

Photochemical reactions of alkynyl iron (II) complexes with carbon disulfide. Insertion of CS₂ into an iron–C(sp) bond

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Abstract

The novel alkynylthiocarboxylate complexes [Fe(η⁵-C₅H₅)(S₂CC≡CR)(dppm-P)] (3a,b) and [Fe(η⁵-C₅H₅)(S₂CC≡CR)(PPh₃)₂] (4a,b) were obtained through the insertion of CS₂ into the iron–alkynyl bond in the complexes [Fe(η⁵-C₅H₅)(C≡CR)(L)(L')] L, L' = dppm R = Ph (1a), ^tBu (1b); L = (CO), L' = (PPh₃) R = Ph (2a), ^tBu (2b). Variable-temperature ³¹P{¹H} NMR studies indicate the presence of two different isomers, [Fe(η⁵-C₅H₅)(η³-S,C,S'-S₂CC≡CR)(L)(L')] and [Fe(η⁵-C₅H₅)(η²-S,S'-S₂CC≡CR)(L)(L')], which rapidly interconvert at room temperature. The synthesis of the precursor complex [Fe(η⁵-C₅H₅)(C≡C^tBu)(CO)(PPh₃)] is also described.

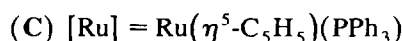
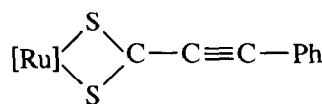
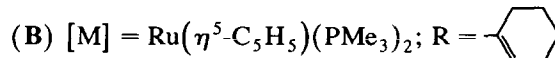
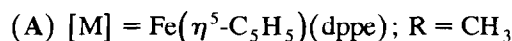
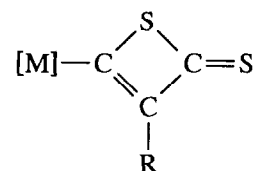
Keywords: Iron (II); CS₂ insertion; Synthesis; NMR; Photochemistry; Alkynyl

1. Introduction

Carbon disulfide is an unsaturated electrophile with an extensive organic and organometallic chemistry [1]. Insertion reactions of CS₂ into transition metal–hydride and carbon (sp³) bonds are well known [2,3], giving dithioformate and dithiocarboxylate complexes respectively. Related complexes are also easily obtained by insertion of CS₂ into transition metal–aryl bonds [4] or metal–oxygen and metal–nitrogen bonds [5]. However, reactions involving M–C(sp²) bonds from alkenyl [6a–c] or alkylidene [6d] derivatives and M–C(sp) bonds from alkylidyne [7] or alkynyl complexes are rare.

In 1982 Selegue [8a] reported the first electrophilic attack of carbon disulfide on the iron alkynyl complex [Fe(η⁵-C₅H₅)(C≡CMe)(dppe)], giving a complex containing a 2H-thiete-2-thione (A). More recently he has also reported the reaction of carbon disulfide with the enynyl derivative [Ru(η⁵-C₅H₅)(C≡C–C=C(H)CH₂–(CH₂)₂CH₂)(PMe₃)₂], leading to a similar thione derivative (B) [8b] in which the pendant alkene is not involved in the electrophilic addition of CS₂. The insertion of carbon disulfide into the compound [Ru(η⁵-

C₅H₅)(C≡CPh)(PPh₃)₂] to give bound phenylthio-propionate S₂CC₂Ph (C) has also been reported [9].

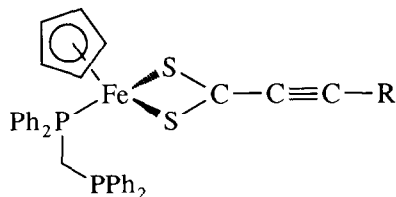


Here we describe the preparation of novel alkynylthiocarboxylate iron(II) complexes obtained through the insertion of CS₂ into the iron–alkynyl bond in the complexes [Fe(η⁵-C₅H₅)(C≡CR)(L)(L')] (L, L' = 2CO; L = CO, L' = PPh₃; L, L' = dppm). The use of different ancillary ligands provides additional information on the mechanism of these particular CS₂ insertion reactions.

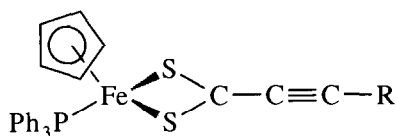
* Corresponding author.

2. Results and discussion

Reaction of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{dppm})]$ $\text{R} = \text{Ph}$ (**1a**), ${}^t\text{Bu}$ (**1b**) [10] and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)]$ $\text{R} = \text{Ph}$ (**2a**), ${}^t\text{Bu}$ (**2b**) (see Section 3) with CS_2 yields the novel alkynyldithiocarboxylate complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{dppm}-\text{P})]$ (**3a,b**) and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{PPh}_3)]$ (**4a,b**).

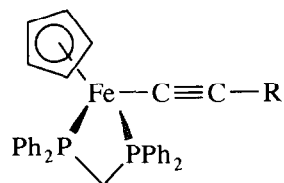


$\text{R} = \text{Ph}$ (**3a**); ${}^t\text{Bu}$ (**3b**)

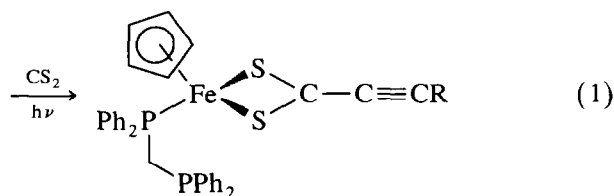


$\text{R} = \text{Ph}$ (**4a**); ${}^t\text{Bu}$ (**4b**)

Irradiation with a UV lamp (400 W) of a CS_2 solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{dppm})]$ (**1a,b**) at -20°C during 4 h leads to a violet–blue solution from which, after chromatography, the complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{dppm}-\text{P})]$ ($\text{R} = \text{Ph}$ (**3a**) or ${}^t\text{Bu}$ (**3b**)) are isolated as the major products in 45 and 65% yields respectively (Eq. (1)). A green solid is also isolated from each by chromatography in ca. 5–10% yield, characterized on the basis of the mass spectra, analytical and spectroscopic data as an adduct of CS_2 with the alkynyl precursor. The ${}^{31}\text{P}\{^1\text{H}\}$ and ${}^1\text{H}$ NMR spectra of the green solid are identical to those of the starting complex but the IR spectra show the characteristic $\nu(\text{CS})$ absorptions at $1000\text{--}1200\text{ cm}^{-1}$ and a peak due to a molecule of CS_2 is shown by the mass spectrum.



$\text{R} = \text{Ph}$ (**1a**); ${}^t\text{Bu}$ (**1b**)

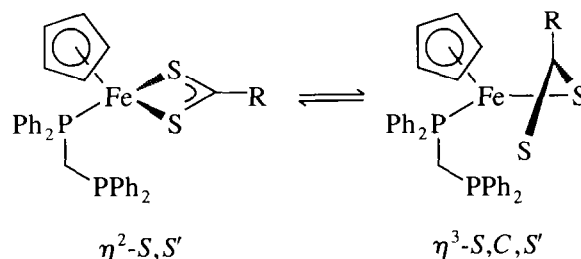


$\text{R} = \text{Ph}$ (**3a**); ${}^t\text{Bu}$ (**3b**)

The alkynyldithiocarboxylate complexes **3a,b** have been characterized by analytical and spectroscopic data. Mass spectra show the molecular ion as well as CS_2 loss, and the IR spectra display the expected $\nu(\text{C}\equiv\text{C})$ and the $\nu(\text{CS})$ absorptions (2063 , 964 and 885 cm^{-1} for **3a**; 2095 , 1026 and 884 cm^{-1} for **3b**).

The ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra at room temperature show two well-separated doublets (AB system) for the phosphorus atoms. One of the doublets is located in the range typical for the coordinated dppm in iron(II) complexes [10] ($\delta = 57.3\text{ ppm}$, ${}^2J(\text{PP}) = 40\text{ Hz}$ for **3a** and $\delta = 59.3\text{ ppm}$, ${}^2J(\text{PP}) = 38\text{ Hz}$ for **3b**). The other doublet appears close to that of free dppm and can be assigned to a non-coordinated phosphorus atom ($\delta = -25.8\text{ ppm}$ for **3a** and -25.7 ppm for **3b**). These ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra rule out monodentate coordination of the dithiocarboxylate and show that it has a greater tendency than dppm to act as a chelating ligand [11] even though the chelate coordination of dppm remains unchanged in a series of reactions performed on the same precursor complexes [10,12].

Variable-temperature ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra show that a fluxional process is taking place, with a mixture of isomers with the alkynyldithiocarboxylate exhibiting $\eta^2\text{-S,S'}$ and $\eta^3\text{-S,C,S'}$ coordination modes.



$\text{R} = \text{C}\equiv\text{CPh}$, $\text{C}\equiv\text{C}{}^t\text{Bu}$

Fig. 1 shows the variable temperature ${}^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3b** in the range $190\text{--}295\text{ K}$. The low field doublet due to the coordinated phosphorus atom disappears as the temperature decreases, and is finally converted at 190 K into two doublets at 46.8 ppm (${}^2J(\text{PP}) = 41\text{ Hz}$) and 67.1 ppm (${}^2J(\text{PP}) = 43\text{ Hz}$) in a ratio of ca. 85:15. The lowest field doublet (67.1 ppm) is assigned to the $\eta^2\text{-S,S'}$ isomer and the higher field signal (46.8 ppm) is assigned to the $\eta^3\text{-S,C,S'}$ isomer, by comparison with the data reported for the analogous isomers $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^2\text{-S,S'}\text{-S}_2\text{CR})(\text{dppm}-\text{P})]$ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\eta^3\text{-S,C,S'}\text{-S}_2\text{CR})(\text{dppm}-\text{P})]$ $\text{R} = \text{Ph}$ or Me [3f]. A similar behaviour is found for the complex **3a** showing a mixture 80:20 $\eta^3\text{-S,C,S'}:\eta^2\text{-S,S'}$ at the same temperature ($\eta^2\text{-S,S'}$ 70.0 ppm , ${}^2J(\text{PP}) = 45\text{ Hz}$; $\eta^3\text{-S,C,S'}$ 52.0 ppm , ${}^2J(\text{PP}) = 40\text{ Hz}$). For both cases the highest field doublet, assigned to the uncoordinated phosphorus, at -25.9 ppm (${}^2J(\text{PP}) = 41\text{ Hz}$) for **3a** and -26.7 ppm (${}^2J(\text{PP}) = 41\text{ Hz}$) for **3b** remains unmodified.

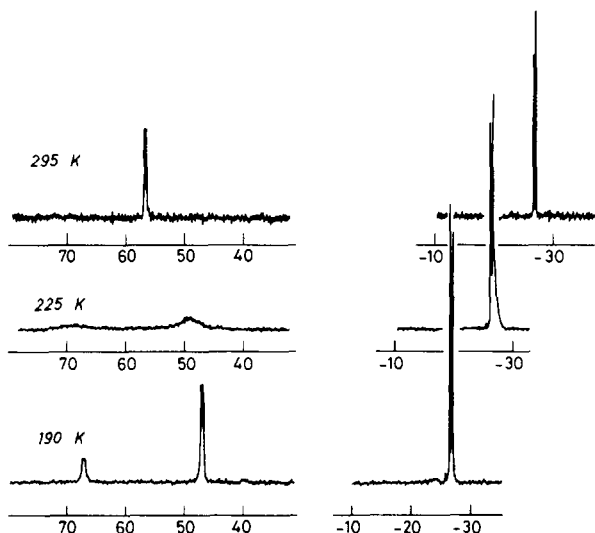
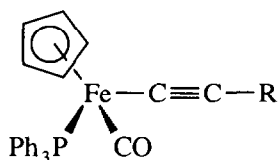


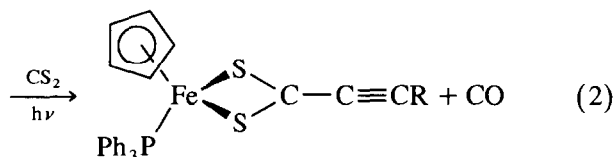
Fig. 1. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{C}^t\text{Bu})(\text{dppm}-P)]$ (**3b**).

The isomer ratios found for these complexes as well as those reported for $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CR})(\text{dppm})]$ ($\text{R} = \text{Me}$ or Ph) [**3f**] and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CH})(\text{dppe}-P)]$ [**3c**] suggest that the size of the R group is important in determining the ratios of isomers.

Irradiation with a UV lamp (400 W) of a CS_2 solution of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)]$ (**2a,b**) during 5–8 h at -10°C leads to the displacement of the carbonyl group to give a blue solution from which the alkyndithiocarboxylate complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{PPh}_3)]$ are isolated in 75% yield for $\text{R} = \text{Ph}$ (**4a**) and 78% yield for $\text{R} = ^t\text{Bu}$ (**4b**). These products are formed by the substitution of CO by one sulfur atom of the inserted CS_2 molecule (Eq. (2)).



$\text{R} = \text{Ph}$ (**2a**); ^tBu (**2b**)



$\text{R} = \text{Ph}$ (**4a**) or ^tBu (**4b**)

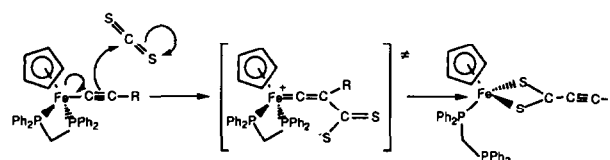
Spectroscopic and analytical data of the complexes **4a** and **4b** are consistent with these formulations. Mass spectra show the molecular ion and the IR spectra exhibit $\nu(\text{C}\equiv\text{C})$ (2163 and 2189 cm^{-1}) and $\nu(\text{CS})$ (854 and 836 cm^{-1}) absorptions for complexes **4a** and **4b** respectively. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra display a signal at

$\delta = 222.3$ for **4a** and 209.2 ppm for **4b** due to the CS_2 carbon nucleus.

However, under similar reaction conditions the dicarbonyl complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})_2]$ ($\text{R} = \text{Ph}$ or ^tBu) [**10**] are unreactive with CS_2 , even after 14 h of irradiation.

Two different mechanisms have been proposed in the reaction of CS_2 with metal-alkynyl complexes: (a) a direct nucleophilic attack on CS_2 by the alkynyl group of the complex $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CMe})(\text{dppe})]$ [**8a**] and (b) the initial coordination of CS_2 to the metal center in the complex $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2]$, followed by an insertion into the metal-alkynyl bond [**9**].

The results reported here seem to support the former mechanism since the greater the electronic richness of the precursor complex, the faster the insertion reactions are. As mentioned above, complexes **3a** and **3b** are formed after 4 h of irradiation, while to accomplish totally the formation of **4a** and **4b**, 5–8 h of irradiation are required. Furthermore, the dicarbonyl complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})_2]$ ($\text{R} = \text{Ph}$ or ^tBu) are unreactive towards CS_2 . This seems to indicate that an intermolecular nucleophilic attack at the central carbon atom of CS_2 occurs in the first step (see Scheme 1). Although we have not attempted the isolation of the intermediates, presumably this addition product undergoes a rapid transformation under the reaction conditions used to form the final complexes, in which a formal insertion process of CS_2 into the metal-alkynyl bond has occurred.



Scheme 1.

3. Experimental section

3.1. General procedures

The reactions were carried out under dry dinitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})_2]$ and $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{dppm})]$ (**1a,b**) were prepared by published procedures [**10**]. Photolysis experiments were performed with external irradiation using a UV lamp (400 W, Applied Photophysics). IR spectra were recorded on a Perkin-Elmer 1720-X FT spectrometer and electron-impact mass spectra were obtained with a Hewlett-Packard 58971 instrument. The C and H analy-

ses were carried out with a Perkin-Elmer 240-B micro-analyzer. NMR spectra were recorded on a Bruker AC300 MHz at 300 MHz (^1H), 121.5 MHz (^{31}P) or 75.4 MHz (^{13}C) using SiMe_4 or 85% H_3PO_4 as standards.

3.2. Preparation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})(\text{PPh}_3)]$ (**2a,b**)

A solution of the alkynyl derivative $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{C}\equiv\text{CR})(\text{CO})_2]$ (2 mmol) and PPh_3 (0.52 g, 2 mmol) in THF (30 ml) was irradiated at 10°C with a UV lamp until the dicarbonyl derivative had disappeared. After 2 h, the solvent was removed and the solid residue extracted with diethyl ether. From the red solution the alkynyl derivatives **2a** and **2b** were isolated as red solids in 72% and 59% yield respectively.

2a: Anal. Found: C, 74.85; H, 4.90. $\text{C}_{32}\text{H}_{25}\text{FeOP}$. Calc.: C, 75.01; H, 4.92%. **2a** shows spectroscopic data according with the reported data [13]. **2b**: Anal. Found: C, 72.95; H, 5.92. $\text{C}_{30}\text{H}_{29}\text{FeOP}$. Calc.: C, 73.18; H, 5.94%. IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2100 (w), $\nu(\text{CO})$ 1926 (s) cm^{-1} . ^1H NMR (C_6D_6): δ 0.96 (s, 9H, ^tBu), 3.92 (s, 5H, C_5H_5), 6.74–7.51 (m, 15H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 76.7.

3.3. Preparation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{dppm-P})]$ (**3a,b**)

General procedure. A solution of the alkynyl derivatives **1a,b** (1 mmol) in CS_2 (20 ml) was irradiated at -20°C with a UV lamp. The reaction was monitored by IR spectroscopy in the $\nu(\text{C}\equiv\text{C})$ region. After 4 h the resulting deep blue solution was evaporated to dryness to give a solid residue which was dissolved in diethyl ether and transferred to an Alox IV/hexane chromatography column. Elution with hexane gave a blue-violet solution which was evaporated to dryness to yield the dithiocarboxylate products **3a,b** as blue solids.

3a: Yield 45%. Mass spectrum 121 [$\text{M}^+ - \text{dppm} - \text{S}_2\text{CC}_2\text{Ph}$]; 440 [$\text{M}^+ - \text{C}_5\text{H}_5 - \text{S}_2\text{CC}_2\text{Ph}$]; 607 [$\text{M}^+ - \text{CS}_2$]; 683 [M^+]. Anal. Found: C, 68.82; H, 4.98. $\text{C}_{39}\text{H}_{32}\text{FeP}_2\text{S}_2$. Calc.: C, 68.62; H, 4.72. IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2063 (w), $\nu(\text{CS})$ 964 and 885 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 2.90 (dd, $^2J(\text{HP}) = 2$ and 8 Hz, 2H, CH_2), 4.15 (s, 5H, C_5H_5), 6.79–7.81 (m, 25H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -25.84 (d, $^2J(\text{PP}) = 40$ Hz), 57.34 (d, $^2J(\text{PP}) = 40$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 24.0 (m, CH_2), 85.3 (C_5H_5), 127.2–139.5 (Ph, $\equiv\text{C}$).

3b: Yield 65%. Mass spectrum 121 [$\text{M}^+ - \text{dppm} - \text{S}_2\text{CC}^t\text{Bu}$]; 440 [$\text{M}^+ - \text{C}_5\text{H}_5 - \text{S}_2\text{CC}^t\text{Bu}$]; 587 [$\text{M}^+ - \text{CS}_2$]; 663 [M^+]. Anal. Found: C, 67.84; H, 5.47. $\text{C}_{37}\text{H}_{36}\text{FeP}_2\text{S}_2$. Calc.: C, 67.07; H, 5.48%. IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2095 (w), $\nu(\text{CS})$ 1026 and 884 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 1.12 (s, 9H, ^tBu), 2.87 (dd, $^2J(\text{HP}) = 2$ and 8 Hz, 2H, CH_2), 4.10 (d, $^3J(\text{HP}) = 1.4$ Hz, 5H, C_5H_5),

6.91–7.81 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ -25.71 (d, $^2J(\text{PP}) = 38$ Hz), 59.28 (d, $^2J(\text{PP}) = 38$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 23.3 (m, CH_2), 27.8 ($\text{C}(\text{CH}_3)_3$), 30.6 (CH_3), 79.8 (C_5H_5), 92.4 ($\equiv\text{C}$), 126.6–132.1 (Ph, $\equiv\text{C}$).

3.4. Preparation of $[\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{S}_2\text{CC}\equiv\text{CR})(\text{PPh}_3)]$ (**4a,b**)

General procedure. A solution of the alkynyl derivatives **2a,b** (1 mmol) in CS_2 (20 ml) was irradiated at -10°C with a UV lamp. The reaction was monitored by IR spectroscopy in the $\nu(\text{C}\equiv\text{C})$ and the $\nu(\text{CO})$ region. After 5–9 h the carbonyl band had disappeared and the resulting deep blue solution was evaporated to dryness to give a residue solid which was extracted with diethyl ether and evaporated to yield the solids **4a** and **4b**. The complex **4b** needed a further purification and was transferred to an Alox IV/hexane chromatography column. Elution with hexane gave a blue violet solution which was evaporated to dryness to yield the dithiocarboxylate product **4b** in high purity.

4a: Reaction time 5 h, yield 75%. Mass spectrum 484 [$\text{M}^+ - \text{C}_5\text{H}_5$]; 497 [$\text{M}^+ - \text{C}_6\text{H}_5$]; 561 [$\text{M}^+ + 1$]. Anal. Found: C, 67.78; H, 4.91. $\text{C}_{32}\text{H}_{25}\text{FePS}_2$. Calc.: C, 68.57; H, 4.49%. IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2163 (w), $\nu(\text{CS})$ 854 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 4.07 (s, 5H, C_5H_5), 6.85–7.75 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 72.9 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 77.4 (C_5H_5), 84.56 ($\equiv\text{C}$), 126.9–136.2 (Ph, $\equiv\text{C}$), 222.3 (CS_2).

4b: Reaction time 9 h, yield 78%. Mass spectrum 464 [$\text{M}^+ - \text{CS}_2$]; 475 [$\text{M}^+ - \text{C}_5\text{H}_5$]; 540 [M^+]. Anal. Found: C, 64.98; H, 5.65. $\text{C}_{30}\text{H}_{29}\text{FePS}_2$. Calc.: C, 66.66; H, 5.40%. IR (KBr) $\nu(\text{C}\equiv\text{C})$ 2189 (w), $\nu(\text{CS})$ 836 (m) cm^{-1} . ^1H NMR (C_6D_6): δ 1.08 (s, 9H, ^tBu), 4.00 (s, 5H, C_5H_5), 7.02–7.70 (m, 15H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6): δ 74.2 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6): δ 28.7 ($\text{C}(\text{CH}_3)_3$), 30.6 (CH_3), 77.4 (C_5H_5), 94.7 ($\equiv\text{C}$), 128.2–137.8 (Ph, $\equiv\text{C}$), 209.2 (CS_2).

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