



**HAL**  
open science

# Modulation of S-Centered Reactivity: Impact of Terminal Ligands on Alkynyl Addition in $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$ Complexes

Ines Bennour, Lucile Chatelain, Philippe Schollhammer

## ► To cite this version:

Ines Bennour, Lucile Chatelain, Philippe Schollhammer. Modulation of S-Centered Reactivity: Impact of Terminal Ligands on Alkynyl Addition in  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$  Complexes. *European Journal of Inorganic Chemistry*, 2024, 10.1002/ejic.202400061 . hal-04568633

**HAL Id: hal-04568633**

**<https://hal.science/hal-04568633v1>**

Submitted on 10 Oct 2024

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial 4.0 International License

# Modulation of S-Centered Reactivity: Impact of Terminal Ligands on Alkynyl Addition in $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$ Complexes

Ines Bennour,<sup>[a]</sup> Lucile Chatelain,<sup>\*[a]</sup> and Philippe Schollhammer<sup>\*[a]</sup>

The reactivity of complexes  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$  ( $\text{L} = \text{CO}$  (1),  $\text{PPh}_3$  (2)), with lithium alkynylide reagents generated in situ, was investigated. The behavior of the  $\text{S}_2$ -bridge in these compounds depends on the substitution at the diiron core. The reaction with the hexacarbonyl derivative 1 leads to the formation of the 1,2-dithiolene bridged complex  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{R})\text{S})(\text{CO})_6]$  ( $3^{\text{R}}$ ) while the molecule  $[\text{Fe}_2(\mu\text{-SH})(\mu\text{-SC}=\text{CR})(\text{CO})_4(\text{PPh}_3)_2]$  ( $5^{\text{R}}$ ), with an open butterfly structure, is isolated when reacting the

disubstituted derivative 2. The disubstituted dithiolene complex  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{Ph})\text{S})(\text{CO})_4(\text{PPh}_3)_2]$  ( $4^{\text{Ph}}$ ) can only be obtained by substitution of carbonyls with  $\text{PPh}_3$  in  $3^{\text{R}}$ . In the presence of piperidine,  $5^{\text{R}}$  isomerizes into the 1,1'-dithiolene bridged derivative  $6^{\text{Ph}}$ . The novel compounds 4–6 were synthesized and characterized by IR and NMR spectroscopies. X-ray crystallographic studies of the dithiolene complexes  $3^{\text{Ph}}$ – $4^{\text{Ph}}$  allowed their structural analysis.

## Introduction

In nature, metalloenzymes containing Fe–S clusters in their cofactor enable the efficient transformation of various small molecules under mild conditions.<sup>[1–4]</sup> Among them, [FeFe]-hydrogenases are a family of enzymes, that allow the reversible conversion of  $\text{H}_2$  to  $\text{H}^+$ . Their active site contains an azadithiolato bridged diiron core whose the coordination sphere is completed with cyanide and carbonyl ligands.<sup>[5,6]</sup> A large variety of bio-inspired Fe–S complexes has been extensively studied to design novel catalysts for the conversion of protons into  $\text{H}_2$ . This is a crucial goal for the use of  $\text{H}_2$  as a green energy carrier.<sup>[5–10]</sup> In this context, the diiron compound  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (1)<sup>[11,12]</sup> is a key precursor for the synthesis of bioinspired diiron species. Indeed, the reduction of 1 into its parent dianion  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]^{2-}$  ( $1^{2-}$ ) affords a general pathway for introducing various functionalized dithiolato bridges.<sup>[7,13,14]</sup> In contrast, the photoactivation of  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (1) in the presence of unsaturated substrates, such as alkene or alkyne, results in a formal [2 + 2] addition at the sulfur atoms.<sup>[15–18]</sup> This photochemical reaction affords a powerful route for preparing the relatively scarce diiron complexes with a 1,2-dithiolene bridge from alkyne.<sup>[16,18–22]</sup> The limited number of such deriva-

tives, compared, for example, to their 1,2-benzenedithiolate analogs<sup>[23]</sup> may be attributed to the low commercial availability of 1,2-dithiolene as well as their relative instability.<sup>[24]</sup> Therefore, the controlled and straightforward synthesis of diiron dithiolenes is challenging.<sup>[15,16,18–21,25–35]</sup> Apart from the [2 + 2] photoaddition of alkyne with 1, an attractive route involving the action of lithium alkynylide reagents on the complex  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (1), followed by a protonation step, was reported in the 80s.<sup>[28,29]</sup>

Moreover, the extension to the chemistry of mono and disubstituted dithiolene bridged derivatives has been limited due to the easy cleavage of dithiolene diiron complexes upon substitution reactions of carbonyl with better  $\sigma$ -donor ligands in  $[\text{Fe}_2(\mu\text{-1,2-dithiolene})(\text{CO})_6]$ .<sup>[34]</sup> To overcome this difficulty, the replacement of carbonyl groups in the precursor 1 before generating the dithiolene bridge was considered. The substitution of CO groups in 1 is a more intriguing process that one might think, due to the presence of the redox active persulfido bridge.<sup>[36]</sup> Recent studies have revealed that the substitution of a CO ligand in the compound  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (1) by a triphenylphosphine does not follow the conventional ligand exchange mechanism on the iron metal, highlighting the non-innocent role of the  $(\mu\text{-S}_2^{2-})$  bridged ligand.<sup>[37]</sup> Further theoretical calculations indicate that the order of the S–S bond depends on the substitution at the iron metal center in complexes  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_{6-x}(\text{L})_x]$  ( $x = 0, 2, 4$ ), that might modify the S-centered reactivity of such substituted species.<sup>[38]</sup>

The literature on the activity of the  $\text{S}_2^{2-}$  ligand coordinated to disubstituted diiron moiety  $\{\text{Fe}_2(\text{CO})_4(\text{L})_2\}^{2+}$  remains limited.<sup>[38,39]</sup> Besides there has not been any reported comparison between the reactivity properties of the two derivatives  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (1) and  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2]$ <sup>[37,39,40]</sup> (2) toward unsaturated substrates.

In the study presented herein, we report the different behavior of complexes  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$  ( $\text{L} = \text{CO}$  (1),  $\text{PPh}_3$  (2)) in the reaction with an lithium alkynylide reagent, selected for

[a] Dr. I. Bennour, Dr. L. Chatelain, Prof. P. Schollhammer  
UMR CNRS 6521 Chimie, Electrochimie Moléculaires et Chimie Analytique  
Univ. Brest  
6 Avenue Victor le Gorgeu, CS93837, 29238 Brest-Cedex 3, France  
E-mail: lucile.chatelain@univ-brest.fr  
philippe.schollhammer@univ-brest.fr

Supporting information for this article is available on the WWW under <https://doi.org/10.1002/ejic.202400061>

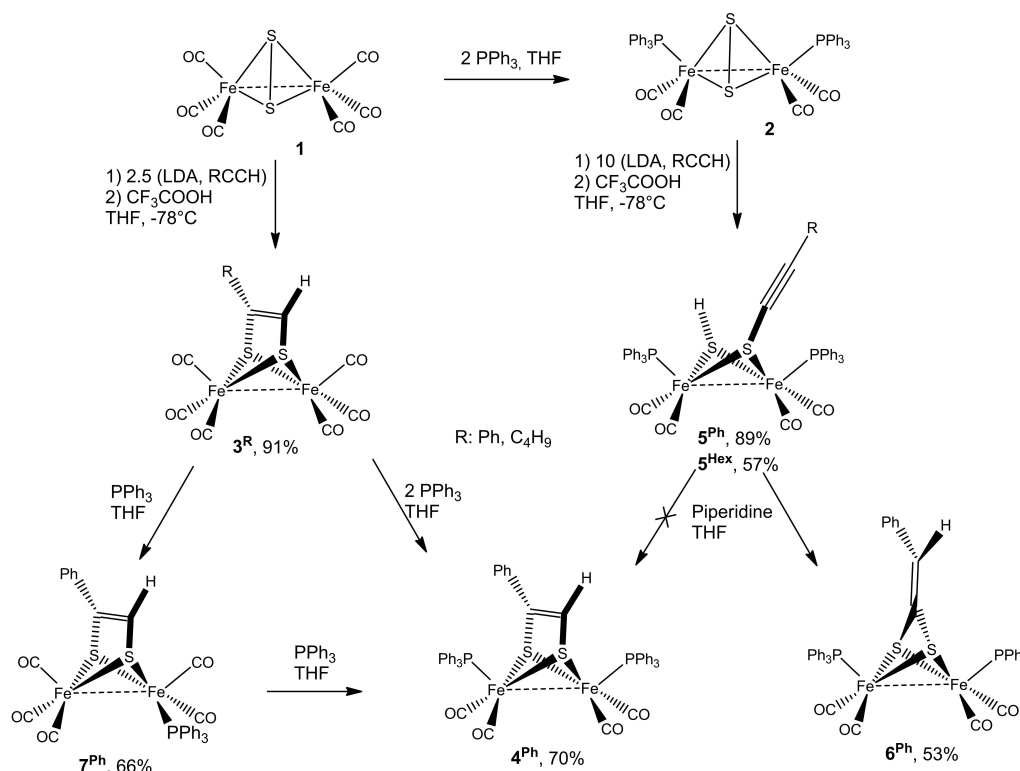
© 2024 The Authors. European Journal of Inorganic Chemistry published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution Non-Commercial NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

preparing compounds with a dithiolene bridge. These results confirm that the coordination environment at the diiron core in  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4\text{L}_2]$  modifies the  $\text{S}_2$ -centered reactivity.

## Results and Discussion

Complexes  $[\text{Fe}_2(\mu\text{-SCH=C(R)S})(\text{CO})_6]$  ( $3^{\text{R}}$ ) ( $\text{R} = \text{Ph}, \text{C}_4\text{H}_9$ ) were synthesized in high yield using a literature procedure.<sup>[28,29]</sup> Their preparation involved the reaction of  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_6]$  (**1**) with an

lithium alkynylide reagent  $\text{RCCLi}$  ( $\text{R} = \text{Ph}, \text{C}_4\text{H}_9$ ), at  $-78^\circ\text{C}$  in THF, followed by the addition of  $\text{CF}_3\text{CO}_2\text{H}$  (Scheme 1). The nature of the substituent on the alkynyl chain did not influence the reaction course, and a 1,2-dithiolene bridging ligand was formed for various R groups. The crystallographic structure of the complex  $3^{\text{Ph}}$  was not reported previously. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of acetonitrile solvent at  $-35^\circ\text{C}$ . The structural determination confirms the formula  $[\text{Fe}_2(\mu\text{-SCH=C(Ph)S})(\text{CO})_6]$  and reveals a butterfly  $\{\text{Fe}_2\text{S}_2\}$  core (Figure 1). The Fe–Fe and dithiolene C=C



Scheme 1. Synthesis of compounds 2–7<sup>Ph</sup>.

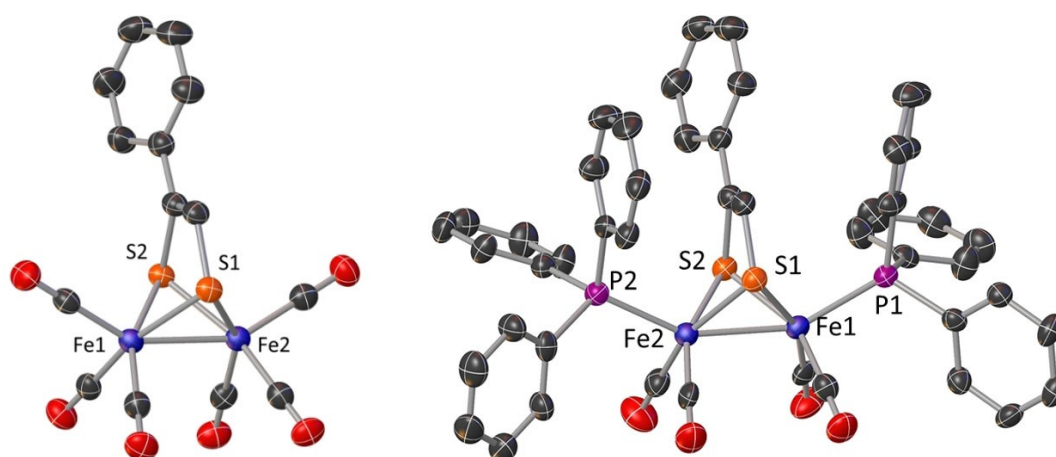


Figure 1. Molecular structures of  $[\text{Fe}_2(\mu\text{-SCH=C(Ph)S})(\text{CO})_6]$   $3^{\text{Ph}}$  (left) and  $[\text{Fe}_2(\mu\text{-SCH=C(Ph)S})(\text{CO})_4(\text{PPh}_3)_2]$   $4^{\text{Ph}}$  (right) with thermal ellipsoids at 40% probability (Hydrogen atoms and co-crystallized solvent molecule are omitted for clarity). Color atom's: carbon in grey, oxygen in red, iron in blue, sulfur in orange, phosphorous in purple. Principal bond distances:  $3^{\text{Ph}}$  Fe1–S1 2.2751(8), Fe1–S2 2.2746(8), Fe2–S1 2.2652(8), Fe2–S2 2.2879(8), mean Fe–CO 1.798(3) Å Fe1–S1 2.291(1), Fe1–S2 2.279(1), Fe2–S1 2.289(1), Fe2–S2 2.283(2), Fe1–P1 2.250(1), Fe2–P2 2.241(1), mean Fe–CO 1.758(5) Å

bond lengths (2.4665(6) and 1.317(4) Å, respectively) are in the range of previously reported hexacarbonyl 1,2-dithiolene complexes (Fe–Fe 2.4755(12)–2.4842(9) Å and C=C 1.313(8)–1.350(6) Å).<sup>[19,21,25,33,35]</sup>

In contrast, the reaction of  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2]$  (**2**) with an excess of  $\text{RCCLi}$  (R: Ph,  $\text{C}_4\text{H}_9$ ), followed by the addition of  $\text{CF}_3\text{CO}_2\text{H}$  did not yield the expected bridged products  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{R})\text{S})(\text{CO})_4(\text{PPh}_3)_2]$  (**4<sup>R</sup>**). Instead, the formation of compounds  $[\text{Fe}_2(\mu\text{-SH})(\mu\text{-SC}\equiv\text{CR})(\text{CO})_4(\text{PPh}_3)_2]$  (**5<sup>R</sup>**) was observed (Scheme 1). Molecules **5<sup>R</sup>** and **5<sup>Hex</sup>** were purified by column chromatography and isolated in good yields. The structure of the compounds **5<sup>R</sup>**, which contains a thiolato and an hydro-sulfido bridges, was proposed in comparing their spectroscopic data with those found in the literature.<sup>[29,39]</sup>

Complexes **5<sup>R</sup>** exhibit similar characteristics. Their IR spectra are typical of those of disubstituted derivatives with three strong bands in the CO stretching vibrations region (1942, 1960 and 2004  $\text{cm}^{-1}$  for **5<sup>R</sup>** and 1942, 1960 and 2003  $\text{cm}^{-1}$  for **5<sup>Hex</sup>** (Figures S3–S4)).<sup>[39]</sup> High field ( $< 0$  ppm)  $^1\text{H}$  NMR signals and two resonances around 85 ppm in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectra correspond to the  $-\text{SH}$  and the triple bond  $\text{C}\equiv\text{C}$  of the  $-\text{S}-\text{C}\equiv\text{C}-\text{R}$  bridging ligands, respectively.<sup>[29,39]</sup> The observation of several resonances in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectra is consistently assigned to the presence of four possible isomers, related to the relative orientations (equatorial or axial) of SH and SR group (Scheme S1 and Figures S11–S15).<sup>[39]</sup> Despite several crystallization attempts, the unstability of compounds **5<sup>R</sup>** stored in solution has prevented the obtention of crystals suitable for XRD analysis. It is worth noting that compounds **3<sup>Hex</sup>** and **5<sup>Hex</sup>** are less stable than their **3<sup>Ph</sup>** and **5<sup>Ph</sup>** counterparts, which hindered further studies.

Piperidine has been used to catalyze the reaction of the complex  $[\text{Fe}_2(\mu\text{-SH})_2(\text{CO})_6]$  with various unsaturated reagents, that afforded bis-thiolato derivatives.<sup>[41]</sup> It was also shown that such a reagent may promote the isomerization of the open form  $[\text{Fe}_2(\mu\text{-SH})(\mu\text{-SR})(\text{CO})_6]$  into dithiolato complexes  $[\text{Fe}_2(\mu\text{-S}_2\text{R})(\text{CO})_6]$  with one or two-carbon bridge between the two sulfur atoms, depending on the nature of the group R.

Following a similar strategy, we observed that adding half an equivalent of piperidine to a THF solution of compound **5<sup>Ph</sup>** at room temperature over several days, resulted in its complete transformation into a novel species. After purification, the main product was not the hoped-for complex **4<sup>Ph</sup>** with a 1,2-dithiolene bridge, but the molecule  $[\text{Fe}_2(\mu\text{-S}_2\text{C}=\text{CH}(\text{Ph}))(\text{CO})_4(\text{PPh}_3)_2]$  (**6<sup>Ph</sup>**) in which the two iron metals are bridged by a 1,1'-dithiolene ligand.<sup>[28,29,42]</sup> The IR spectrum of **6<sup>Ph</sup>** displays  $\nu_{\text{CO}}$  bands very close to those of **2** and **5<sup>Ph</sup>** (Figure S5). The assignment of the bridge to a 1,1'-dithiolene rather than a 1,2-dithiolene group was achieved through  $^{13}\text{C}\{-^1\text{H}\}$  and  $^{13}\text{C}\{-^1\text{H}\}$  HMQC NMR spectra (Figures S16–S19). The downfield resonance at 149.7 ppm in the  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum corresponds to the  $-\text{C}(\text{S}_2)=$  carbon, while the resonance at 115.8 ppm is attributed to the  $=\text{CH}(\text{Ph})$  carbon.  $^{13}\text{C}\{-^1\text{H}\}$  HMQC NMR spectrum shows that this later signal is correlated with the resonance at 4.38 ppm in the  $^1\text{H}$  NMR spectrum, which allows to identify the sole non-aromatic proton of this ligand. The presence of two isomers is suggested by the two resonances observed in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR

spectrum at both room and low temperatures. Their structures are proposed in Scheme S2. Upon increasing the temperature, no isomerization process was detected but decomposition of **6<sup>Ph</sup>** arose.

Noting that this pathway with the disubstituted disulfido complex  $[\text{Fe}_2(\mu\text{-S}_2)(\text{CO})_4(\text{PPh}_3)_2]$  (**2**) as precursor, failed to lead to the desired substituted 1,2-dithiolene product **4<sup>Ph</sup>**, we investigated the reactions of substitution in the hexacarbonyl 1,2-dithiolene compound **3<sup>Ph</sup>**. The addition of one equivalent of  $\text{PPh}_3$  to a THF solution of **3<sup>Ph</sup>** resulted in the substitution of one CO by the phosphine, which afforded the complex  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{Ph})\text{S})(\text{CO})_5(\text{PPh}_3)]$  (**7<sup>Ph</sup>**) in good yield. In the presence of an excess of  $\text{PPh}_3$  in THF the molecule **7<sup>Ph</sup>** was slowly and quantitatively transformed into  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{Ph})\text{S})(\text{CO})_4(\text{PPh}_3)_2]$  (**4<sup>Ph</sup>**). Heating the solution at 40 °C moderately accelerated the reaction time without decomposition into monometallic species, as previously reported for such 1,2-dithiolene bimetallic complexes.<sup>[34,43]</sup> The IR spectrum of **7<sup>Ph</sup>** shows, in the  $\nu_{\text{CO}}$  region, a typical pattern for monosubstituted derivatives  $[\text{Fe}_2(\mu\text{-dithiolate})(\text{CO})_5(\text{L})]$ , with four strong bands at 2051, 1993, 1980 (sh) and 1936  $\text{cm}^{-1}$  (Figure S6). The  $^1\text{H}$  NMR spectrum in  $\text{CD}_2\text{Cl}_2$  is consistent with the formula  $[\text{Fe}_2(\mu\text{-SCH}=\text{C}(\text{Ph})\text{S})(\text{CO})_5\text{L}]$ , with a singlet resonance of  $\text{SCH}=\text{C}$  observed at 5.69 ppm. The  $^{13}\text{C}\{-^1\text{H}\}$  NMR spectrum supports also the presence of a 1,2-dithiolene ligand. The resonances of the carbon atoms of the  $=\text{CH}$  and  $=\text{CPh}$  groups is attributed through  $^{13}\text{C}\{-^1\text{H}\}$  NMR correlation analysis (134.9 ppm for  $=\text{CH}$  and 159.0 ppm for  $=\text{CPh}$ ). At room temperature, only one resonance is observed in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR spectrum. Upon, decreasing the temperature this signal splits into three singlets, which are assigned to three isomers of **7<sup>Ph</sup>** related to the position (apical or basal) of  $\text{PPh}_3$  and the relative orientation of the dithiolene  $\text{R}-\text{C}=\text{C}-\text{H}$  group (Figures S20–S23).

The IR spectrum of **4<sup>Ph</sup>** displays three strong bands in the carbonyl region at 2000, 1954 and 1936  $\text{cm}^{-1}$  (Figure S2), consistent with a symmetrically disubstituted diiron complex. One resonance is detected in the  $^{31}\text{P}\{-^1\text{H}\}$  NMR whatever the temperature, which suggests that only one isomer, with a symmetrical geometry is favored. It is noteworthy that the resonance of the  $-\text{SCH}=\text{C}$  group is shielded of about 1 ppm, at 4.80 ppm, compared to **3<sup>Ph</sup>** and **7<sup>Ph</sup>**. The  $^{13}\text{C}\{-^1\text{H}\}$  spectrum is consistent with 1,2-dithiolene features (Figures S7–S10). Single crystals of complex **4<sup>Ph</sup>** were grown at  $-35^\circ\text{C}$  in a THF/Toluene solution. In accordance with the spectroscopic data, the X-ray structure reveals the presence of the symmetrical di-apical isomer (Figure 1). Each iron center adopts a distorted square pyramidal geometry with a  $\text{PPh}_3$  in apical position, the two sulfur atoms of the 1,2-dithiolene bridge and two carbonyl ligands in basal position. Their coordination sphere is supplemented with a Fe–Fe single bond according to the effective atomic number rule. The Fe–Fe bond distance of 2.4939(8) Å and the C=C bond length of the 1,2-dithiolene (1.315(5) Å) are within the range of those observed for analogous structures from 2.4797(1) to 2.525(2) Å, and 1.303(8) to 1.3273(5) Å, respectively.<sup>[31,34]</sup>

The two phosphine ligands are in an eclipsed orientation in the apical position. As shown in Figure S1, the replacement of

two CO by PPh<sub>3</sub> has a slight effect on the Fe–Fe and S–S distances in **1** and **2**. The Fe–Fe and the average of Fe–S lengths are longer by 0.007(1) Å and 0.016(1) Å, respectively, in **2** compared to **1**. The Fe–C distances are shorter by 0.023(1) Å (Table 1 in SI) in **2** than in **1** due to the expected better π-back donation from the iron centers to the carbonyl groups. The S–S bond is increased by 0.008(1) Å in **2** compared to **1**. When comparing the molecular structures of complexes **3**<sup>Ph</sup> and **4**<sup>Ph</sup>, or those of other derivatives with ethanedithiolate (edt<sup>2-</sup>) or benzenedithiolate (bdt<sup>2-</sup>) bridges (Table 1 in SI), similar structural changes are observed upon the replacement of two CO by two PPh<sub>3</sub>. A lengthening of 0.0273(7) Å and 0.010(4) Å is observed for the Fe–Fe and the Fe–S bonds, respectively, in **4**<sup>Ph</sup> compared to **3**<sup>Ph</sup>.

This study reveals the significant difference in the reactivity of compounds **1** and **2** toward lithium alkynylide reagents. In the case of **1**, a 1,2-dithiolene is obtained, while starting from **2**, no reaction occurred with less than 10 equivalents of RCCLi and no bridging 1,2-dithiolene is formed. Instead, the formation of a bimetallic complex with two different bridges (μ-SH and μ-S–C≡C–Ph) is observed. The rationalization of some aspects of the reactivity of the S<sub>2</sub>-bridged diiron moiety [Fe<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>6</sub>], reported in pioneering works, remained obscure until recently.<sup>[37–39]</sup> The formation of ‘closed’ or ‘open’ isomers, 1,2-dithiolene, 1,1-dithiolene or (μ-SH)(μ-S–C≡CR), depends on the stability of the anionic intermediate species formed upon the addition of the lithium alkynylide reagent, which are C- or S-centered (Scheme 2), as well as the nature of the electrophile added in the second step.<sup>[29]</sup> Obviously, the difference of reactivity between **1** and **2** arises from the different substitution at the diiron core in those complexes. The replacement of two CO in **2** by PPh<sub>3</sub> ligands, in apical position, increases both the steric congestion of the μ-S<sub>2</sub> site and the electron density at the diiron core, which favor the cleavage of the S–S bond and the stabilization of the S-centered anionic intermediate, preventing its transformation into 1,2-dithiolene upon protonation. Such a rationalization of the different pathways of this reaction depending on the substitution at the diiron core is reminiscent

of the recent computational study.<sup>[38]</sup> It demonstrated that the conversion of the tetrahedrane persulfido form {Fe<sub>2</sub>(μ-S<sub>2</sub>)} into its butterfly bis-sulfido {Fe<sup>II</sup><sub>2</sub>(μ-S<sub>2</sub>)} in [Fe(μ-S<sub>2</sub>)(CO)<sub>6-x</sub>(PME<sub>3</sub>)<sub>x</sub>] species is favored upon substitution of CO by phosphine. The addition of such σ-donor ligands increases the electron density at the diiron core and stabilizes the disulfide-Fe<sup>II</sup>Fe<sup>II</sup> redox state. Finally, the isomerization of **5**<sup>Ph</sup> to **4**<sup>Ph</sup> was ruled out in presence of piperidine. Instead, bridging 1,1'-dithiolene **6**<sup>Ph</sup> was obtained. This result may be attributed to the easier rearrangement formed by the addition of the deprotonated sulfido ligand on the linear –C≡C–Ph fragment (transformation B to C in Scheme 2). Furthermore, the aromatic group is located outwards from the {Fe<sub>2</sub>S<sub>2</sub>} core in a less sterically crowded environment in **6**<sup>Ph</sup>, as shown in the crystallographic structure of complex [Fe<sub>2</sub>(μ-SCH=C(Ph)S)(CO)<sub>6</sub>] (**3**<sup>Ph</sup>), compared to **4**<sup>Ph</sup>.<sup>[42]</sup>

## Conclusions

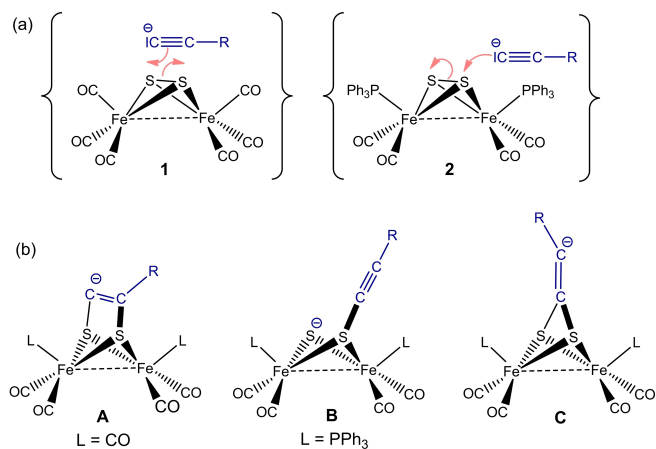
The reactivity of the two complexes, [Fe<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>4</sub>L<sub>2</sub>] (L = CO (**1**); PPh<sub>3</sub> (**2**)) with RCCLi reagents was considered to prepare 1,2-dithiolene compounds [Fe<sub>2</sub>(μ-dithiolene)(CO)<sub>4</sub>L<sub>2</sub>] (L = PPh<sub>3</sub>) with an electron-rich diiron site. This unsaturated dithiolene bridge can be post-functionalized for introducing various features in the second sphere of coordination of those dinuclear complexes. Our study revealed that the nature of the terminal ligands at the diiron core (CO vs PPh<sub>3</sub>) in the compounds [Fe<sub>2</sub>(μ-S<sub>2</sub>)(CO)<sub>4</sub>L<sub>2</sub>] orientates differently their S<sub>2</sub>-centered reactivity. The pathway, which allows the formation of 1,2-dithiolene bridge, requires the introduction of this bridge before the substitution of CO groups by better σ-donor ligands, even if the last step of this sequence may induce the cleavage of the dinuclear framework in reason of the electron-withdrawing properties of such unsaturated dithiolene bridge.

Further studies are now ongoing to functionalize 1,2-dithiolene complexes with Lewis acidic function to extend a strategy recently established in our group for H<sub>2</sub> activation.<sup>[44]</sup>

## Experimental Section

### General Experimental Details

All reactions were carried out under an atmosphere of Ar or N<sub>2</sub> using Schlenk or glovebox techniques for the syntheses. Anhydrous toluene, THF, pentane and hexane were distilled over sodium, degassed and stored under Ar. CH<sub>2</sub>Cl<sub>2</sub> were distilled over CaH<sub>2</sub>, degassed and stored under Ar. Deuterated solvent were degassed by a minimum of three freeze-pump-thaw cycles and dried over activated molecular sieves (3 Å or 4 Å). Lithium diisopropylamide solution (2 M in THF), trifluoroacetic acid and PPh<sub>3</sub> were used as received from Acros Organics, Sigma Aldrich or Baker. PhCCH, hexyne and piperidine were degassed and dried over molecular sieves prior to use. The complex **2** was synthesized following literature procedure.<sup>[39]</sup> Complexes **3**<sup>R</sup> were synthesized according to the literature.<sup>[29]</sup> The NMR spectra (<sup>1</sup>H, <sup>13</sup>C-<sup>1</sup>H, <sup>31</sup>P-<sup>1</sup>H)) were respectively recorded at room temperature in deuterated solvents with a Bruker Avance 400 or Avance III HD 500 spectrometer of the ‘Service RMN-SM de l’Université de Bretagne Occidentale’. They were referenced to SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C), H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Variable Temper-



**Scheme 2.** (a) Mechanistic proposition for the acetylide addition to the μ-S<sub>2</sub> site in **1** and **2**; (b) Possible C- and S-centered monoanionic intermediates resulting from addition of lithium alkynylide to complexes **1**–**2**.



ature-NMR experiments were performed with a Bruker Avance III HD 500 spectrometer. The infrared spectra were recorded with PerkinElmer spectrometer in solution. Chemical analyses were made by the "Service d'Analyses – Chromato – Masse BioClS – UMR 8076", Châtenay-Malabry (France). Single-crystal X-ray diffraction data were collected at 150–170 K on an Oxford Diffraction X-Calibur-2 CCD diffractometer, equipped with a jet cooler device and a graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  0.71073). Deposition Numbers 2324412 (for 3<sup>Ph</sup>), 2324411 (for 4<sup>Ph</sup>) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

### Synthesis and Characterization of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (4<sup>Ph</sup>)

705.7 mg of PPh<sub>3</sub> (2.69 mmol, 3 eq.) were added to a solution of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>6</sub>] (3<sup>Ph</sup>) (400 mg, 0.897 mmol, 1 eq.) in 40 mL of THF. The mixture was stirred at 40 °C for one week. The solvent was evaporated to dryness under reduced pressure. The obtained residue was chromatographed using pentane as an eluent. CH<sub>2</sub>Cl<sub>2</sub> was slowly added to the eluent to accelerate the migration of the products. The main fraction with red color was collected and the solvent was removed to give 580 mg (70%) of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (4<sup>Ph</sup>) as a sensitive brown-red solid. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{co}}$  (cm<sup>-1</sup>): 2000, 1954, 1936. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K):  $\delta$  (ppm) = 4.80 (s, 1H, =CH), 6.6–7.06 (m, 5H, Ph–C), 7.28–7.62 (m, 30H, Ph–P). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K):  $\delta$  (ppm) = 60.04 ppm (s, PPh<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz, 298 K):  $\delta$  (ppm) = 125.4–134.0 (Ph), 135.6 (s, =CH), 137 (d, P–C,  $J_{\text{PC}}$  = 42 MHz), 156.5 (s, =CPh), 216.1 (m, CO). Elemental analysis: C, H, N analysis calculated for C<sub>48</sub>H<sub>36</sub>Fe<sub>2</sub>O<sub>4</sub>P<sub>2</sub>S<sub>2</sub>: C 63.04%, H 3.97%; found C 62.80%, H 4.09%.

### Synthesis and Characterization of [Fe<sub>2</sub>( $\mu$ -SH)( $\mu$ -SC=CPh)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5<sup>Ph</sup>) and [Fe<sub>2</sub>( $\mu$ -SH)( $\mu$ -SC=C(C<sub>4</sub>H<sub>9</sub>))(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5<sup>Hex</sup>)

An alkynylidene solution, prepared from the addition of lithium diisopropylamide (0.62 mL, 2 M in THF, 1.23 mmol, 10 eq.) to a solution of phenylacetylene (0.140 mL, 1.27 mmol, 10 eq.) or hexyne (0.146 mL, 1.27 mmol, 10 eq.) in 10 mL of THF at room temperature, was cannulated to a cold solution (–78 °C) of [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>)] (2) (100.0 mg, 0.123 mmol, 1 eq.) in 20 mL of THF, which turned dark yellow. (Note: The use of 2.5 equivalents lead to unreacted precursor together with decomposed products.) This reaction mixture was stirred for 30 min at –78 °C. Then, 0.1 mL (1.30 mmol, 10.6 eq.) of trifluoroacetic acid, was added, causing an immediate red color change. Stirring was continued, at –78 °C, for 30 min and then at room temperature for further 30 min prior to removal of the solvent. The remaining black solid was filtrated on a silica gel column using a cold mixture of pentane and dichloromethane (4:3) as eluent, which afforded a red solution of 5<sup>Ph</sup>. After removing the solvent, [Fe<sub>2</sub>( $\mu$ -SH)( $\mu$ -SC=CPh)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] were obtained as an air-sensitive red oily-powder. Relevant elemental analysis and single crystals for XRD of 5<sup>Ph</sup> could not be obtained due to their instability.

Data for 5<sup>Ph</sup>: 100 mg, 89%. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{co}}$ (cm<sup>-1</sup>) = 2004, 1960, 1942. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K):  $\delta$  (ppm) = –3.97 (t, <sup>3</sup>J<sub>(PH)}</sub> = 5.85 Hz, SH), –1.32 (t, <sup>3</sup>J<sub>(PH)}</sub> = 4.89 Hz, SH), –0.86 (br m, SH), –0.43 (br m, 1H, SH), 7.31–7.53 (m, 35H, Ph). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K):  $\delta$  (ppm) = 57.7, 56.6, 54.2, 53.7, 51.2 (s, PPh<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz, 298 K):  $\delta$  (ppm) = 81.8, 89.4 (s, C=C), 123.9–136.6 (Ph), 216.9, 217.3 (m, CO).

Data for 5<sup>Hex</sup>: 41 mg, 57%. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{co}}$ (cm<sup>-1</sup>) = 2003, 1960, 1942. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K):  $\delta$  (ppm) = –4.14 (t, <sup>3</sup>J<sub>(PH)}</sub> = 5.9 Hz, SH), –1.23 (t, <sup>3</sup>J<sub>(PH)}</sub> = 4.9 Hz, SH), –0.93 (br. t, SH), –0.45 (t, <sup>3</sup>J<sub>(PH)}</sub> = 1.7 Hz, SH), 0.92 (t, 3H, CH<sub>3</sub>), 1.39–1.55 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>), 2.24 (–CH<sub>2</sub>–S), 7.42–7.57 (m, 30H, Ph). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K):  $\delta$  (ppm) = 57.2, 54.4, 51.4 (s, PPh<sub>3</sub>).

### Synthesis and Characterization of [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>C=CH(Ph))(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (6<sup>Ph</sup>)

5  $\mu$ L of piperidine (0.051 mmol, 0.5 eq) were added to a solution of [Fe<sub>2</sub>( $\mu$ -SH)( $\mu$ -SC=CPh)(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (5<sup>Ph</sup>) (100.0 mg, 0.109 mmol, 1 eq.) in 20 mL of THF. The color of the reaction solution immediately changed from light red to dark red. After stirring in the dark, at room temperature, for one week, the solvent was evaporated to dryness under reduced pressure. The resulting residue was chromatographed on a silica gel column with a mixture of pentane:dichloromethane (10:2). After removing the solvent, 53 mg of [Fe<sub>2</sub>( $\mu$ -S<sub>2</sub>C=CH(Ph))(CO)<sub>4</sub>(PPh<sub>3</sub>)<sub>2</sub>] (6<sup>Ph</sup>) were obtained as a red powder (53%). No crystals suitable for XRD analysis were obtained. IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{co}}$ (cm<sup>-1</sup>) = 2000, 1954, 1938. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K):  $\delta$  (ppm) = 4.38 (s, 1H, =CH), 6.62–7.08 (m, 5H, Ph–C), 7.32–7.61 (m, 30H, Ph–P). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K):  $\delta$  (ppm) = 55.2, 57.7 ppm (s, PPh<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz, 298 K):  $\delta$  (ppm) = 115.8 (s, CH(Ph)=), 125.9–136.3 (Ph), 135.9, 136.3 (P–C), 149.7 (C(S<sub>2</sub>)=), 216.9, 218.6 (m, CO).

### Synthesis and Characterization of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>] (7<sup>Ph</sup>)

58.8 mg of PPh<sub>3</sub> (0.224 mmol, 1 eq.) were added to a solution of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>6</sub>] (3<sup>Ph</sup>) (100.0 mg, 0.224 mmol, 1 eq.) in 20 mL of THF at room temperature. This mixture was stirred for 5 days. The solvent was then evaporated to dryness under reduced pressure. The resulting residue was chromatographed on a silica gel column with a mixture of hexane:dichloromethane (10:1) as eluent. The first collected orange fraction corresponds to the unreacted precursor [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>6</sub>] (3<sup>Ph</sup>). A second brown fraction was collected and afforded, after removing the solvent, 100 mg of [Fe<sub>2</sub>( $\mu$ -SCH=C(Ph)S)(CO)<sub>5</sub>(PPh<sub>3</sub>)<sub>2</sub>] (7<sup>Ph</sup>) as an air-sensitive brown solid (66%). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu_{\text{co}}$  (cm<sup>-1</sup>): 2051, 1993, 1980, 1936. <sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz, 298 K):  $\delta$  (ppm) = 5.69 (s, 1H, =CH), 6.97–7.21 (m, 5H, Ph–C), 7.35–7.42 (m, 15H, Ph–P). <sup>31</sup>P-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz, 298 K):  $\delta$  (ppm) = 63.06 ppm (s, PPh<sub>3</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.8 MHz, 298 K):  $\delta$  (ppm) = 125.0–133.8 (Ph), 134.9 (s, =CH), 135.8 (d, P–C,  $J_{\text{PC}}$  = 42 MHz), 159.0 (s, =CPh), 209 (s, CO), 213.5 (d,  $J_{\text{PC}}$  = 7.12 MHz, CO), 213.8 (d,  $J_{\text{PC}}$  = 7.54 MHz, CO). Elemental analysis: C, H, N analysis calculated for C<sub>31</sub>H<sub>21</sub>Fe<sub>2</sub>O<sub>5</sub>P<sub>1</sub>S<sub>2</sub>. (C<sub>6</sub>H<sub>14</sub>)<sub>0.2</sub>: C 55.45%, H 3.44%; found C 55.29%, H 3.38%.

## Supporting Information

IR and NMR spectra are reported in the supporting information.

## Acknowledgements

The authors thank Drs. G. Simon and S. Cérantola, and Dr. F. Michaud for their help in recording NMR and XRD experiments at the 'Service Général des Plateformes, Brest' (SGPLAT), respectively. L.C. thanks the ANR (Agence Nationale de Recherche) for funding the project JCJC OxySplit-H2 (ANR-20-

CE07-0027-01). I. B. and L. C. acknowledge the support of the Region Bretagne for funding the project SAD ConvCatH.

## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

**Keywords:** bioinspired model of hydrogenases · di-substituted carbonyl diiron complex · 1,2-dithiolene ligand · phosphine

- [1] H. Beinert, R. H. Holm, E. Münck, *Science*. **1997**, *277*, 653–659.
- [2] F. Möller, S. Piontek, R. G. Miller, U.-P. Apfel, *Chem. Eur. J.* **2018**, *24*, 1471–1493.
- [3] M. Giedyk, K. Goliszewska, D. Gryko, *Chem. Soc. Rev.* **2015**, *44*, 3391–3404.
- [4] T. Rouault, In *Iron-Sulfur Clusters in Chemistry and Biology*, De Gruyter, **2014**.
- [5] D. Schilter, J. M. Camara, M. T. Huynh, S. Hammes-Schiffer, T. B. Rauchfuss, *Chem. Rev.* **2016**, *116*, 8693–8749.
- [6] F. Wittkamp, M. Senger, S. T. Stripp, U.-P. Apfel, *Chem. Commun.* **2018**, *54*, 5934–5942.
- [7] Y. Li, T. B. Rauchfuss, *Chem. Rev.* **2016**, *116*, 7043–7077.
- [8] C. Elleouet, F. Y. Pétillon, P. Schollhammer, in *Advances in Bioorganometallic Chemistry* (Eds.: T. Hirao, T. Moriuchi), Elsevier, **2019**, pp. 347–364.
- [9] J. T. Kleinhaus, F. Wittkamp, S. Yadav, D. Siegmund, U.-P. Apfel, *Chem. Soc. Rev.* **2021**, *50*, 1668–1784.
- [10] G. Hogarth, *Coord. Chem. Rev.* **2023**, *490*, 215174.
- [11] W. Hieber, J. Gruber, *Z. Anorg. Allg. Chem.* **1958**, *296*, 91–103.
- [12] C. H. Wei, L. F. Dahl, *Inorg. Chem.* **1965**, *4*, 1–11.
- [13] P. Buday, C. Kasahara, E. Hofmeister, D. Kowalczyk, M. K. Farh, S. Riediger, M. Schulz, M. Wächtler, S. Furukawa, M. Saito, D. Ziegenbalg, S. Gräfe, P. Bäuerle, S. Kupfer, B. Dietzek-Ivanšić, W. Weigand, *Angew. Chem. Int. Ed.* **2022**, *61*, e202202079.
- [14] M. E. Ahmed, S. Dey, M. Y. Darensbourg, A. Dey, *J. Am. Chem. Soc.* **2018**, *140*, 12457–12468.
- [15] H. Adams, M. J. Morris, C. C. Robertson, H. C. I. Tunnicliffe, *Organometallics* **2019**, *38*, 665–676.
- [16] K. Charretre, M. Kdider, J.-F. Capon, F. Gloaguen, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Inorg. Chem.* **2010**, *49*, 2496–2501.
- [17] L. Bertini, P. Fantucci, L. De Gioia, *Organometallics* **2011**, *30*, 487–498.
- [18] S. Aguado, L. Casarrubios, C. R. de Arellano, M. A. Sierra, *RSC Adv.* **2020**, *10*, 29855–29867.
- [19] P. Mathur, R. S. Ji, D. K. Rai, A. Raghuvanshi, S. M. Mobin, *J. Cluster Sci.* **2012**, *23*, 615–625.
- [20] D. Seyferth, R. S. Henderson, *J. Organomet. Chem.* **1979**, *182*, C39–C42.
- [21] P. Mathur, V. K. Singh, A. K. Singh, S. M. Mobin, C. Thöne, *J. Organomet. Chem.* **2006**, *691*, 3336–3342.
- [22] P. Mathur, S. Boodida, R. S. Ji, S. M. Mobin, *J. Organomet. Chem.* **2009**, *694*, 3043–3045.
- [23] S. Gao, Y. Liu, Y. Shao, D. Jiang, Q. Duan, *Coord. Chem. Rev.* **2020**, *402*, 213081.
- [24] T. B. Rauchfuss, in *Dithiolene Chemistry*, John Wiley & Sons, Ltd, **2003**, pp. 1–54.
- [25] H. Mousser, A. Darchen, A. Mousser, *J. Organomet. Chem.* **2010**, *695*, 786–791.
- [26] R. B. King, *J. Am. Chem. Soc.* **1963**, *85*, 1584–1587.
- [27] G. N. Schrauzer, V. P. Mayweg, H. W. Finck, W. Heinrich, *J. Am. Chem. Soc.* **1966**, *88*, 4604–4609.
- [28] D. Seyferth, G. G. Womack, L. C. Song, *Organometallics* **1983**, *2*, 776–779.
- [29] D. Seyferth, G. B. Womack, *Organometallics* **1986**, *5*, 2360–2370.
- [30] D. Touchard, J. L. Fillaut, P. Dixneuf, C. Mealli, M. Sabat, L. Toupet, *Organometallics* **1985**, *4*, 1684–1686.
- [31] D. Touchard, J. L. Fillaut, D. V. Khasnis, P. H. Dixneuf, C. Mealli, D. Masi, L. Toupet, *Organometallics* **1988**, *7*, 67–75.
- [32] P. Mathur, A. K. Dash, *J. Cluster Sci.* **1998**, *9*, 131–143.
- [33] R. Siebenlist, H.-W. Frühauf, H. Kooijman, N. Veldman, A. L. Spek, K. Goubitz, J. Fraanje, *Inorg. Chim. Acta.* **2002**, *327*, 66–89.
- [34] N. B. Makouf, H. B. Mousser, A. Darchen, A. Mousser, *J. Organomet. Chem.* **2018**, *866*, 35–42.
- [35] A. Q. Daraosheh, H. Abul-Futouh, N. Murakami, K. M. Ziems, H. Görls, S. Kupfer, S. Gräfe, A. Ishii, M. Celeda, G. Mlostoń, W. Weigand, *Materials* **2022**, *15*, 2867.
- [36] S. Lounissi, J.-F. Capon, F. Gloaguen, F. Matoussi, F. Y. Pétillon, P. Schollhammer, J. Talarmin, *Organometallics* **2010**, *29*, 1296–1301.
- [37] F. Zhang, T. J. Woods, T. B. Rauchfuss, F. Arrigoni, G. Zampella, *Chem. Commun.* **2021**, *57*, 5079–5081.
- [38] F. Arrigoni, G. Zampella, F. Zhang, H. N. Kagalwala, Q.-L. Li, T. J. Woods, T. B. Rauchfuss, *Inorg. Chem.* **2021**, *60*, 3917–3926.
- [39] H. N. Kagalwala, N. Lalaoui, Q.-L. Li, L. Liu, T. Woods, T. B. Rauchfuss, *Inorg. Chem.* **2019**, *58*, 2761–2769.
- [40] R. Rossetti, G. Gervasio, P. L. Stanghellini, *Inorg. Chim. Acta.* **1979**, *35*, 73–78.
- [41] Dietmar. Seyferth, G. B. Womack, R. S. Henderson, Martin. Cowie, B. W. Hames, *Organometallics*. **1986**, *5*, 1568–1575.
- [42] X. Wang, Z. Wei, X. Jiang, J. Zhao, X. Liu, *Inorg. Chim. Acta.* **2012**, *392*, 112–117.
- [43] M. Kdider, C. Elleouet, F. Y. Pétillon, P. Schollhammer, *Molbank*. **2023**, M1719.
- [44] L. Chatelain, J.-B. Breton, F. Arrigoni, P. Schollhammer, G. Zampella, *Chem. Sci.* **2022**, *13*, 4863–4873.

Manuscript received: January 31, 2024  
Revised manuscript received: March 29, 2024  
Accepted manuscript online: April 10, 2024  
Version of record online: May 8, 2024