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Communication

Mono- and Dinuclear Carbonyl Dithiolene Complexes Related to the [FeFe]-Hydrogenases

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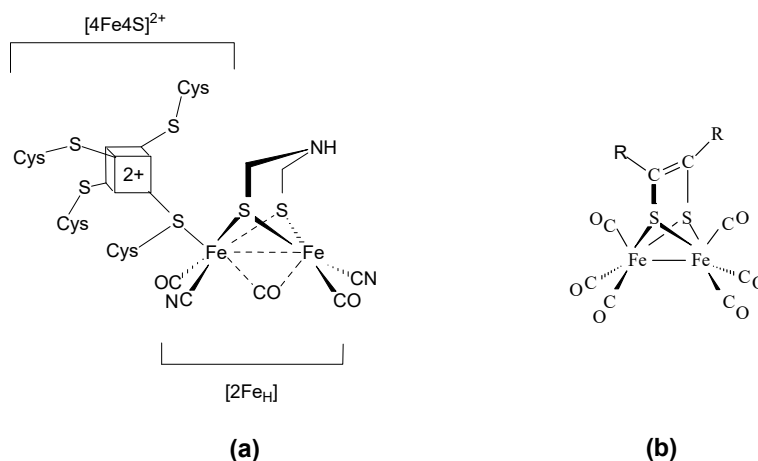
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Abstract: The di-iron carbonyl dithiolene bridged complex $[\text{Fe}_2(\text{CO})_6(\mu\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ (**1**) reacts with 1 equivalent of phosphane PR_3 ($\text{R} = \text{Ph}, \text{OMe}$) to give, as major products, monosubstituted derivatives $[\text{Fe}_2(\text{CO})_5\text{L}(\mu\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ ($\text{L} = \text{PPh}_3$ (**2**), P(OMe)_3 (**3**)). In the presence of an excess (3–4 equiv.) of P(OMe)_3 , the cleavage of **1** arises partly and a mixture of the mononuclear species $[\text{Fe}(\text{CO})(\text{P(OMe)}_3)_2(\kappa^2\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ (**4**) and **3** is obtained. The compounds **2–4** were analyzed by IR and ^1H , $^{31}\text{P}\{-^1\text{H}\}$ NMR spectroscopies. Their structures in solid state were determined by X-ray diffraction analyses, which accord with their spectroscopic characteristics.

Keywords: dinuclear complexes; iron; dithiolene bridge; carbonyl; phosphane; metal–sulfur; hydrogenases; bioinspiration

1. Introduction

The chemistry of carbonyl dithiolato di-iron complexes $[\text{Fe}_2(\text{CO})_{6-x}\text{L}_x(\mu\text{-dithiolato})]$ has attracted a lot of attention during the two last decades in reason of the resemblance of such compounds with the active site of [FeFe]-hydrogenases (H-cluster) (Scheme 1a) and in view to obtain efficient bioinspired non-noble metal electrocatalysts for the reversible H^+/H_2 conversion [1–5]. A wide number of di-iron systems with various combinations of thiolate bridges and terminal ligands have been studied in order to tune the electronic and steric properties of the dinuclear site as well as to functionalize the second sphere of coordination with non-innocent functionalities (redox and proton relays) [6].



Scheme 1. Representation of the H-cluster (a) and a dinuclear carbonyl alkenedithiolate complex (b).



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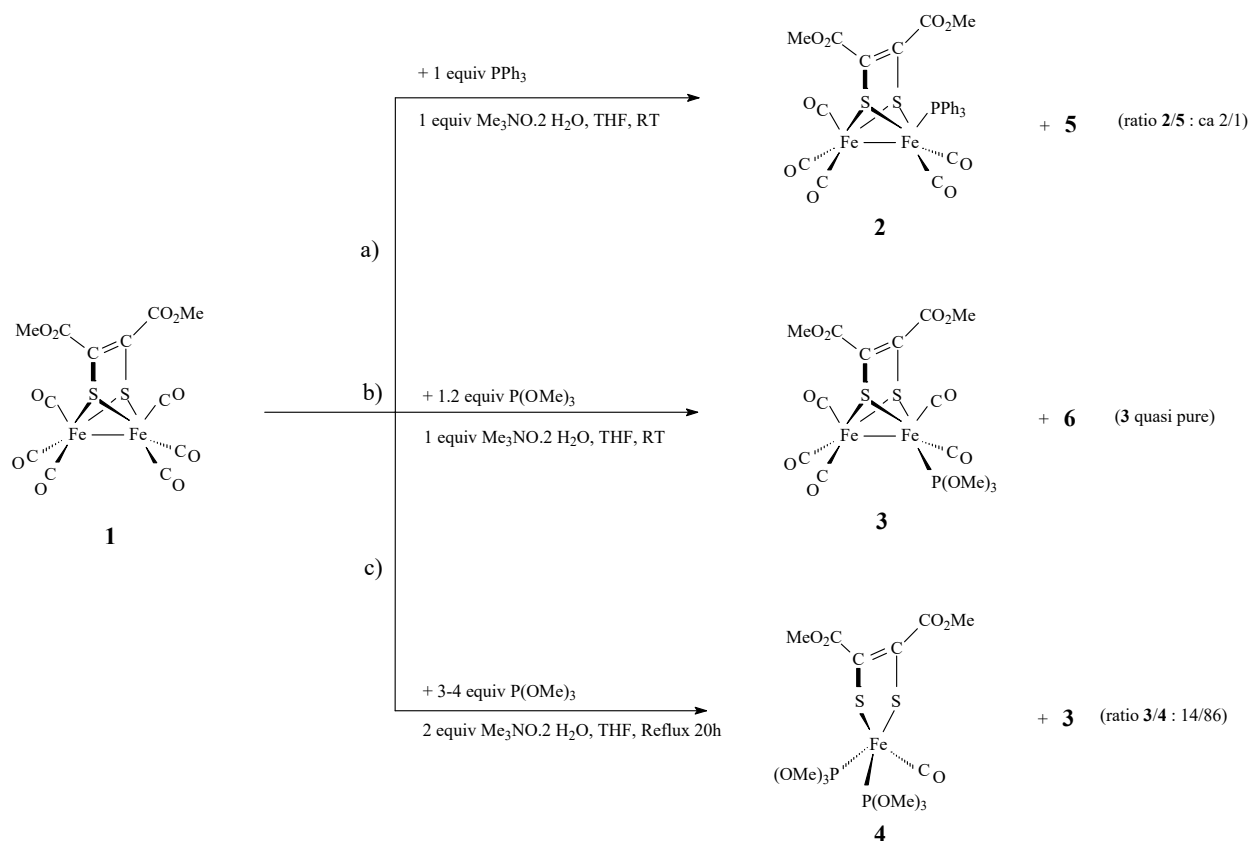


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Within the course of our research in this topic, we have been interested to study di-iron complexes with a dithiolene (alkene dithiolate) bridge (Scheme 1b) bearing an electron-withdrawing group, such as CO₂Me, in reason of the capacity of this bridge to act as a redox active ligand as well as its electronic effect on the di-iron framework which allows us to decrease the potential of reduction of such derivatives and to stabilize reduced species [7]. Relatively few examples of di-iron complexes [Fe₂(CO)_{6-x}L_x(μ-dithiolene)] have been reported [7–12]. The hexacarbonyl precursors can be prepared following various pathways, which have been previously reported in the literature [1–4,11]. The substitution of carbonyl groups by phosphanes, through photochemical, thermal or electrochemical activation, allows us to prepare monosubstituted [Fe₂(CO)₅L(μ-dithiolene)] and symmetrically disubstituted [Fe₂(CO)₄L₂(μ-dithiolene)] derivatives (one CO being replaced at each iron atom). However, clean substitution processes are often limited by the fragmentation of the dinuclear entity into mononuclear complexes, [Fe(CO)_{3-x}L_x(κ²-dithiolene)] (x = 0–2) in the reaction conditions [10,11]. Herein, we report our preliminary attempts to prepare substituted di-iron derivatives by reacting the hexacarbonyl precursor [Fe₂(CO)₆(μ-S₂C₂(CO₂Me)₂)] (**1**) with PPh₃ and P(OMe)₃.

2. Results and Discussion

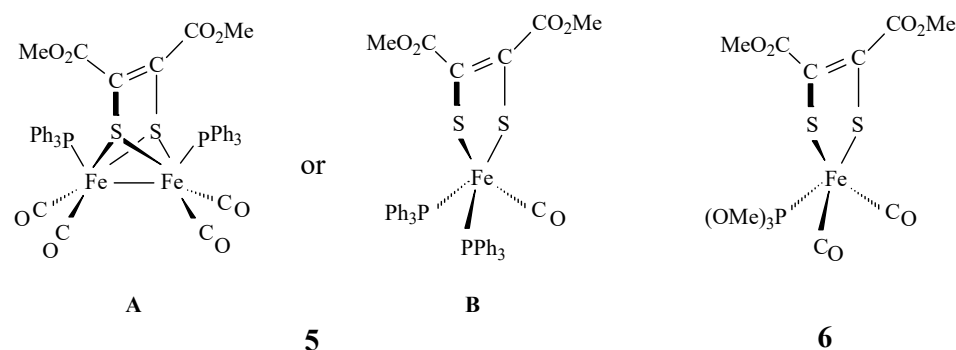
The complex [Fe₂(CO)₆(μ-S₂C₂(CO₂Me)₂)] (**1**) was reacted with one equivalent of phosphane (PPh₃ or P(OMe)₃) to give, according to the experimental conditions, the monosubstituted derivatives [Fe₂(CO)₅L(μ-S₂C₂(CO₂Me)₂)] (L = PPh₃ (**2**), P(OMe)₃ (**3**)) as the major products of the reaction (Scheme 2, Appendix A). The formation of side products **5,6** were also detected. When a large excess of P(OMe)₃ was used, only one product, **4**, could be isolated together with a small amount of **3**. It was assigned to the mononuclear iron derivative [Fe(CO)(P(OMe)₃)₂(κ²-S₂C₂(CO₂Me)₂)] (Scheme 2, Appendix A).



Scheme 2. Reactivity of **1** towards PPh₃ (a) and P(OMe)₃ (b,c). The ratios given for complexes have been determined by NMR and correspond to those of the major fractions collected after purification by chromatography.

Compounds **2–4** were characterized by spectroscopic analyses (IR, NMR) and their structures were confirmed by X-ray analyses of single crystals. The infrared spectra of **2** and **3** recorded in CH₂Cl₂ display a similar pattern in the terminal $\nu(\text{CO})$ region, which is typical of an {Fe₂(CO)₅L(μ -dithiolate)} framework with four bands at 2058(s), 2002(s), 1988(m, sh), 1946(w) cm⁻¹ and 2061(s), 2008(vs), 1989(s), 1955(w) cm⁻¹, respectively. Their ¹H NMR spectra in CDCl₃ exhibit one singlet at 3.48 ppm (for **2**) and 3.66 ppm (for **3**) which is assigned to two equivalent methyl groups of the dithiolate ligand, which accords with a position of the C=C axis of the dithiolene bridge perpendicular to the Fe-Fe bond. The signals of the phosphanes PR₃ (R = Ph, OMe) were detected at the expected chemical shifts with related proton integrations. The ³¹P-{¹H} NMR spectra of **2** and **3** show one singlet at 60.8 or 172.1 ppm for PPh₃ and P(OMe)₃, respectively. The IR spectrum of **4**, in CH₂Cl₂, presents in the carbonyl region one single band at 1971 (vs) cm⁻¹. Its ¹H NMR spectrum displays, in the alkyl region, a singlet at 3.91 ppm assigned to the methyl group of the chelating dithiolene, and a multiplet at 3.43 ppm is attributed to two phosphite ligands. In the ³¹P-{¹H} NMR spectrum, a single resonance at 175.0 ppm was observed for the P(OMe)₃ groups. The formation of the analogous compound [Fe(CO)(P(OMe)₃)₂(κ^2 -S₂C₂Ph₂)] was observed together with a disubstituted complex [Fe₂(CO)₄(P(OMe)₃)₂(μ -S₂C₂Ph₂)] when [Fe₂(CO)₆(μ -S₂C₂Ph₂)] is warmed in the presence of an excess of P(OMe)₃ in refluxing toluene [10].

The co-products **5** and **6** were detected in the ¹H and ³¹P-{¹H} NMR spectra of **2** and **3**, respectively. Unfortunately, we have been unable to separate them satisfactorily by chromatography from their mixture with **2** and **3**. It was not possible on the basis of the spectroscopic data of **5** to distinguish a disubstituted di-iron structure with two PPh₃ in symmetrical position (Scheme 3(5A)) from a mononuclear geometry with two equivalent phosphines (Scheme 3(5B)), its IR pattern being overlapped with that of **2**. The geometry of **6** was ascertained as [Fe(CO)₂(P(OMe)₃)₂(κ^2 -S₂C₂(CO₂Me)₂)] (Scheme 3) by the presence of two $\nu(\text{CO})$ bands at 2036(s) and 1988(s) cm⁻¹ in its infrared spectrum, as well as by the observation in the ¹H NMR spectrum of a doublet (³J_{P-H} = 12.0 Hz) at 3.45 ppm counting for nine protons with respect to six protons of the methyls of the dithiolene group. The formation of the analogous complex [Fe(CO)₂(PPh₃)₂(κ^2 -S₂C₂Ph₂)] was proposed to arise from the decomposition of the air-sensitive disubstituted species [Fe₂(CO)₄(PPh₃)₂(μ -S₂C₂Ph₂)] [11].



Scheme 3. Proposed geometries for **5** and **6** on the basis of their spectroscopic data.

Single crystals of **2–4** suitable for X-ray diffraction studies were obtained from diethyl ether solutions of the complexes, at -15 °C (Figure 1, Table 1 and Tables S1–S3).

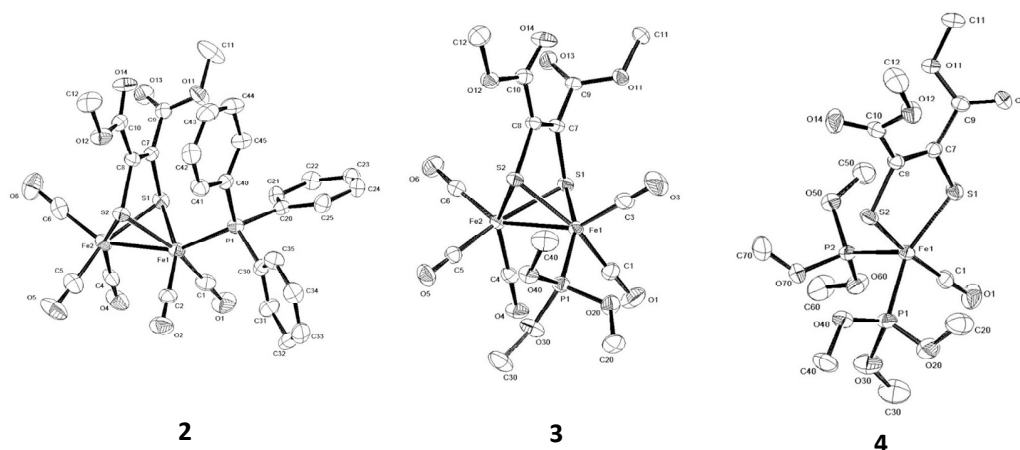


Figure 1. Molecular structure of compounds **2**, **3** and **4** with thermal ellipsoids at 30% probability.

Table 1. Selected bond lengths (Å) and angles (°) of **2–4**.

| | 2 | 3 | 4 |
|-----------------------|-------------|-------------|-------------|
| Fe(1)-Fe(2) | 2.4834 (6) | 2.4772 (6) | |
| P(1)-Fe(1) | 2.2496 (8) | 2.1651 (9) | 2.1621 (9) |
| P(2)-Fe(1) | | | 2.1214 (9) |
| S(1)-Fe(1) | 2.2852 (8) | 2.2762 (9) | 2.1762 (8) |
| S(1)-Fe(2) | 2.2886 (8) | 2.2908 (9) | |
| S(2)-Fe(1) | 2.2872 (8) | 2.2810 (9) | 2.1983 (8) |
| S(2)-Fe(2) | 2.2742 (8) | 2.2667 (9) | |
| C(1)-Fe(1) | 1.771 (3) | 1.786 (4) | 1.768 (3) |
| C(2/3)-Fe(1) | 1.769 (3) | 1.778 (4) | |
| C(4)-Fe(2) | 1.794 (3) | 1.789 (3) | |
| C(5)-Fe(2) | 1.776 (3) | 1.793 (3) | |
| C(6)-Fe(2) | 1.812 (3) | 1.811 (3) | |
| C(7)-C(8) | 1.323 (4) | 1.329 (4) | 1.354 (4) |
| Fe(1)-S(1)-Fe(2) | 65.77 (2) | 65.69 (3) | |
| Fe(1)-S(2)-Fe(2) | 65.97 (2) | 66.01 (3) | |
| C(1)-Fe(1)-S(1) | 90.95 (9) | 90.42 (11) | |
| C(1)-Fe(1)-S(2) | 161.07 (10) | 163.16 (12) | 170.23 (10) |
| C(2/3)-Fe(1)-S(1) | 156.84 (10) | 105.76 (12) | |
| P(1)-Fe(1)-S(1) | 106.47 (3) | 156.95 (4) | 151.49 (4) |
| P(2)-Fe(1)-S(1) | | | 116.47 (4) |
| P(1)-Fe(1)-S(2) | 102.98 (3) | 95.07 (3) | |
| P(2)-Fe(1)-S(2) | | | 96.24 (3) |
| P(1)-Fe(1)-C(1) | 95.94 (10) | 87.60 (11) | 90.95 (11) |
| P(2)-Fe(1)-C(1) | | | 93.47 (10) |
| P(1)-Fe(1)-C(2/3) | 96.26 (9) | 97.27 (12) | |
| P(1)-Fe(1)-P(2) | | | 93.98 (3) |
| C(1)-Fe(1)-C(2/3) | 91.30 (3) | 97.09 (17) | |
| S(1)-Fe(1)-S(2) | 79.80 (9) | 80.62 (3) | |
| C(4)-Fe(2)-C(5) | 91.19 (13) | 90.11 (14) | |
| C(4)-Fe(2)-S(1) | 91.50 (9) | 92.81 (10) | |
| C(4)-Fe(2)-S(2) | 154.58 (10) | 146.25 (11) | |
| C(5)-Fe(2)-S(1) | 159.48 (11) | 164.82 (11) | |
| C(5)-Fe(2)-S(2) | 88.98 (9) | 88.71 (11) | |
| C(6)-Fe(2)-Fe(1) | 149.44 (10) | 148.77 (11) | |
| P(1)/C(3)-Fe(1)-Fe(2) | 153.93 (3) | 150.45 (12) | |

The $[\text{Fe}_2\text{S}_2]$ core in these complexes adopts a butterfly conformation as previously observed, for example, in related crystallographically characterized monosubstituted di-iron compounds $[\text{Fe}_2(\text{CO})_5(\text{L})\{\mu\text{-}(\text{SCH}_2)_2(\text{Ph})\text{P}=\text{O}\}]$ (L = PPh_3 , and $\text{P}(\text{OEt})_3$) [13]. The

local environment of each iron atom is a square pyramid supplemented by a metal–metal bond. In both complexes **2** and **3**, the two iron atoms are bridged by the dithiolene linker, whose C=C bond lies perpendicularly to the iron–iron axis. The PR₃ ligand coordinated to the Fe(1) atom lies in apical position in **2** and in a basal one in **3**. The Tolman's angles, θ , of PPh₃ and P(OMe)₃ are, respectively, 145° [14] and 107° [15]. The more crowded PPh₃ ligand in **2** lying in an apical position, the basal position of P(OMe)₃, observed in **3**, is probably due to a higher repulsion between the CO₂Me functionality of the dithiolene ligand and the methoxy group of P(OMe)₃, than that between the apical PPh₃ and CO₂Me in **2**. Thus, the apical/basal positions in **2** (PPh₃) and **3** (P(OMe)₃), respectively, differ from the apical/apical ones observed in solid state in the two di-iron complexes [Fe₂(CO)₅(L){ μ -(SCH₂)₂(Ph)P=O}] [13] with L = PPh₃, and P(OEt)₃ (θ = 109° [14]). This difference could mainly be due to a steric effect rather than an electronic one, when one compares such an effect in the two series of complexes implying, respectively, a bridging electron-withdrawing dithiolene ligand in **2** and **3**, and the bridging phosphine oxide dithiolato moiety in [Fe₂(CO)₅(L){ μ -(SCH₂)₂(Ph)P=O}] [13]. In the case of these latter complexes, the P=O bridging head of the dithiolate orientates in the opposite direction of the iron atom bearing the phosphane, thus allowing its apical position.

The Fe-Fe bond distances in complexes **2**, and **3**, 2.4834 (6) Å and 2.4772 (6) Å, respectively, are slightly shortened than that observed in their hexacarbonyl precursor **1** (2.4870 (19) Å [7]). A similar trend is observed for the two dithiolene compounds [Fe₂(CO)₆(μ -S₂C₂Ph₂)] and [Fe₂(CO)₄{P(OMe)₃}₂(μ -S₂C₂Ph₂)] for which the Fe-Fe distances are 2.4821(8) Å [9] and 2.4797 Å [10], respectively. In the case of the complexes [Fe₂(CO)₅(L){ μ -(SCH₂)₂(Ph)P=O}], the distances Fe-Fe are 2.5148(9) Å, 2.5006 (14) Å and 2.5152 (8) Å when L = CO [16], PPh₃ [13] and P(OEt)₃ [13], respectively. It is obvious that the replacement of one carbonyl by various phosphanes affects the Fe-Fe bond lengths and could be tentatively related to their σ -electron-donor power (pKa(PPh₃) = 2.73 and (pKa(P(OMe)₃) = 2.6) [17]. On the other hand, it should also be noted that reverse effects on the Fe-Fe distance are observed for di-substituted derivatives in other close di-iron species, for example, the compounds [Fe₂(CO)₄L₂(μ -bdtf) (bdtf = 3,4 dimercaptobenzaldehyde) (L = PPh₃, P(OMe)₃) [18]. This shows that such slight effects are the result of very fine electronic and steric balance depending on the nature of the thiolate bridge, the characteristics (θ , pKa) of the phosphanes, their number and the geometry of the considered isomer, rendering rationalization quite intricate. The Fe-C(O) and C-O bond lengths for **2** and **3**, reported in Table S4, are very close and do not reflect noticeable changes of electron density at the iron core and electron back donation from the iron atom to carbonyl group when substituting PPh₃ with P(OMe)₃.

The structural analysis of **4** reveals a pentagonal geometry similar to that of the analogous compound [Fe(CO)(P(OMe)₃)₂(κ^2 -S₂C₂Ph₂)] [10]. The dithiolene ligand adopts a bidentate geometry through the coordination of its two sulfur atoms. The coordination sphere of the iron atom is completed with one carbonyl and two P(OMe)₃ ligands. An average value of the calculated Addison parameters of 0.84 indicates that **4** adopts a distorted trigonal-pyramid geometry [19].

3. Materials and Methods

All the experiments were carried out under an inert atmosphere, using Schlenk techniques for the syntheses. Solvents were deoxygenated and dried according to standard procedures. The literature method was used for the preparation of the starting compound [Fe₂(CO)₆](μ -S₂C₂(CO₂Me)₂) (**1**) [8]. All other reagents were commercially available and used as purchased. NMR spectra (¹H, ³¹P-{¹H}) were recorded at room temperature with Bruker AMX 400 or AC 300 spectrometers (Billerica, MA, USA) of the "Service général des plateformes, Université de Bretagne Occidentale, Brest" and were referenced to SiMe₄ (¹H) and H₃PO₄ (³¹P). The infrared spectra were recorded with Bruker Vertex 70 and FT IR Perkin Elmer spectrum 2 spectrometer. In a typical experiment, single crystals of **2–4** were obtained from solutions prepared by solubilization of partially purified residues of

2–4 (10 mg), which were obtained after chromatography, in degassed diethyl ether (5 mL) in Schlenk tubes. These solutions were stored, at $-15\text{ }^{\circ}\text{C}$, overnight or for several days. Crystal data of compounds 2–4 were collected with an Oxford Diffraction X—Calibur-2 CCD diffractometer, equipped with a jet cooler device and graphite-monochromated Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$). The structures were solved and refined by standard procedures [20]. Deposition numbers CCDC 2277613, 2277614, and 2277616 contain the supplementary crystallographic data for 2, 3 and 4. These data can also be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (accessed on 28 June 2023).

4. Conclusions

These preliminary results show that the formation of monosubstituted dithiolene complexes $[\text{Fe}_2(\text{CO})_5\text{L}(\mu\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ ($\text{L} = \text{PPh}_3$, and $\text{P}(\text{OMe})_3$) arises easily in mild reaction conditions, at room temperature in the presence of one equivalent of phosphane, while disubstituted species $[\text{Fe}_2(\text{CO})_4\text{L}_2(\mu\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ turn out to be more difficult to prepare because of the readily decomposition of the dinuclear entity, with an electron-withdrawing dithiolene group, into mononuclear species $[\text{Fe}(\text{CO})_{3-x}\text{L}_x(\kappa^2\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ when harsher reaction conditions are set (thermolysis and an excess of phosphane). This suggests that photolytic or electrochemical activation could be more suitable than thermolysis for preparing polysubstituted dithiolene derivatives $[\text{Fe}_2(\text{CO})_{6-x}\text{L}_x(\mu\text{-S}_2\text{C}_2(\text{CO}_2\text{Me})_2)]$ ($x > 1$).

Supplementary Materials: The following supporting information are available online, Table S1: Crystal data and structure refinement for complex 2; Table S2: Crystal data and structure refinement for complex 3; Table S3: Crystal data and structure refinement for complex 4; Table S4: Comparison of the Fe-C(O) and C-O bond lengths (\AA) in complexes 2 and 3; Figure S1: IR spectrum in CH_2Cl_2 of 2 (carbonyl bands of 5 are overlapped); Figure S2: ^1H NMR (CDCl_3) mixture of 2 + 5: (a) aromatic and methyl groups chemical shifts region; (b) complete spectrum; Figure S3: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) mixture of 2 + 5; Figure S4: IR spectrum in CH_2Cl_2 of 3; Figure S5: IR spectrum in CH_2Cl_2 of 6 (3 as impurity); Figure S6: ^1H NMR (CDCl_3) of 3: (a) methyl group chemical shift region; (b) complete spectrum; Figure S7: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 3; Figure S8: ^1H NMR (CDCl_3) of 6: (a) methyl groups chemical shifts region; (b) complete spectrum; Figure S9: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 3; Figure S10: IR spectrum in CH_2Cl_2 of 4; Figure S11: $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3) of 4.

Author Contributions: M.K. prepared and characterized the compounds 1–4. P.S. supervised the syntheses and X-ray, spectroscopic characterizations. C.E., F.Y.P. and P.S. contributed to the writing of the manuscript. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

Appendix A

-Reaction of 1 with 1 equiv. of PPh_3 . To a solution of 1 (50 mg, 0.10 mmol) in THF (30 mL), 1 equiv. of PPh_3 (27 mg, 0.10 mmol) and 1 equiv. of $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$ were added. The mixture was stirred at room temperature, and the progress of the reaction was monitored by IR until the $\nu(\text{CO})$ bands of the starting complex 1 have totally disappeared (~ 6 h). After evaporation of the solvent, the residue was purified by chromatography on a silica gel column. An orange band was eluted with pure dichloromethane. Removal of volatiles afforded an orange powder ($m = 45$ mg). Analysis of CDCl_3 solution of this solid by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated the presence of two products in the 2/1 ratio. The major compound was identified as a monosubstituted di-iron complex 2, while the

minor one can be attributed to either a disubstituted di-iron or a mono-iron complex **5**. Attempts to separate the two products by chromatography by varying the relative amounts of CH₂Cl₂-hexane eluents failed. Only crystals of the major complex **2** were grown from a diethyl ether solution of the mixture of the two products.

Complex **2**: IR (CH₂Cl₂, cm⁻¹): ν(CO) 2058 (s), 2002 (s), 1988 (m, sh), 1946 (w), 1719 (w, CO₂Me). ¹H NMR (CDCl₃, δ, ppm): 7.68–7.36 (m, 15H, Ph), 3.48 (s, 6H, CO₂Me). ³¹P-{¹H} NMR (CDCl₃, δ, ppm): 60.8 (s).

Complex **5**: IR (CH₂Cl₂, cm⁻¹): ν(CO), bands overlapped with those of **2**. ¹H NMR (CDCl₃, δ, ppm): 7.68–7.36 (m, 30H, Ph), 3.17 (s, 6H, CH₃). ³¹P-{¹H} NMR (CDCl₃, δ, ppm) 57.5 (s).

-Reaction of **1** with 1.2 equiv. P(OMe)₃. To a THF (30 mL) solution of **1** (90 mg, 0.185 mmol), 1.2 equiv. of P(OMe)₃ (0.025 mL, 0.222 mmol) and 1 equiv. of Me₃NO·2H₂O were added. The mixture was stirred at room temperature for 12 h. After evaporation of the solvent, the residue was purified by chromatography on a silica gel column. Two bands were eluted with a dichloromethane-hexane-THF (90/5/5) mixture. The first eluted orange band gave, after evaporation of the volatiles, a quasi-pure solid **3** as the major product of the reaction (70 mg). A second eluted garnet-red band afforded a mixture of **3** and **6** in the ratio 1/24. Single crystals of **3**, suitable for X-ray diffraction studies, were grown from a diethyl ether solution at -15 °C.

Complex **3**: IR (CH₂Cl₂, cm⁻¹): ν(CO) 2061 (s), 2008 (vs), 1989 (s), 1955 (w), 1717 (w, CO₂Me). ¹H NMR (CDCl₃, δ, ppm): 3.80 (d, *J* = 12.0 Hz, 9H, P(OMe)₃), 3.66 (s, 6H, CO₂Me). ³¹P-{¹H} NMR (CDCl₃, δ, ppm): 172.1 (s).

Complex **6**: IR (CH₂Cl₂, cm⁻¹): ν(CO) 2036 (s), 1988 (s). ¹H NMR (CDCl₃, δ, ppm): 3.93 (s, 6H, CO₂Me), 3.45 (d, *J* = 12.0 Hz, 9H, P(OMe)₃). ³¹P-{¹H} NMR (CDCl₃, δ, ppm): 168.2 (s).

-Reaction of **1** with 3 equiv. of P(OMe)₃. To a solution of **1** (93 mg, 0.191 mmol) in THF (30 mL), 3 equiv. of P(OMe)₃ (0.062 mL, 0.555 mmol) and 2 equiv. of Me₃NO·2H₂O were added. The mixture was stirred under reflux condition for 2 hrs. After evaporation of the solvent, the residue was purified by chromatography on a silica gel column. A garnet-red main band was eluted with a CH₂Cl₂-hexane-THF mixture in the 90/5/5 ratio, affording after evaporation to dryness a powder (40 mg) that contains a mixture of **4** and **3** in a ratio 86/14 according to NMR analysis.

Complex **4**: IR (CH₂Cl₂, cm⁻¹): ν(CO) 1971 (vs), 1731 (w, CO₂Me). ¹H NMR (CDCl₃, δ, ppm): 3.91 (s, 6H, CO₂Me), 3.43 (m, 18H, P(OMe)₃). ³¹P-{¹H} NMR (CDCl₃, δ, ppm): 175.0 (s).

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