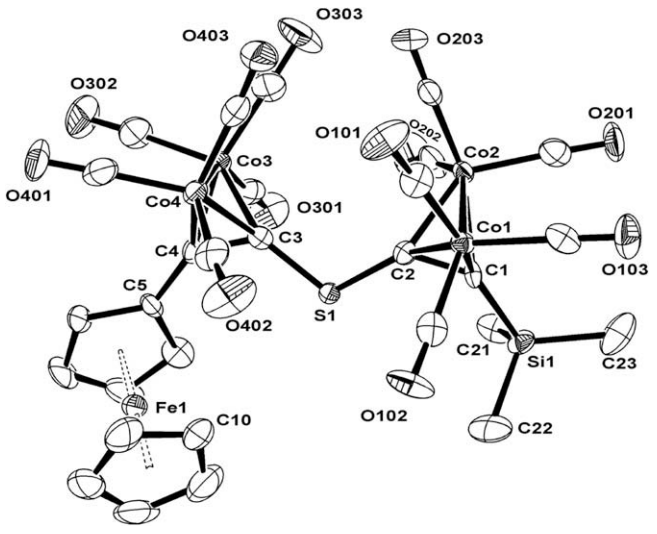
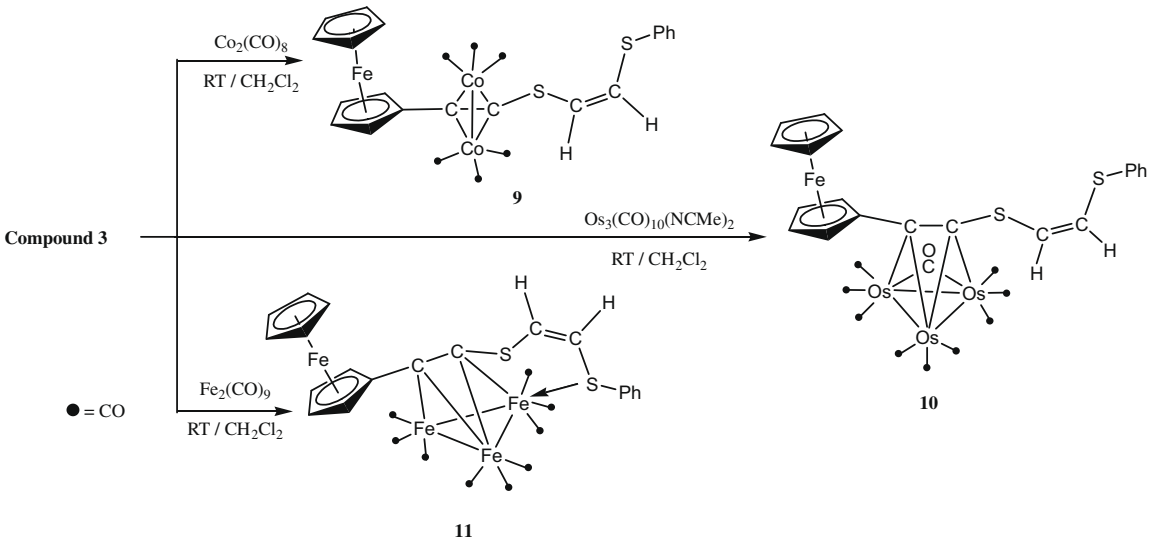


Fig. 3. Molecular structure of **7**. Selected lengths (Å) and angles (°): C(1)–C(2) 1.377(10), C(3)–C(4) 1.378(10), C(2)–S(1) 1.739(7), C(3)–S(1) 1.724(8), Co(1)–Co(2) 2.501(2), Co(3)–Co(4) 2.491(2), C(3)–S(1)–C(2) 109.1(4). Ellipsoids are drawn at the 50% probability level.



Scheme 2.

[(*Z*)-{Co_2-$(CO)_6$}(μ-η^2-FcCCSC(H)=C(H)SPh)] **9** and [(*Z*)-$Os_3(CO)_9$(μ-CO){μ_3-η^2-FcCCSC(H)=C(H)(SPh)}] **10** (Scheme 2).

Thus, the IR spectra for compounds **9** [ν_{CO} (cm^{-1}) 2088m, 2054s, 2037s, 2027vs] and **10** [ν_{CO} (cm^{-1}): 2088w, 2064vs, 2047s, 2025m, 2005s, 1996sh, 1976w, 1845vw] show the expected carbonyl pattern for the $Co_2(CO)_6$ and $Os_3(CO)_9$(μ-CO) fragments, respectively, and the ^{13}C NMR resonances of the C≡C carbon atoms [117.9 and 84.4 ppm] for **9** and [137.0 and 135.8 ppm] for **10** appear in the characteristic range for an alkyne group acting as four electron donor [8,12,21c,23].

The structure of compound [(*Z*)-{$Fe_3(CO)_9$}[μ_3,η^3-(*CCS*)-FcCCSC(H)=C(H)(SPh)] **11** has been suggested taking into account that: (a) only one of the olephinic resonances appear shifted downfield (138.1, 124.9 ppm), as compared to the resonances for the free ligand **3** (125.6, 124.2 ppm), indicating that one of the two sulfur atoms is participating in the coordination to the metal cluster, (b) on the other hand, the fact that the alkyne group is acting as a 4-electron donor is justified according to its signals in ^{13}C NMR spectrum (209.6, 95.8 ppm). The assignment of these signals was based on the spectroscopic data reported for similar $Fe_3(CO)_9$(μ_3,η^2-alkyne) complexes [24], (c) our experience using the alkyne thioether $C_5H_5FeC_5H_4C{\equiv}CSC{\equiv}CSiMe_3$ as ligand in cluster chemistry has revealed that when this ligand is coordinated through the C–C triple bond, the adjacent sulfur atom is unable to coordinate to another metal centre, probably due to a decrease in its donor ability as a consequence that the sulfur atom is giving electronic density to the C≡C bond [25] and finally, (d) the presence in the FAB^+ mass spectrum of the molecular peak [797 (M^++H)] and those corresponding to the successive loss of the nine carbonyls [768–544 (M^+-nCO, n = 1–9)]. Additionally, the IR spectrum in the CO region show a typical pattern for a closed $Fe_3(CO)_9$ moiety [24].

These results reveal that the formation of compounds **9** and **10** implies the substitution of two CO or two NCMe ligands while cleavage and formation of Fe–Fe bonds in the precursor $Fe_2(CO)_9$ is required to obtain compound **11**. The occurrence of this ruptures justifies the low yield for the latter compound. Compounds **9–11** maintain the *cis* geometry of the olephinic protons of the starting vinyl-sulfide [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3**.

3. Conclusions

New vinyl-sulfides and ethers containing a ferrocenyl group have been prepared by addition of thiols and alcohols to the alkyne groups in compound FcC≡CSC≡CH **1**. In all cases, the hydroalkoxylation and hydrothiolation processes follow the anti-Markovnikov rule yielding only to the *Z* isomer.

As far as we know, vinyl-sulfides and ether containing an organometallic substituent are scarce, being the compound [(*Z*)-FcC≡CSC(H)=C(H)(OMe)] **2a** the first organometallic vinyl ether whose structure has been crystallographically studied.

Preliminary studies on [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** reveal its multifunctional ability only in the formation of compound {Fe_3-$(CO)_9$}[μ_3,η^3-(*CCS*)-FcCCSC(H)=C(H)(SPh)] **11**.

4. Experimental

4.1. General procedures

All reactions were carried out under argon atmosphere. Solvents were dried using standard methods. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrophotometer using NaCl cells. ^1H and $^{13}C\{^1H\}$ NMR spectra were registered on a Bruker AMX-300 and DRX-500 instrument, respectively. Elemental analyses were performed on an Elemental Analyzer LECO CHNS-932. FAB, MALDI and ESI mass spectra were carried out on a WG Autospec Spectrometer, a 4700 Proteomics Analyzer (Applied Biosystems) and on a QSTAR (Applied Biosystems) using 3-nitrobenzyl alcohol, ditranol or acetonitrile as matrix, respectively. $C_5H_5FeC_5$- $H_4C{\equiv}CSC{\equiv}CSiMe_3$ was prepared according to published procedures [7].

4.2. Synthesis of Compound FcC≡CSC≡CH *1*

To a solution of FcC≡CSC≡$CSiMe_3$ (100 mg, 0.3 mmol) in THF (10 mL) was added KF (19 mg, 0.33 mmol) dissolved in MeOH (1.9 mL). The mixture was stirred 1 h and then the solvent was removed under vacuum. The product was extracted with $CHCl_3/H_2O$. The organic layer was dried over $MgSO_4$ and filtered. Compound [FcC≡CSC≡CH] **1** was isolated in 90% yield (72 mg, 0.27 mmol).

Spectral data for compound ***1***: ^1H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 4.49 (t, 4H, C_5H_4, J = 1.9 Hz), 4.25 (t, 4H, C_5H_4, J = 1.9 Hz), 4.24 (s, 5H, C_5H_5), 3.00 (s, 1H, ≡CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 95.7 [FcC≡C], 68.7, 66.2 [CSC], 83.5 [C≡CH], 72.3, 69.5, 63.1 [C_5H_4], 70.1 [C_5H_5]. MS (FAB^+) m/z: 266 [M^+]. Anal. Calc. for $C_{14}H_{10}SFe$: C, 63.18; H, 3.79; S, 12.05. Found: C, 63.40; H, 3.75; S, 11.88%.

4.3. Synthesis of compound FcC≡CSC(H)=C(H)(OR) [R = Me (**2a**), Et (**2b**)]

To a solution of FcC≡CSC≡CH **1** (100 mg, 0.38 mmol) in 20 mL of ROH (R = Me or Et, respectively) was added a saturated solution of K_2CO_3 in the same solvent (2.5 mL). The mixture was heated at 60 °C for 48 h. The orange mixture was evaporated to dryness and chromatographed by TLC using hexane/toluene (5:1) as eluent giving an orange band corresponding to compound [(*Z*)-FcC≡CSC(H)=C(H)(OR)] R = Me (**2a**) (85 mg, 0.28 mmol, 95%), R = Et (**2b**) (84 mg, 0.27 mmol, 90%). Single crystals of compound **2a** were grown from hexane/CH_2Cl_2 at −20 °C.

*Spectral data for compound **2a***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 6.24 (d, 1H, =C(H)OMe, J = 5.2 Hz), 5.09 (d, 1H, C(H)=C, J = 5.2 Hz), 4.43 (t, 2H, C_5H_4, J = 1.9 Hz), 4.20 (m, 7H, C_5H_4 + C_5H_5), 3.73 (s, 3H, OCH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 147.7 [=*C*H(OMe)], 97.1 [SC(H)=C], 91.3 [FcC≡C], 64.8 [FcC≡*C*], 72.0, 68.9, 60.5 [C_5H_4], 70.0 [C_5H_5], 30.3 [O*C*H$_3$]. MS (FAB$^+$) m/z: 298 [M$^+$]. Anal. Calc. for $C_{15}H_{14}OSFe$: C, 60.40; H, 4.76; S, 10.74. Found: C, 60.61; H, 4.90; S, 10.44%.

*Spectral data for compound **2b***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 6.30 [d, 1H, =C(H)(OEt), J = 5.2 Hz], 5.07 [d, 1H, C(H)=C, J = 5.2 Hz], 4.43 [t, 2H, C_5H_4, J = 1,8 Hz], 4.20 [m, 7H, C_5H_4 + C_5H_5], 3.93 [qu, 2H, OCH_2, J = 7.1 Hz], 1.31 [t, 3H, CH_3, J = 7.1 Hz]. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 146.3, [=*C*H(OEt)], 97.0 [SC(H)=C], 91.2 [FcC≡C], 64.8 [FcC≡*C*], 71.9, 68.9, 64.9 [C_5H_4], 69.9 [C_5H_5], 29.7 [O*C*H$_2$], 15.2 [*C*H$_3$]. MS(FAB$^+$) m/z 312 (M$^+$). Anal. Calc. for $C_{16}H_{16}OSFe$: C, 61.53; H, 5.13; S, 10.26. Found: C, 61.57; H, 5.16; S, 9.76%.

4.4. Reaction of FcC≡CSC≡CH **1** with HSPh

4.4.1. Stoichiometry 1:5

To a solution of compound [FcC≡CSC≡CH] **1** (100 mg, 0.38 mmol) in THF (20 mL) was added 6 mL of a saturated solution of K_2CO_3 in THF and HSPh (0.20 mL, 1.9 mmol). The mixture was stirred for 14 h. After this time, the solvent was removed in vacuo and the residue was purified by TLC using hexane/toluene (5:2) as eluent. Compound [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** (87 mg, 0.23 mmol, 61%) was obtained as an orange solid.

*Spectral data for **3***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.40–7.24 (m, 5H, Ph), 6.48 [d, 1H, SC(H)=C, J = 8.3 Hz], 6.45 [d, 1H, =C(H)(SPh), J = 8.3 Hz], 4.46 (t, 2H, C_5H_4, J = 1.9 Hz), 4.24 (t, 2H, C_5H_4, J = 1.9 Hz), 4.23 (s, 5H, C_5H_5). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 134.7, 129.5, 129.2, 127.1 [C_6H_5], 125.6, 124.2 [*C*=*C*], 93.9 [FcC≡C], 71.5, [FcC≡*C*], 72.1, 69.2, 64.2 [C_5H_4], 70.1 [C_5H_5,]. MS (FAB$^+$) m/z: 376 [M$^+$]. Anal. Calc. for $C_{20}H_{16}S_2Fe$: C, 63.83; H, 4.29; S, 17.04. Found: C, 63.17; H, 4.42; S, 16.46%.

4.4.2. Excess of HSPh

To a solution of compound [FcC≡CSC≡CH] **1** (50 mg, 0.19 mmol) in THF (10 mL) was added 3 mL of a saturated solution of K_2CO_3 in THF and HSPh (0.38 mL, 3.8 mmol). The mixture was stirred for 3 days. After this time, the solvent was removed in vacuo and the residue was purified by TLC using hexane/toluene (10:1) as eluent. Compound [(*Z*,*Z*)-FcC(SC_6H_5)=C(H)SC(H)=C(H)SC_6H_5] **4** (40 mg, 0.08 mmol, 44%) was obtained as an orange solid.

*Spectral data for **4***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.51–7.24 (m, 10H, Ph), 7.00 (s, 1H, =C(H)S), 6.55 (d, 1H, SC(H)=C, J = 8.5 Hz), 6.45 (d, 1H, =C(H)(SPh), J = 8.5 Hz), 4.44 (t, 2H, C_5H_4, J = 1.9 Hz), 4.22 (t, 2H, C_5H_4, J = 1.9 Hz), 4.14 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 135.4, 129.3, 128.5, 126.5 [C_6H_5], 130.8 [=*C*(H)S], 128.0 [*C*(SPh)=CH], 124.4, 124.0 [*C*H=*C*H], 70.2, 69.0, 66.9 [C_5H_4], 69.6 [C_5H_5]. MS (FAB$^+$) m/z: 486 [M$^+$]. Anal. Calc. for $C_{26}H_{22}S_3Fe$: C, 64.20; H, 4.53; S, 19.75. Found: C, 64.76; H, 4.68; S, 19.75%.

4.5. Reaction of FcC≡CSC≡CH **1** with HSC_6F_5

4.5.1. Stoichiometry 1:5

The experimental procedure is analogous to the before mentioned for HSPh, although in this case the reaction was stirred for 22 h. The crude was chromatographed on silica gel. Elution with hexane/CH_2Cl_2 50:1 gave a mixture of isomers of the compound [(*Z*)-FcC≡CSC(H)=C(H)SC_6F_5] **5** (87 mg, 0.23 mmol, 61%) in a 2:1 ratio.

*Spectral data for **5***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 6.61 (d, 1H, SC(H)=C, J = 8.0 Hz, isomer a), 6.56 (d, 1H, SC(H)=C, J = 8.0 Hz, isomer b), 6.27 (d, 1H, =C(H)S, J = 8.0 Hz, isomer a), 6.19 (d, 1H, =C(H)S, J = 8.0 Hz, isomer b), 4.45 (t, 2H, C_5H_4, J = 1.9 Hz), 4.24 (d, 2H, C_5H_4, J = 1.9 Hz), 4.21 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 149.5–125.0 [C_6F_5, both isomers], 130.7, 119.0 [*C*H=*C*H, isomer a], 129.7, 120.2 [*C*H=*C*H, isomer b], 94.9 [*C*≡CS, isomer a], 94.6 [C≡*C*S, isomer b], 72.1, 69.3, 63.8 [C_5H_4, both isomers], 70.3 [C≡*C*S, isomer b], 70.2 [C≡*C*S, isomer a], 70.0 [C_5H_5, both isomers]. MS (FAB$^+$) m/z: 466 [M$^+$]. Anal. Calc. for $C_{20}H_{11}F_5FeS_2 \cdot 1/4\ CH_2Cl_2$: C, 49.91; H, 2.36; S, 13.13. Found: C, 50.06; H, 2.58; S, 13.13%.

4.5.2. Excess of HSC_6F_5

The procedure is analogous to the before mentioned for HSPh. The solvent was removed in vacuo and the residue was chromatographed by TLC using hexane/THF (30:1) as eluent. An orange-red band gave a mixture of isomers [(*Z*,*Z*)-FcC(SC_6F_5)=C(H)SC(H)=C(H)SC_6F_5] **6** in a 2:1 ratio.

*Spectral data for **6***: ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.17 [s, 1H, C=C(H)S, isomer a], 6.98 [s, 1H, C=C(H)S, isomer b], 6.66 [d, 1H, SC(H)=C, J = 8.1 Hz, isomer b], 6.56 [d, 1H, =C(H)S, J = 8.1 Hz, isomer a], 6.14 [d, 1H, =C(H)(SC_6F_5), J = 8.1 Hz, isomer b], 6.08 [d, 1H, =C(H)(SC_6F_5), J = 8.1 Hz, isomer a], 4.78 [m, 2H, C_5H_4, isomer a], 4.71 [m, 2H, C_5H_4, isomer b], 4.38 [m, 2H, C_5H_4, isomer a], 4.36 [m, 2H, C_5H_4, isomer a], 4.21 [s, 5H, C_5H_5, isomer a], 4.18 [s, 5H, C_5H_5, isomer b]. ^{13}C NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 151.5 [*C*(SC_6F_5)=CH, isomer a], 149.0–136.1 [C_6F_5, both isomers], 140.9 [*C*(SC_6F_5)=CH, isomer b], 139.8 [=*C*(H)S, isomer b], 135.8 [=*C*(H)S, isomer a], 128.2, 118 [*C*H=*C*H, isomer a], 128.1, 120.5 [*C*H=*C*H, isomer b], 70.4, 70.2, 70.0, 69.4 [C_5H_4, both isomers], 69.5 [C_5H_5, both isomers]. MS(FAB$^+$) m/z 666 (M$^+$). Anal. Calc. for $C_{28}H_{17}F_{10}FeS_3 \cdot 1/2\ CH_2Cl_2$: C, 44.90; H, 1.85; S, 13.85. Found: C, 45.27; H, 1.98; S, 13.52%.

4.6. Synthesis of [{$Co_2(CO)_6$}$_2$(-η^2:η^2-FcCCSCCSiMe$_3$)] **7**

$Co_2(CO)_8$ (513 mg, 1.5 mmol) was added to a solution of [FcC≡CSC≡CSiMe$_3$] (200 mg, 0.6 mmol) in hexane (30 mL) and the mixture was stirred for 1.5 h. The resulting green solution was dried under vacuum and the residue was purified by column chromatography. Elution with hexane/toluene (100:1) gave the green compound [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCSiMe$_3$)] **7** (439 mg, 0.48 mmol, 81%). Suitable crystals of compound **7** were grown from hexane at −20 °C.

*Spectral data of **7***: IR(hexane) ν_{CO} (cm^{-1}): 2097m, 2083w, 2061vs, 2026s. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 4.49 [m, 2H, C_5H_4], 4.42 [m, 2H, C_5H_4], 4.28 [s, 5H, C_5H_5], 0.42 [s, 9H, $SiMe_3$]. ^{13}C NMR ($CDCl_3$, 500 MHz, 22 °C) δ: 199.3, 198.7 [CÓs], 105.9, 99.3, 92.7, 87.8 [C≡C], 85.1, 69.3, 69.2 [C_5H_4], 69.7 [C_5H_5,], 0.1 [Si(CH_3)$_3$]. MS(FAB$^+$) m/z: 910 [M$^+$], 826–574 [M$^+$−nCO, n = 3–12]. Anal. Calc. for $C_{29}H_{18}O_{12}SSiCo_4Fe \cdot 1/2\ CH_2Cl_2$: C, 37.19; H, 2.01; S, 3.32. Found: C, 37.40; H, 2.36; S, 3.76%.

4.7. Synthesis of [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCH)] **8**

To a solution of [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCSiMe$_3$)] **7** (50 mg, 0.06 mmol) in THF (8 mL) was added KF (3.8 mg, 0.07 mmol) dissolved in MeOH (0.4 mL). The mixture was stirred 18 h and then the solvent was removed under vacuum. The product was chromatographed by TLC using hexane/dichloromethane (5:1) as eluent. Compound [{$Co_2(CO)_6$}$_2$(μ-η^2:η^2-FcCCSCCH)] **8** was isolated in 95% yield (44 mg, 0.05 mmol).

Spectral data of ***8***: IR (hexane) ν_{CO} (cm^{-1}): 2099w, 2086m, 2064vs, 2037s, 2026vs. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 6.57 (s, 1H, C≡CH), 4.46 (m, 2H, C_5H_4), 4.41 (m, 2H, C_5H_4), 4.30 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, 500 MHz, 22 °C) δ: 198.7 [CÓs], 90.0, 89.8, 84.5, 74.4 [C≡C], 69.7 [C_5H_5,], 69.6, 69.3, 69.2 [C_5H_4]. MS (FAB$^+$) *m*/*z*: 838 [M$^+$], 754–502 [M−*n*CO, *n* = 3–12]. Anal. Calc. for $C_{26}H_{10}O_{12}SCo_4Fe{\cdot}1/2\ CH_2Cl_2$: C, 36.14; H, 1.25; S, 3.63. Found: C, 36.28; H, 1.55; S, 3.76%.

4.8. Reaction of [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** with $Co_2(CO)_8$

To a solution of [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** (112 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) was added $Co_2(CO)_8$ (103 mg, 0.30 mmol) and the mixture was stirred for 2 h. The solvent was removed under vacuum and the residue was chromatographed by TLC using hexane/toluene (5:2) as eluent. Compound [(*Z*)-{Co_2-$(CO)_6$}(μ-η^2-FcCCSC(H)=C(H)SPh)] **9** was isolated as a dark green solid (135 mg, 0.20 mmol, 68%).

Spectral data for ***9***: IR (hexane) ν_{CO} (cm^{-1}): 2088m, 2054s, 2037s, 2027vs. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.45–7.29 (m, 5H, Ph), 6.76 (d, 1H, SC(H)=C, *J* = 8.3 Hz), 6.56 (d, 1H, =C(H)S, *J* = 8.3 Hz), 4.47 (t, 2H, C_5H_4, *J* = 1.9 Hz), 4.40 (t, 2H, C_5H_4, *J* = 1.9 Hz), 4.31 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$, 500 MHz, 22 °C) δ: 206.7 [CÓs], 134.8, 129.7, 129.2, 125.7 [C_6H_5], 128.3, 126.9 [C=C], 117.9, 84.4 [C≡C], 72.0, 69.5, 69.4 [C_5H_4], 69.7 [C_5H_5,]. MS (FAB$^+$) *m*/*z*: 662 [M$^+$], 634–494 [M$^+$−*n*CO, *n* = 1–6]. Anal. Calc. for $C_{26}H_{16}O_6S_2Co_2Fe{\cdot}1/4\ CH_2Cl_2$: C, 46.15; H, 2.41; S, 9.37. Found: C, 46.30; H, 2.72; S, 9.82%.

4.9. Reaction of [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** with $Os_3(CO)_{10}(MeCN)_2$

[(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** (70 mg, 0.19 mmol) dissolved in 5 mL of CH_2Cl_2 was added to a solution of $Os_3(CO)_{10}(MeCN)_2$ (230 mg, 0.19 mmol) in CH_2Cl_2 (15 mL). The mixture was stirred for 2 h and then it was taken to dryness and the crude was chromatographed by TLC using hexane/CH_2Cl_2 (10:3) as eluent. The red compound [(*Z*)-$Os_3(CO)_9$(μ-CO){μ_3-η^2-FcCCSC(H)=C(H)(SPh)}] **10** was obtained as a mixture of isomers in a 3:1 ratio. (105 mg, 0.09 mmol, 45%).

Spectral data for ***10***: IR (hexane) ν_{CO} (cm^{-1}): 2088w, 2064vs, 2047s, 2025m, 2005s, 1996sh, 1976w, 1845vw. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.45–7.28 [m, 5H, Ph], 6.85 [d, 1H, SC(H)=C, *J* = 8.0 Hz, isomer a], 6.65 [d, 1H, SC(H)=C, *J* = 8.3 Hz, isomer b], 6.39 [d, 1H, C=C(H)S, *J* = 8.0 Hz, isomer a], 6.21 [d, 1H, SC(H)=C, *J* = 8.3 Hz, isomer b], 4.43 [t, 2H, C_5H_4, *J* = 1.9 Hz, isomer a], 4.35 [m, 2H, C_5H_4, isomer b], 4.33 [t, 2H, C_5H_4, *J* = 1.9 Hz, isomer a], 4.24 [m, 2H, C_5H_4, isomer b], 4.26 [s, 5H, C_5H_5, isomer a], 4.13 [s, 5H, C_5H_5, isomer b]. ^{13}C NMR ($CDCl_3$, 500 MHz, 22 °C) δ: 178.9 [CÓs], 130.6, 130.0, 129.2, 127.1 [C_6H_5], 127.2, 126.4 [C=C], 137.0, 135.8 [C≡C], 70.6, 69.8, 68.9 [C_5H_4], 70.2 [C_5H_5,]. MS(FAB$^+$) *m*/*z*: 1200–948 [M$^+$−*n*CO, *n* = 1, 2, 4–10].

4.10. Reaction of [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** with $Fe_2(CO)_9$

$Fe_2(CO)_9$ (196 mg, 0.54 mmol) was added to a solution of [(*Z*)-FcC≡CSC(H)=C(H)SPh] **3** (100 mg, 0.27 mmol) in THF (20 mL) and the reaction is stirred for 2.5 h. The mixture was taken to dryness and extracted with hexane. The green compound [(*Z*)-{Fe_3-$(CO)_9$}[μ_3,η^3-(*CCS*)-FcCCSC(H)=C(H)(SPh)] **11** (61 mg, 0.08 mmol, 28%) crystallized from this solution at −20 °C.

Spectral data for ***11***: IR (hexane) ν_{CO} (cm^{-1}): 2072w, 2042vs, 2026s, 2002m, 1985w, 1970w. ^{1}H NMR ($CDCl_3$, 300 MHz, 22 °C) δ: 7.46–7.32 [m, 5H, Ph], 6.91 [d, 1H, SC(H)=C, *J* = 8.4 Hz], 6.28 [d, 1H, SC(H)=C, *J* = 8.4 Hz], 5.42 [m, 2H, C_5H_4], 5.0 [m, 2H, C_5H_4], 4.22 [s, 5H, C_5H_5]. ^{13}C NMR ($CDCl_3$, 500 MHz, 22 °C) δ: 210.7, 210.6, 210.2 [CÓs], 138.1, 124.9 [C=C], 132.8, 130.6, 129.3, 127.7, [C_6H_5], 209.6, 108.5, 95.8 [C≡C], 74.5, 74.3, 74.0, 71.4, 70.8 [C_5H_4], 71.1 [C_5H_5,]. MS(FAB$^+$) *m*/*z*: 797 [M$^+$+H], 768–544 [M$^+$−*n*CO, *n* = 1–9]. Anal. Calc. for $C_{29}H_{16}Fe_4O_9S_2$: C, 43.75; H, 2.01; S, 8.04. Found: C, 43.62; H, 2.44; S, 8.20%.

Table 1
Crystal data and structure refinement for **2a** and **7**.

Compound	**2a**	**7**
Empirical formula	$C_{15}H_{14}FeOS$	$C_{29}H_{18}Co_4FeO_{12}SSi$
Formula weight	298.17	910.15
T [K]	200(2)	200(2)
Wavelength (Mo Kα) [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*21/*a*	*C*2/*c*
a [Å]	9.714(4)	30.773(6)
b [Å];	14,045(6)	15.912(4)
c [Å];	11.226(5)	15.390(4)
β (°)	114.93(3)	107.94(4)
V [Å^3]; *Z*	1388.9(10); 4	7169(3); 8
D_{calc} [g cm^{-3}]	1.426	1.686
μ [mm^{-1}]	1.22	2.355
F(0 0 0)	616	3616
Crystal size [mm]	0.41 × 0.28 × 0.16	0.21 × 0.16 × 0.12
θ Range (°)	3.52–27.52	3.27–27.52
Index ranges	−12 to 11, −18 to 18, 0 to 14	−39 to 39, −20 to 20, −19 to 19
Collected reflections	32 096	81 435
Independent reflections	3204	8212
Goodness-of-fit (GOF) on F^2	1.201	1.270
Final *R* indices [$F > 4\sigma(F)$]	R_1 = 0.070, wR_2 = 0.133	R_1 = 0.091, wR_2 = 0.217
R indices (all data)	R_1 = 0.092, wR_2 = 0.141	R_1 = 0.127, wR_2 = 0.235
Largest difference in peak/hole [e Å^{-3}]	0.623/−0.621	1.197/−1.029

4.11. X-ray crystallographic studies

Crystals of complexes **2a** and **7** were grown as described in Section 4, removed from the Schlenks and covered with a layer of a viscous perfluoropolyether (Fomblin®Y). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected at 200 K on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. Crystallographic data for all the complexes are presented in Table 1. The structures were solved, using the WINGX package [26], by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97) [27]. All non-hydrogen atoms were anisotropically refined. All the hydrogen atoms were positioned geometrically and refined by using a riding model in **7**. The hydrogen atoms of **2a** were directly located in the Fourier map and isotropically refined, except those of the C41 methyl group, which were positioned geometrically and refined by using a riding model.

5. Supplementary material

CCDC 746242 and 746241 contain the supplementary crystallographic data for **2a** and **7**. These data can be obtained free of charge

from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

We thank the Dirección General de Universidades e Investigación, Comunidad de Madrid (Project S-0505/PPQ/0328) and Factoría de Cristalización (CONSOLIDER-INGENIO 2010) for financial aid.

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