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C–C bond formation through olefin–thiocarbyne coupling in diiron complexes

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Abstract

The bridging diiron thiocarbyne complex $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) reacts with activated olefins (methyl acrylate, acrylonitrile, styrene, diethyl maleate), in the presence of Me_3NO and NaH, to give the corresponding μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R'' = CO_2Me$, $R' = H$, **3a**; $R'' = CN$, $R' = H$, **3b**; $R'' = C_6H_5$, $R' = H$, **3c**; $R'' = R' = CO_2Et$, **3d**). The coupling reaction of olefin with thiocarbyne is regio- and stereospecific, leading to the formation of only one isomer. C–C bond formation occurs between the less substituted alkene carbon and the thiocarbyne. Moreover, olefinic hydrogens of the bridging ligands are mutually *trans*.

The reactions of **3a**–**b** with $MeSO_3CF_3$ result, selectively, in the formation of the cationic μ-sulphonium allylidene complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ ($R = CO_2Me$, **4a**; $R = CN$, **4b**). Compound **4a** undergoes displacement of the SMe_2 group by nucleophiles such as $NaBH_4$, NBu_4CN and NaOMe, affording the complexes $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(R)C_\beta(H)C_\gamma(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R = H$, **5a**; $R = CN$, **5b**; $R = OMe$, **5c**), respectively. The molecular structures of **3a** and **5a** have been determined by X-ray diffraction studies.

Keywords: Thiocarbyne; Diiron complexes; Allylidene; Olefin insertion; C–C bond formation

1. Introduction

Dinuclear complexes with adjacent metal atoms have provided valuable models for investigating C–C bond formation reactions, which are relevant to hydrocarbon chain growth in the Fischer–Tropsch chemistry [1]. Our interest in this area has been focused on the diiron and diruthenium complexes containing bridging alkylidene and alkylidyne ligands [2]. Among these, the μ-thiocarbyne complex $[Fe_2\{\mu\text{-}CS(Me)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**1**) (Chart 1) has offered a number of new C–C bond forming reactions, which take advantage of the strong electrophilic character of the bridging ligand and are based on the addition of carbon nucleophiles (e.g. organo-lithium, organocopper, and Grignard reagents) [3].

On the other hand, studies on the related μ-aminocarbyne complex $[Fe_2(\mu\text{-}CNMe_2)(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (**2**) (Chart 1) have revealed a further possibility to generate C–C bonds and transform the C_1 into a C_3 bridging frame, consisting in the insertion of alkynes in the metal-carbyne bond [4].

Herein we report on an extension of these studies, aimed at investigating possible C–C bond forming reactions by coupling of olefins with the thiocarbyne ligand in complex **1**.

2. Results and discussion

The bridging diiron thiocarbyne complex **1** reacts with olefins (methyl acrylate, acrylonitrile, styrene, diethyl

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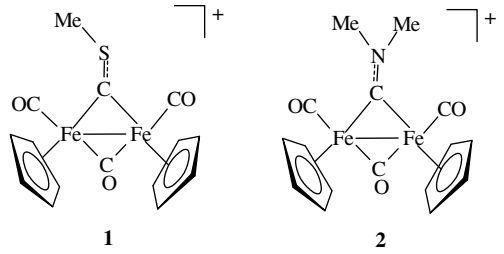
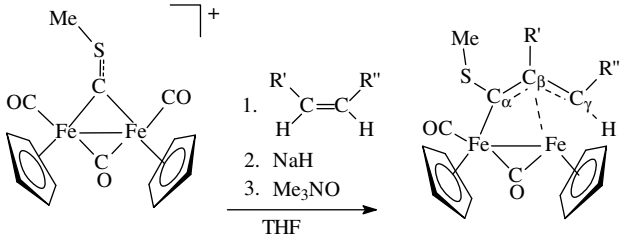


1 **2**

Chart 1.



1	R"	R'	
	CO_2Me	H	**3a**
	CN	H	**3b**
	C_6H_5	H	**3c**
	CO_2Et	CO_2Et	**3d**

Scheme 1.

maleate), in the presence of Me_3NO and NaH, to give the μ-allylidene complexes $[Fe_2\{\mu\text{-}\eta^1{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)\text{-}(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R'' = CO_2Me$, $R' = H$, **3a**; $R'' = CN$, $R' = H$, **3b**; $R'' = C_6H_5$, $R' = H$, **3c**; $R'' = R' = CO_2Et$, **3d**) (Scheme 1). The reactions were carried out in THF solution at room temperature; **3a**–**d** were purified by chromatography on alumina and isolated in about 80% yield.

Compounds **3a**–**d** were characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the molecular structure of **3a**, determined by the X-ray diffraction, is reported in Fig. 1. The main bond lengths and bond angles are reported in Table 1. The molecule is composed by a *cis*-$[Fe_2(\mu\text{-}CO)(CO)(Cp)_2]$ moiety to which is coordinated a bridging $\mu\text{-}\eta^1{:}\eta^3$-C(SMe)CHCH($CO_2Me$) ligand. The latter closely resembles other organic unsaturated fragments previously found coordinated to diiron frames and obtained by addition of nucleophiles (i.e. hydrides, cyanides, acetylides) to vinyliminium complexes [5]. All these ligands have been usually described as the result of the contribution of a bridging allylidene (Structure A in Chart 2) and a bridging vinylalkylidene (B) form. Depending on the substituents present on the ligand, one of the two forms can be predominant. In the present case, since both the C–C bonds within the ligand [C(13)–C(14) 1.415(4) Å, C(14)–C(15) 1.422(4) Å] and the Fe–C interactions between the ligand and the diiron frame [Fe(1)–C(13) 2.049(3) Å, Fe(1)–C(14) 2.026(3) Å, Fe(1)–C(15) 2.068(3) Å] are very

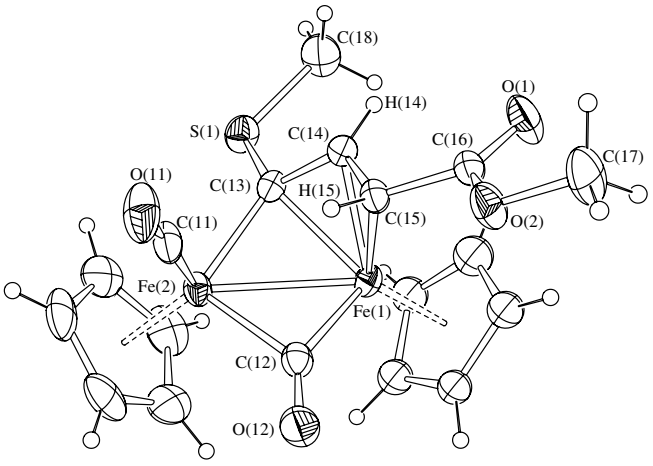


Fig. 1. Molecular structure of **3a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level. Only the main image of the Cp ligand bonded to Fe(1) is drawn.

Table 1
Selected bond lengths (Å) and angles (deg) for **3a**

Fe(1)–Fe(2)	2.5502(5)	C(12)–O(12)	1.165(4)
Fe(2)–C(11)	1.756(3)	C(13)–C(14)	1.415(4)
Fe(1)–C(12)	1.870(3)	C(14)–C(15)	1.422(4)
Fe(2)–C(12)	1.982(3)	C(13)–S(1)	1.758(3)
Fe(2)–C(13)	1.955(3)	S(1)–C(18)	1.802(4)
Fe(1)–C(13)	2.049(3)	C(15)–C(16)	1.471(4)
Fe(1)–C(14)	2.026(3)	C(16)–O(1)	1.204(4)
Fe(1)–C(15)	2.068(3)	C(16)–O(2)	1.341(4)
C(11)–O(11)	1.142(4)	O(2)–C(17)	1.450(4)
Fe(1)–C(12)–Fe(2)	82.87(12)	C(13)–C(14)–C(15)	121.1(3)
Fe(1)–C(13)–Fe(2)	79.09(10)	C(14)–C(15)–C(16)	117.9(3)
Fe(2)–C(13)–C(14)	123.5(2)	C(13)–S(1)–C(18)	107.02(16)

similar, it seems reasonable to conclude that the ligand can be mainly described as a bridging allylidene (A). It is noteworthy that the two hydrogen atoms within the ligand, *i.e.* H(14) and H(15), are in mutually *trans* position.

The IR spectra of **3a**–**d** (in CH_2Cl_2 solution) show the typical ν-CO band pattern consisting of one absorption for the terminal carbonyl (*e.g.* at 1960 cm^{-1} for **3a**) and one for the bridging carbonyl (*e.g.* at 1785 cm^{-1} for **3a**). Additional bands are observed in the case of **3a** and **3d**, due to the carboxylate (*e.g.* at 1698 cm^{-1} for **3a**), or attributable to the CN group (at 2209 cm^{-1} for **3b**).

For the complexes **3a**–**d** several isomeric forms are in theory possible. Indeed, complexes obtained by reaction with asymmetric alkenes might exhibit two regio-isomers

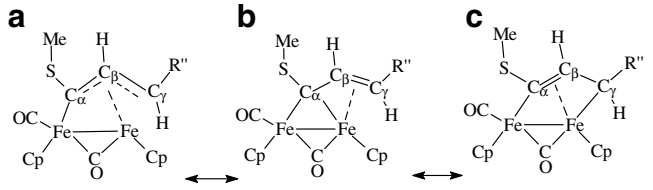


Chart 2.

depending on which of the two non equivalent alkene carbons forms the C–C bond with the thiocarbyne ligand. Moreover, when the coupling involves the CH_2 termination of the olefin, each of the two geminal hydrogen should undergo deprotonation. Therefore, the C_β-H and C_γ-H hydrogens in type 3 complexes, might result on the same or on the opposite side of the C_β–C_γ double bond, generating *E* or *Z* isomers. Finally, as for other complexes containing the $Fe_2Cp_2(\mu\text{-CO})$ framework, further isomers should arise from possible *cis–trans* isomerization (*cis* and *trans* are referred in this case to the mutual Cp position). In spite of these possibilities the ^1H NMR spectra of **3a–d** (in $CDCl_3$) indicate the presence of a single isomer, indicating that the olefin addition to the bridging ligand is both regio- and stereo-specific. The NMR data indicate that **3a–d**, in solution, adopt the same geometry observed in the solid. In particular, the C–C bond formation occurs between the less substituted alkene carbon and the thiocarbyne ligand. Indeed, the spectra of **3a–c** show two doublets, attributable to the C_β H and C_γ H protons, respectively, with coupling constant (*e.g.* 8.2 Hz for **3a**) which indicates that these hydrogens are mutually *trans,* as found in the X-ray structure of **3a**. Likewise, NOE investigations on **3a–d** reveal that the Cp rings are *cis*. Finally, the C_γ H proton resonance is shifted to low frequencies (*e.g.* −0.79 ppm for **3a**), accordingly to the proximity and the shielding effect exerted by the metal centre.

Relevant feature in the ^{13}C NMR spectra include the typical resonances due to the C_α, C_β and C_γ of the bridging allylidene (*e.g.* for **3a**, at 189.2, 74.8 and 43.1 ppm, respectively).

Consistent with their nature, the bridging ligands in **3a–d** (Chart 2) can be considered as the result of a nucleophilic addition of a vinyl group to the bridging carbyne carbon (Chart 2, **B**) or, alternatively, as derived from olefin insertion into the metal bridging-carbyne ligand and proton loss (Chart 2, **C**). This latter point is noteworthy because olefin insertion in the metal-carbon bond, which is a relevant step in various important catalytic cycles [6], is rarely observed in bridging ligands. Indeed, there are few examples of reactions involving olefins and bridging alkylidyne [7] and alkylidene ligands [8]. In particular, the formation of **3a–d** closely resembles the reaction between the μ-ethylidyne complex $[Ru_2\{\mu\text{-C(Me)}\}(\mu\text{-CO})(CO)_2(Cp)_2]^+$ and $MeCH{=}CH_2$, which also required photolytic conditions and deprotonation in order to form the bridging allylidene complex $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Me)C(Me)CH}_2\}(\mu\text{-CO})(CO)(Cp)_2]$ [7a].

Several bridging allylidene dinuclear complexes, analogous to **3a–d**, are known, but these compounds are normally obtained by reactions of bridging alkylidenes with alkynes [9] rather than be formed from alkenes.

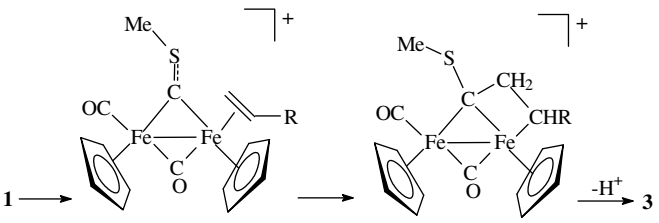
Some aspects concerning the reaction of the thiocarbyne **1** with olefins should be pointed out. First, the reaction requires the displacement of a CO ligand, which is accomplished by the use of Me_3NO. The generation of a vacant coordination site is presumably necessary to allow olefin coordination as initial reaction step. This is consistent with the fact that, in related dinuclear complexes, other insertion reactions of alkynes into the metal carbon bond of bridging ligands require photolytic conditions or the presence of labile ligands in order to provide a vacant coordination site [4,9].

A second requirement is the presence of a base (NaH) in order to remove a proton from the olefin. Strictly related to this point is the observation that the reaction proceeds only with olefins activated by electron-withdrawing groups. In fact, yields are high (80–90%) with olefins activated by CO_2R or CN groups, and lower in the case of styrene (50% yield), whereas non-activated olefins, both linear (2-butene) and cyclic (cyclopentene, cyclohexene) are completely unreactive. Moreover, it has to be noted that attempts to obtain **3b** by treatment of $[Fe_2\{\mu\text{-CS(Me)}\}(\mu\text{-CO})(CO)(NCMe)(Cp)_2][SO_3CF_3]$ with the vinyl anion, generated by treatment of $CH_2{=}CHCN$ with BuLi, were unsuccessful. This further suggests that a preliminary olefin coordination is necessary to promote the reaction.

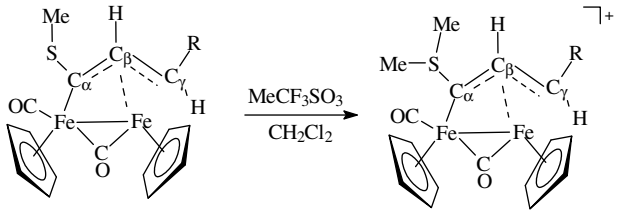
Interestingly, the reaction of **1** with diethyl maleate generates **3d** in high yield, whereas the corresponding reaction with diethyl fumarate does not take place, suggesting the importance of steric effects.

These findings suggest that the reaction sequence should include, as initial step, the η^2-olefin coordination at the site made available by CO removal. Consequent olefin–thiocarbyne coupling might proceed by formation of a metallacyclobutane intermediate (Scheme 2), as proposed by Knox to explain the formation of $[Ru_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-C(Me)C(Me)CH}_2\}(\mu\text{-CO})(CO)(Cp)]$ [7a]. The following deprotonation and rearrangement steps should directly involve the metallacyclobutane intermediate, or take place by a different sequence, like the β-elimination route suggested by Knox for the diruthenium compound. However, other possibilities can not be excluded. Indeed, deprotonation should take place on the coordinated olefin and the resulting vinyl intermediate should rearrange and undergo intramolecular coupling with the thiocarbyne ligand, since similar rearrangements involving terminally cordinated C(O)H or $C(O)OCH_3$ ligands and the μ-thiocarbyne have been reported previously [3].

The reactivity of complexes of type **3** was then investigated. In particular, we have found that the reaction of compounds **3a–b** with methyl triflate in dichloromethane solution at room temperature results selectively in the S-methylation, with formation of the cationic μ-sulphonium

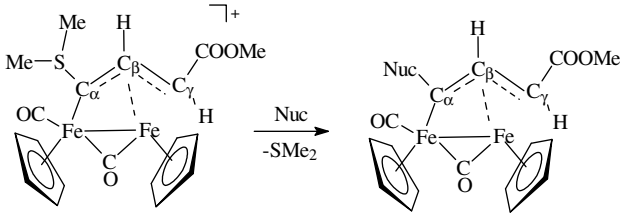


Scheme 2.



	R	
3a	CO_2Me	**4a**
3b	CN	**4b**

Scheme 3.



	Nuc	Reactive	
4a	H^-	$NaBH_4$	**5a**
4a	CN^-	NBu_4^nCN	**5b**
4a	MeO^-	MeONa	**5c**

Scheme 4.

allylidene complexes **4a**–**b**, in nearly quantitative yields (Scheme 3).

Compounds **4a**–**b** have been purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis.

The IR spectra (in CH_2Cl_2 solution) of **4a**–**b** exhibit absorptions due to the terminal and bridging carbonyls (*e.g.* at 1989 and 1823 cm^{-1} for **4a**), which are shifted to higher frequencies (*ca.* 30 cm^{-1}) compared to those of the parent complexes, as effect of the positive charge in **4a**–**b**. Additional bands are observed for **4a**, due to the CO_2Me (at 1708 cm^{-1}) and, for **4b**, attributable to a CN group (at 2220 cm^{-1}).

The ^1H NMR spectra ($CDCl_3$, r.t.) of **4a**–**b** reveal the presence of a single isomer. In particular, the SMe_2 group gives rise to one singlet signal in both ^1H and ^{13}C NMR spectra (*e.g.* for **4a** at δ 3.67 and 52.0 ppm, respecively). The equivalence of the two Me groups is due to the free rotation of the SMe_2 unit around the μ-C–S bond.

Methylation at the S atom does not modify significantly the ^{13}C NMR resonance pattern for the carbons of the C_3 bridging group: C_α gives rise to a low frequency resonance (194 ppm for **4a**), whereas C_β and Cγ resonances occur in 85–30 ppm range.

Bridging sulphonium alkylidene complexes of the type $[Fe_2\{\mu\text{-}C(SMe_2)(X)\}(\mu\text{-}CO)(CO)_2(Cp)_2][SO_3CF_3]$ (X = CN, H) have been previously described [10]. These compounds have been shown to act as precursors of a variety of bridging alkylidene complexes *via* the displacement of SMe_2 by nucleophiles including: amines, alcohols, thiols, phosphines and carbon nucleophiles [11]. Therefore, we have investigated the reactivity of **4a** towards nucleophilic reagents, in order to demonstrate the possibility to accomplish further modifications of the bridging C_3 frame, *via* nucleophilic displacement of SMe_2. Unfortunately, complex **4a** appeared considerably less reactive compared to the sulphonium alkylidene complexes mentioned above. SMe_2 displacement takes place in good yield only in the reactions with $NaBH_4$ or NBu_4^nCN which afforded the complexes **5a** and **5b**, respectively (Scheme 4).

The reaction of **4a** with MeONa in methanol affords **5c** (Scheme 4) in poor yield because the nucleophilic addition is accompanied by demethylation, leading to the formation of the parent compound **3a**. Demethylation becomes even more evident in the reactions with amines (e.g. pyrrolidine, pyrimidine, triethyl amine), which almost quantitatively reverse the reaction with $MeSO_3CF_3$. Finally, attempts to replace the SMe_2 group by other carbon nucleophiles (acetylides, organolithium and Grignard reagents), failed to generate the expected complexes and yielded mixtures of decomposition products.

Compounds **5a**–**c** have been purified by chromatography on alumina and characterized by IR and NMR spectroscopy, and elemental analysis. Moreover, the X-ray structure of **5a** has been determined.

The IR spectra of **5a**–**c** (in CH_2Cl_2 solution), show absorptions attributable to the terminal and bridging CO (*e.g.* for **5a** at 1960 and 1781 cm^{-1}, respectively) and bands due to the COOMe (*e.g.* at 1700 cm^{-1} for **5a**), or, in the case of **5b**, attributable to the CN group (at 2160 cm^{-1}).

The ^1H NMR spectra of **5a**–**c** (in $CDCl_3$) indicate the presence of a single isomeric form, which, presumably, maintains the same conformation of the parent complex **4a**. In fact, only one set of resonances is observed and the signals generated by $C_\beta H$ and $C_\gamma H$ protons present, again, a value for $^3J_{HH}$ typical of olefin protons mutually *trans* (*e.g.* 8.0 Hz for **5a**). Interestingly, in compound **5a**, each carbon of the C_3 bridging chain displays a hydrogen substituent, characterized by well distinct resonance. In fact, signals are observed at 12.04, 5.68 and −0.73 ppm, corresponding to C_α–H, C_β–H and C_γ–H, respectively.

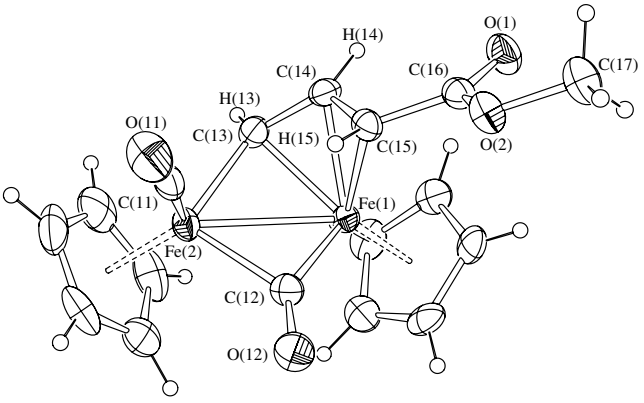


Fig. 2. Molecular structure of **5a**, with key atoms labelled. Displacement ellipsoids are at 30% probability level.

Table 2
Selected bond lengths (Å) and angles (deg) for **5a**.

Fe(1)–Fe(2)	2.5423(6)	C(11)–O(11)	1.148(4)
Fe(2)–C(11)	1.741(3)	C(12)–O(12)	1.168(3)
Fe(1)–C(12)	1.868(3)	C(13)–C(14)	1.396(4)
Fe(2)–C(12)	1.987(3)	C(14)–C(15)	1.415(4)
Fe(2)–C(13)	1.926(3)	C(15)–C(16)	1.470(4)
Fe(1)–C(13)	2.006(3)	C(16)–O(1)	1.213(3)
Fe(1)–C(14)	2.033(3)	C(16)–O(2)	1.333(4)
Fe(1)–C(15)	2.101(3)	O(2)–C(17)	1.445(4)
Fe(1)–C(12)–Fe(2)	82.47(12)	C(13)–C(14)–C(15)	121.4(3)
Fe(1)–C(13)–Fe(2)	80.53(11)	C(14)–C(15)–C(16)	117.9(3)
Fe(2)–C(13)–C(14)	126.9(2)		

Finally, NOE investigations indicate the presence, in solution, of only the *cis* isomer: indeed a significant NOE effect has been revealed between the Cp resonances.

The molecular structure of **5a** is reported in Fig. 2, whereas the main bond lengths and bond angles are summarised in Table 2. The bonding parameters of **5a** closely resembles the ones described for **3a** and, therefore, this molecule can also be described as a bridging allylidene diiron complex. The hydrogen atoms H(13) and H(14) are in mutual *cis* position, whereas H(14) and H(15) are *trans*, as found in **3a**.

3. Conclusions

The bridging thiocarbyne ligand in **1** reacts with olefins in the presence of base generating a bridging allylidene ligand. The reactions are regio and stereo specific and represent a rare example of olefin incorporation into a bridging ligand producing a C_1 to C_3 chain growth. Since proton removal is required in order to accomplish the reaction, this latter is limited to olefins containing electronwithdrawing groups.

The study has evidenced that the bridging C_3 frame, obtained by alkene-carbyne coupling, can be further modified by methylation of the S atom and displacement of the SMe_2 group. This approach provides a route for replacing the μ-C–S bond with a μC–C or μC–H bond. Therefore, the results herein presented reinforce our findings on the very rich chemistry of bridging diiron thiocarbyne and promises further developments in the synthesis of new highly functionalized organic frames, bridging Fe atoms.

4. Experimental details

4.1. General

All reactions were routinely carried out under a nitrogen atmosphere, using standard Schlenk techniques. Solvents were distilled immediately before use under nitrogen from appropriate drying agents. Chromatography separations were carried out on columns of deactivated alumina (4% w/w water). Glassware was oven-dried before use. Infrared spectra were recorded at 298 K on a Perkin–Elmer Spectrum 2000 FT-IR spectrophotometer and elemental analyses were performed on a ThermoQuest Flash 1112 Series EA Instrument. All NMR measurements were performed at 298 K on Mercury Plus 400 instrument. The chemical shifts for ^1H and ^{13}C were referenced to internal TMS. The spectra were fully assigned *via* DEPT experiments and ^1H, ^{13}C correlation through gs-HSQC and gs-HMBC experiments [12]. NOE measurements were recorded using the DPFGSE-NOE sequence [13]. All the reagents were commercial products (Aldrich) of the highest purity available and used as received. $[Fe_2(CO)_4(Cp)_2]$ was purchased from Strem and used as received. Compound **1** was prepared by published methods [14].

4.2. Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe)C_\beta(R')C_\gamma(H)(R'')\}(\mu\text{-}CO)(CO)(Cp)_2]$ ($R'' = CO_2Me$, $R' = H$, **3a**; $R'' = CN$, $R' = H$, **3b**; $R'' = C_6H_5$, $R' = H$, **3c**; $R'' = R' = CO_2Et$, **3d**)

To a solution of **1** (534 mg, 1.0 mmol) in THF (20 mL) were successively added: methyl acrylate (0.9 mL, 10 mmol), NaH (120 mg, 5.0 mmol), and Me_3NO (100 mg, 1.5 mmol). The mixture was stirred at room temperature for 15 min and then filtered on a celite pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green/brown solid, corresponding to **3a**. Crystals suitable for X-ray analysis were obtained by a dichloromethane solution, layered with petroleum ether, at −20 °C. Yield: 390 mg, 89%. Anal. Calc. for $C_{18}H_{18}Fe_2O_4S$: C, 48.87; H, 4.10. Found: C, 48.91; H, 4.08%. IR (CH_2Cl_2) ν(CO) 1960 (vs), 1785 (s), 1698 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.33 (d, 1H, $^3J_{HH} = 8.2$ Hz, $C_\beta H$); 4.89 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.63 (s, 3H, CO_2Me); 2.96 (s, 3H, S*Me*); −0.79 (d, 1H, $^3J_{HH} = 8.2$ Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$)δ 264.9 (μ-CO); 213.8 (CO); 189.2 (C_α); 162.4 (CO_2Me); 88.3 (Cp); 85.5 (Cp); 74.8 (C_β); 51.4 (CO_2Me); 43.1 (C_γ); 21.0 (S*Me*).

Compounds **3b–d** were prepared with the same procedure described for **3a**, by reacting **1** with NaH, Me_3NO and the appropriate olefin.

3b (yield: 85%; colour: green). Anal. Calc. for $C_{17}H_{15}Fe_2NO_2S$: C, 49.88; H, 3.70. Found: C, 49.84; H, 3.73%. IR (CH_2Cl_2)ν(CN) 2209 (w), ν(CO); 1965 (vs), 1797 (s) cm^{-1}. ^1H NMR ($CDCl_3$)δ 5.01 (d, 1H, $^3J_{HH} = 7.8$ Hz, $C_\beta H$); 4.91 (s, 5H, Cp); 4.55 (s, 5H, Cp); 2.93 (s, 3H, S*Me*); −1.41 (d, 1H, $^3J_{HH} = 7.8$ Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 264.3 (μ-CO); 213.1 (CO); 189.6 (C_α); 124.9 (CN); 88.7 (Cp); 86.3 (Cp); 74.3 (C_β); 22.2 (C_γ); 21.0 (S*Me*).

3c (yield: 51%; colour: green/brown). Anal. Calc. for $C_{22}H_{20}Fe_2O_2S$: C, 57.39; H, 4.38. Found: C, 57.33; H, 4.41%. IR (CH_2Cl_2) ν(CO) 1949 (vs), 1775 (s) cm^{-1}. ^1H NMR ($CDCl_3$)δ 7.21–7.07 (m, 5H, Ph); 5.36 (d, 1H, $^3J_{HH} = 9.6$ Hz, $C_\beta H$); 4.87 (s, 5H, Cp); 4.17 (s, 5H, Cp); 3.01 (s, 3H, S*Me*); 1.06 (d, 1H, $^3J_{HH} = 9.6$ Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$)δ 264.5 (μ-CO); 213.5

(CO); 189.4 (C_α); 131.6 (C_{ipso}); 128.7 (C_{orto}); 125.9 (C_{meta}); 125.3 (C_{para}); 88.2 (Cp); 85.9 (Cp); 73.2 (C_β); 37.5 (C_γ); 21.1 (S*Me*).

3d (yield: 84%; colour: brown). Anal. Calc. for $C_{22}H_{24}Fe_2O_6S$: C, 50.00; H, 4.58. Found: C, 49.96; H, 4.53%. IR (CH_2Cl_2) *v*(CO) 1980 (vs), 1810 (s), 1716 (m) cm^{-1}. ^1H NMR ($CDCl_3$)δ 4.88 (s, 5H, Cp); 4.80 (s, 5H, Cp); 4.27-3.74 (m, 4H, $CO_2CH_2CH_3$); 2.26 (s, 3H, S*Me*); 1.49–1.10 (m, 6H, $CO_2CH_2CH_3$); −0.74 (s, 1H, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.0 (CO); 191.2 (C_α); 162.4 ($CO_2CH_2CH_3$); 162.6 ($CO_2CH_2CH_3$); 91.3 (Cp); 88.2 (Cp); 86.5 (C_β); 59.2 ($CO_2CH_2CH_3$); 58.7 ($CO_2CH_2CH_3$); 34.5 (C_γ); 21.1 (S*Me*); 14.7 ($CO_2CH_2CH_3$); 14.5 ($CO_2CH_2CH_3$).

4.3. Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(SMe_2)C_\beta(H)C_\gamma(H)(R)\}(\mu\text{-}CO)(CO)(Cp)_2][SO_3CF_3]$ (R = CO_2Me, **4a**; R = CN, **4b**)

Methyl triflate (0.13 mL, 1.1 mmol) was added to a solution of **3a** (442 mg, 1.0 mmol) in CH_2Cl_2 (20 mL) and the resulting solution was stirred at room temperature for 4 h. removal of the volatile material under reduced pressure and chromatography of the residue on an alumina column, with methanol as eluent, afforded a dark brown solid, corresponding to **4a**. Yield: 527 mg, 87%. Anal. Calc. for $C_{20}H_{21}F_3Fe_2O_7S_2$: C, 39.61; H, 3.49. Found: C, 39.68; H, 3.46%. IR (CH_2Cl_2) *v*(CO) 1989 (vs), 1823 (s), 1708 (m) cm^{-1}. ^1H NMR ($CDCl_3$) δ 5.57 (d, 1H, $C_\beta H$, $^3J_{HH} = 8.2$ Hz); 5.13 (s, 5H, Cp); 4.75 (s, 5H, Cp); 3.67 (s, 6H, SMe_2); 3.52 (s, 3H, CO_2Me); −0.65 (d, 1H, $C_\gamma H$, $^3J_{HH} = 8.2$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 265.0 (μ-CO); 213.4 (CO); 194.1 (C_α); 162.5 (CO_2CH_3); 88.9 (Cp); 85.5 (Cp); 83.7 (C_β); 52.0 (SMe_2); 46.5 (C_γ); 39.7 (CO_2CH_3).

Compound **4b** was prepared with the same procedure described for **4a**, by treating **3b** with methyl triflate in dichloromethane solution.

4b (yield: 86%; colour: dark brown). Anal. Calc. for $C_{19}H_{18}F_3Fe_2NO_5S_2$: C, 39.80; H, 3.17. Found: C, 39.81; H, 3.14%. IR (CH_2Cl_2)*v*(CN) 2220 (w), *v*(CO) 1993 (vs), 1829 (s) cm^{-1}. ^1H NMR ($CDCl_3$)δ 5.26 (d, 1H, $C_\beta H$, $^3J_{HH} = 7.8$ Hz); 5.15 (s, 5H, Cp); 4.92 (s, 5H, Cp); 3.68 (s, 6H, SMe_2); −1.20 (d, 1H, $C_\gamma H$, $^3J_{HH} = 7.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$)δ 265.0 (μ-CO); 213.5 (CO); 195.0 (C_α); 125.3 (*C*N); 89.1 (Cp); 86.5 (Cp); 84.1 (C_β); 52.4 (SMe_2); 28.8 (C_γ).

4.4. Synthesis of $[Fe_2\{\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_\alpha(R)C_\beta(H)C_\gamma(H)(CO_2Me)\}(\mu\text{-}CO)(CO)(Cp)_2]$ (R = H, **5a**; R = CN, **5b**; R = OMe, **5c**)

Complex **4a** (605 mg, 1.0 mmol) was dissolved in THF (20 mL) and treated with $NaBH_4$ (190 mg, 5.0 mmol) was added. The mixture was stirred at room temperature for 30 min and then filtered on an alumina pad. Removal of the solvent and chromatography of the residue on an alumina column, with CH_2Cl_2 as eluent, afforded a green/brown solid, corresponding to **5a**. Yield: 355 mg, 90 %. Anal. Calc. for $C_{17}H_{16}Fe_2O_4$: C, 51.52; H, 4.07. Found: C, 51.50; H, 4.01%.

IR (CH_2Cl_2): *v* 1960 vs (t-CO); 1781 s (μ-CO); 1700 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 12.04 (d, 1H, $^3J_{HH} = 6.4$ Hz, $C_\alpha H$); 5.68 (t, 1H, $^3J_{HH} = 7.2$ Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.62 (s, 3H, CO_2Me); −0.73 (d, 1H, $^3J_{HH} = 8.0$ Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$)δ (ppm): 267.5 (μ-CO); 213.7 (t-CO); 176.2 (CO_2Me); 174.4 (C_α); 87.4 (C_β); 87.1 (Cp); 83.4 (Cp); 51.4 (CO_2Me); 44.3 (C_γ).

Compounds **5b** and **5d** were prepared with the same procedure described for **5a**, by treating **3a** with NBu^n_4CN and MeONa, respectively. Sodium methoxyde was freshly obtained from Na and MeOH. For both **5b** and **5d** longer reaction time (4 h) were required.

5b (yield: 84%; colour: green/brown). Anal. Calc. for $C_{18}H_{15}Fe_2NO_4$: C, 51.31; H, 3.59; N, 3.33. Found: C, 51.25; H, 3.65; N, 3.31%.

IR (CH_2Cl_2): *v* 2160 w (CN); 1964 vs (t-CO); 1785 s (μ-CO); 1704 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 5.86 (d, 1H, $^3J_{HH} = 7.6$ Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.68 (s, 3H, CO_2Me); −0.90 (d, 1H, $^3J_{HH} = 7.6$ Hz, $C_\gamma H$). ^{13}C $\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 267.5 (μ-CO); 213.5 (t-CO); 174.0 (CO_2Me); 150.4 (C_α); 135.1 (CN); 89.6 (C_β); 87.5 (Cp); 85.3 (Cp); 52.2 (CO_2Me); 44.9 (C_γ).

5c (yield: 34%; colour: brown). Anal. Calc. for $C_{18}H_{18}Fe_2O_5$: C, 50.71; H, 4.26. Found: C, 50.64; H, 4.25%.

IR (CH_2Cl_2): *v* 1961 vs (t-CO); 1783 s (μ-CO); 1702 m (CO_2Me) cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 5.72 (d, 1H, $^3J_{HH} = 7.6$ Hz, $C_\beta H$); 4.80 (s, 5H, Cp); 4.40 (s, 5H, Cp); 3.86 (s, 3H, O*Me*); 3.60 (s, 3H, CO_2Me); −0.82 (d, 1H, $^3J_{HH} = 7.6$ Hz, $C_\gamma H$). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ (ppm): 267.5 (μ-CO); 213.5 (t-CO); 168.8 (CO_2Me); 164.0 (C_α); 88.7 (C_β); 87.9 (Cp); 84.6 (Cp); 63.5 (O*Me*); 50.9 (CO_2Me); 43.7 (C_γ).

4.5. X-ray crystallography for **3a** and **5a**

Crystal data for **3a** and **5a** were collected at room temperature on a Bruker APEX II CCD diffractometer using graphite monochromated Mo Kα radiation. Structures were solved by direct methods and structures refined by full-matrix least-squares based on all data using F^2 [15] Crystal data are listed in Table 3. Non-H atoms were refined anisotropically, unless otherwise stated. H-atoms were placed in calculated positions, except position of H(14) and H(15) in **3a** and H(13), H(14) and H(15) in **5a** which were located in the Fourier map. H-atoms were treated isotropically using the 1.2 fold U_{iso} value of the parent atom except methyl protons, which were assigned the 1.5 fold U_{iso} value of the parent C-atom. The crystals of **3a** are twinned by inversion with a refined Flack parameter of 0.144(16) (1928 Friedel pairs used for refinement) [16]. The TWIN routine of SHELX97 was used during the refine-

Table 3
Crystal data and experimental details for **3a** and **5a**

Complex	**3a**	**5a**
Empirical formula	$C_{18}H_{18}Fe_2O_4S$	$C_{17}H_{41}ClFe_2N_2O_2$
F_w	442.08	396.00
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	Cc	$P2_1/c$
a (Å)	13.3520(8)	9.8980(10)
b (Å)	12.3123(7)	19.741(2)
c (Å)	11.6974(7)	8.0365(8)
β (°)	112.1770(10)	96.248(2)
Cell volume (Å^3)	1780.72(18)	1561.0(3)
Z	4	4
D_c (g cm^{-3})	1.649	1.685
μ (mm^{-1})	1.766	1.875
$F(000)$	904	808
Crystal size (mm)	$0.32 \times 0.26 \times 0.22$	$0.23 \times 0.20 \times 0.16$
θ Limits (°)	2.23–27.10	2.06–27.00
Reflections collected	9533	16920
Independent reflections [R_{int}]	3891 [0.0151]	3406 [0.0396]
Data/restraints/parameters	3891/50/231	3406/3/218
Goodness on fit on F^2	1.094	1.116
R_1 ($I > 2\sigma(I)$)	0.0284	0.0356
wR_2 (all data)	0.0758	0.0821
Largest difference peak and hole (e Å^{-3})	0.460/−0.486	0.311/−0.341

ment. The Cp ring bonded to Fe(1) in **3a** is disordered. Disordered atomic positions were split and refined isotropically using similar distance and similar U restraints and one occupancy parameter per disordered group.

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Appendix A. Supplementary material

CCDC 632860 and 632861 contain the supplementary crystallographic data for **3a** and **5a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.01.052.

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