# Synthesis, Structure and Reactivity of Sulfur-Rich [Fe($L^1$)($L^2$)('tp$S_4$')] Complexes with Rigid [Fe('tp$S_4$')] Cores and σ−π Co-Ligands ('tp$S_4$'$^{2-}$ = 1,2-Bis(2-mercaptophenylthio)phenylene(2−); $L^1$, $L^2$ = CO, $PR_3$, NO)[‡]

Dieter Sellmann,*[a] David C. F. Blum,[a] Frank W. Heinemann,[a] and Jörg Sutter[a]

*Dedicated to Professor Gottfried Huttner on the occasion of his 65th birthday*

**Keywords:** Helical structures / Iron / S ligands

Optimisation of synthesis and purification steps has made the new ligand 'tp$S_4$'$^{2-}$ available in preparative amounts. Treatment of $FeCl_2·4H_2O$ with 'tp$S_4$'-$Li_2$ or 'tp$S_4$'-$Na_2$ yielded [Fe('tp$S_4$')] (**1**), which in the solid state and in the absence of co-ligands probably trimerises to give paramagnetic [Fe('tp$S_4$')]$_3$. The [Fe('tp$S_4$')] fragment displays helical coordination of the 'tp$S_4$'$^{2-}$ ligand and binds σ–π ligands such as CO, NO and phosphanes to give diamagnetic 18-valence-electron complexes of general formula [Fe($L^1$)($L^2$)('tp$S_4$')]. The *cis*-dicarbonyl complex [Fe$(CO)_2$('tp$S_4$')] (**2**) is labile and readily dissociates CO to give dinuclear [Fe(CO)('tp$S_4$')]$_2$ (**3**). Simultaneous coordination of CO and phosphanes yielded [Fe(CO)($PR_3$)('tp$S_4$')] with R = Me (**4**), Et (**5**), Pr (**6**) and Bu (**7**), but it proved impossible to obtain analogous complexes with bulky $PPh_3$ or $PCy_3$ ligands. Bis(phosphane) complexes could be obtained only with $PMe_3$ and the bidentate dppe, which yielded [Fe$(PMe_3)_2$('tp$S_4$')] (**8**) and [Fe(dppe)('tp$S_4$')] (**11**). Alkylphosphanes with longer alkyl substituents, such as P*n*$Pr_3$ and P*n*$Bu_3$, gave the labile derivatives [Fe$(PR_3)_2$('tp$S_4$')] with R = *n*Pr (**9**) and *n*Bu (**10**). Complexes **9** and **10** reversibly dissociate one $PR_3$ ligand, yielding diamagnetic [Fe($PR_3$)('tp$S_4$')] fragments. These findings explain the decisive and hitherto inexplicable influence of $PPr_3$ and $PBu_3$ ligands upon the stabilisation of $N_2H_2$ in the diazene complexes [μ-$N_2H_2${Fe($PR_3$)('tp$S_4$')}$_2$] with R = Pr, Bu. Treatment of [Fe('tp$S_4$')] (**1**) or [Fe(CO)('tp$S_4$')]$_2$ (**3**) with NO or $NO^+$ yielded [Fe$(NO)_2$('tp$S_4$')] (**12**). The molecular structures of **3**, **4**, **7** and **8** were determined by X-ray structure analysis. Spectroscopic and structural results indicate that the differences in reactivity between [Fe($L^1$)($L^2$)('tp$S_4$')] and homologous [Fe($L^1$)($L^2$)('$S_4$')] complexes can be traced back to subtle electronic and structural effects.
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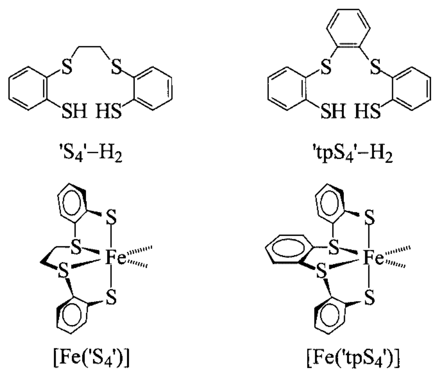
## Introduction

The goal of modelling and understanding the activation and turnover of small molecules at the metal/sulfur sites of nitrogenases and hydrogenases accounts for much of the interest in low-molecular-weight iron complexes with sulfur-dominated coordination spheres that are able to bind molecules relevant to enzyme activity.[1,2] In the search for such complexes we have found that iron complexes with the [Fe('$S_4$')] fragment (Scheme 1) are capable in particular of binding CO, NO, $N_2H_2$, $N_2H_4$ and $NH_3$, though not yet $N_2$.[3] It was also found that the '$S_4$'$^{2-}$ ligand in the resulting [Fe('$S_4$')] complexes exhibits a pronounced tendency to release the $C_2H_4$ bridge, yielding 1,2-benzenedithiolate ligands, under photolytic and/or strongly reducing reaction conditions.[4] These findings and the well-known fact that steric constraints exerted by ligands can have a marked influence upon the reactivity of otherwise identical complexes prompted us to synthesise 'tp$S_4$'-$H_2$ = 1,2-bis(2-mercaptophenylthio)phenylene (Scheme 1).[5]



Scheme 1. Ligands and iron complex fragments with $S_4$ donor atom sets

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[‡] Transition Metal Complexes with Sulfur Ligands, 156. Part 155: Ref.[6]

[a] Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstraße 1, 91058 Erlangen, Germany
Fax: (internat.) + 49-9131/852-7367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

The ‘tp$S_4$’$^{2-}$ anion is analogous to the ‘$S_4$’$^{2-}$ anion, but has a rigid *o*-phenylene group in place of the flexible $C_2H_4$ bridge and exclusively aromatic C−S bonds, which are significantly more stable towards C−S cleavage.

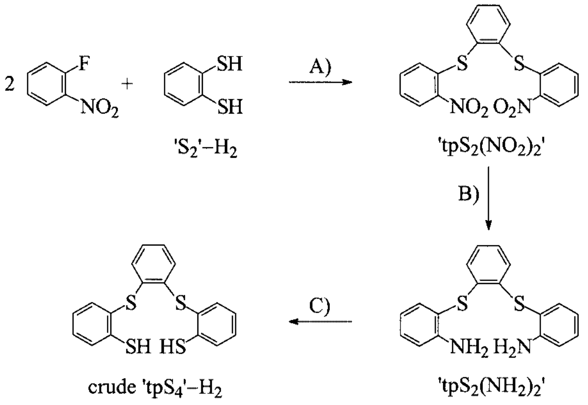
In our recent first paper on [Fe(‘tp$S_4$’)] complexes we reported the diazene complexes [μ-$N_2H_2${Fe($PR_3$)(‘tp$S_4$’)}$_2$] with R = Pr, Bu.[6] A strange and previously inexplicable result was that these complexes were accessible only with $PPr_3$ and $PBu_3$, but not with smaller or larger phosphanes such as $PMe_3$ or $PPh_3$. Another characteristic feature of these diazene complexes is their tendency to form hydrogen-bridge diastereomers, and [μ-$N_2H_2${Fe($PPr_3$)(‘tp$S_4$’)}$_2$] is the first example for which these diastereomers have been characterised by X-ray structure analysis.

In this paper we report an optimised synthesis of ‘tp$S_4$’-$H_2$ and give an account of the general reactivity of [Fe(‘tp$S_4$’)] complex fragments with CO and phosphanes, emphasizing the similarities as well as the differences between [Fe(‘$S_4$’)] and [Fe(‘tp$S_4$’)] complexes.

## Results and Discussion

### Optimisation of the Synthesis of ‘tp$S_4$’-$H_2$

The synthesis of ‘tp$S_4$’-$H_2$ is a multistep procedure comprising aromatic substitution, reduction, diazotisation and diazonium salt substitution reactions, as shown in Scheme 2.[5]



Scheme 2. Synthesis of crude ‘tp$S_4$’-$H_2$: (A) + 2 NaOMe, MeOH, 12 h reflux; (B) Zn, $NH_4Cl$, THF, 3 h reflux; (C) (a) $H_2SO_4$, $NaNO_2$, $H_2O$, 0 °C; (b) + KSC(S)OEt, $H_2O$, 85 °C; (c) + KOH, EtOH, 19 h reflux; (d) + HCl, $H_2O$

Polyfunctional species are involved in all these steps, and the final crude product was usually heavily contaminated by side-products. Removal of these side-products had previously been achievable only in a very laborious way that included treatment of the crude ‘tp$S_4$’-$H_2$ with LiOMe to give crude ‘tp$S_4$’-$Li_2$, and the synthesis of the nickel complex [Ni(‘tp$S_4$’)]$_2$. Recrystallisation of this nickel complex was the essential purification step. Acidolysis of [Ni(‘tp$S_4$’)]$_2$ finally yielded pure ‘tp$S_4$’-$H_2$, which could be converted into pure ‘tp$S_4$’-$Li_2$ as a storable form. In the end, pure ‘tp$S_4$’-$H_2$ or ‘tp$S_4$’-$Li_2$ were obtained only in 100 mg amounts and yields that rarely exceeded 20%.[6]

In optimisation of the reaction conditions we have now found that the steps A and B of Scheme 1 can be scaled up and improved such that the intermediates ‘tp$S_2$($NO_2$)$_2$’ and ‘tp$S_2$($NH_2$)$_2$’ are obtained in nearly quantitative yields. The steps leading to ‘tp$S_4$’-$H_2$ can also be scaled up, and the resulting crude product is obtained in a form that directly gives white ‘tp$S_4$’-$Na_2$ in yields of ca. 70% and in gram amounts upon treatment with NaOH. The procedure described here (cf. Exp. Sect.) now makes ‘tp$S_4$’-$H_2$ readily available in preparative amounts for the synthesis of metal complexes.

### Syntheses of [Fe(‘tp$S_4$’)] Complexes

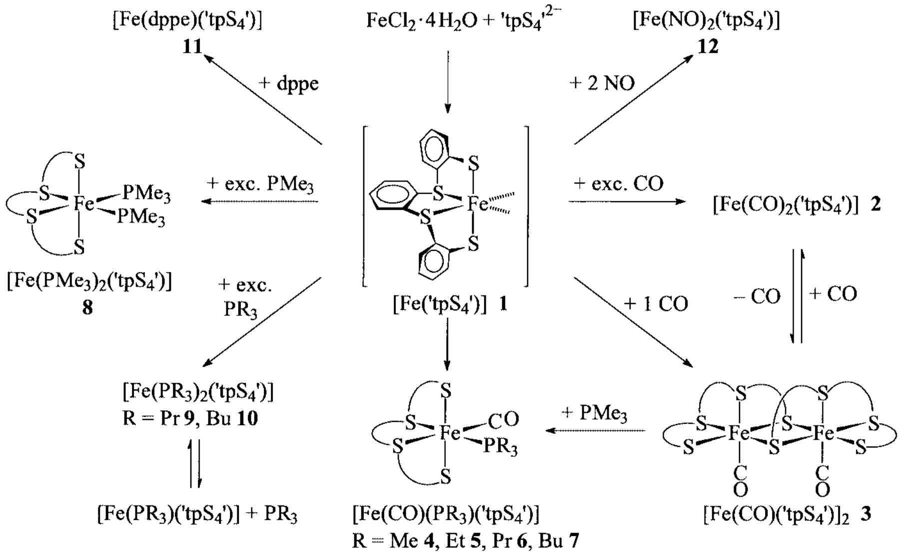
Scheme 3 summarises the syntheses of [Fe(‘tp$S_4$’] complexes.

Coordination of anionic ‘tp$S_4$’$^{2-}$ to $Fe^{II}$ centres was readily achieved by treating methanolic solutions of ‘tp$S_4$’-$Li_2$ (or ‘tp$S_4$’-$Na_2$) with $FeCl_2{\cdot}4H_2O$. Light brown [Fe(‘tp$S_4$’)] (**1**) was obtained. This is soluble in coordinating solvents such as THF or MeOH, but also in noncoordinating $CH_2Cl_2$. In this regard, [Fe(‘tp$S_4$’)] (**1**) differs remarkably from tetranuclear [Fe(‘$S_4$’)]$_4$, which is practically insoluble in all common organic solvents.[7] This solubility in THF, MeOH and $CH_2Cl_2$ made [Fe(‘tp$S_4$’)] (**1**) the best-suited precursor for [Fe($L^1$)($L^2$)(‘tp$S_4$’)] complexes.

The nuclearity of [Fe(‘tp$S_4$’)] (**1**) remained undetermined. FD mass spectra of **1** showed peaks at $m/z$ = 412, 824 and 1236, assignable to mono-, di- and trinuclear [Fe(‘tp$S_4$’)] species. The mass peak at $m/z$ = 1236 is compatible with the assumption that in the solid state and in the absence of co-ligands, [Fe(‘tp$S_4$’)] (**1**) trimerises through thiolate bridges in such a way that coordinatively saturated hexacoordinate iron centres result. All X-ray structure determinations of [Fe($L^1$)($L^2$)(‘tp$S_4$’)] complexes established a helical coordination of ‘tp$S_4$’$^{2-}$ to the Fe centre (vide infra). Such a coordination can also be assumed for [Fe(‘tp$S_4$’)] (**1**), the fifth and sixth coordination sites of which may be occupied by solvent molecules in solution. In the solid state, complex **1** is paramagnetic and exhibits $\mu_{eff}$ = 3.13 $\mu_B$ at room temperature.

Treatment of **1** in THF solution with an excess of CO yielded the *cis*-dicarbonyl complex [Fe(CO)$_2$(‘tp$S_4$’)] (**2**), as indicated by two ν(CO) bands at 2047 and 2004 cm$^{-1}$ in the IR spectrum. In stark contrast to the analogous [Fe(CO)$_2$(‘$S_4$’)],[8] which is stable in solution and in the solid state, [Fe(CO)$_2$(‘tp$S_4$’)] (**2**) is highly labile and could not be isolated in the solid state. Attempts to separate **2** from solution always yielded red-brown powders with IR spectra exhibiting strong ν(CO) bands at 1979 cm$^{-1}$, indicating that complex **2** had dissociated one CO ligand and that the resulting complex fragments had dimerised to give [Fe(CO)(‘tp$S_4$’)]$_2$ (**3**).

This indication could be corroborated by independent experiments. Treatment of an MeOH solution of **1** with exactly 1 equiv. of CO directly gave [Fe(CO)(‘tp$S_4$’)]$_2$ (**3**). Complex **3** is sparingly soluble in all common solvents and



Scheme 3. Synthesis of [Fe(‘tpS$_4$’)] complexes

precipitated from solution. Its dinuclear structure was established by X-ray crystallography.

The dissociation of CO from [Fe(CO)$_2$(‘tpS$_4$’)] (**2**) is reversible. Treatment of an MeOH or THF suspension of **3** with an excess of CO gave a clear solution of [Fe(CO)$_2$(‘tpS$_4$’)] (**2**), from which **3** precipitated again when the atmosphere of CO was replaced by N$_2$. These observations enabled us to conclude that an equilibrium exists between **2**, **3** and CO. This is driven in the direction of **3** by that compound’s low solubility when the partial pressure of CO is decreased.

One more possible reason for the labile bonding of CO in [Fe(CO)$_2$(‘tpS$_4$’)] (**2**) could be the electron density at the iron centre. Comparison of the ν(CO) bands (in KBr) of [Fe(CO)$_2$(‘tpS$_4$’)] and [Fe(CO)$_2$(‘S$_4$’)] (2048/2002 cm$^{-1}$ vs. 2036/1992 cm$^{-1}$) and [Fe(CO)(‘tpS$_4$’)]$_2$ and [Fe(CO)(‘S$_4$’)]$_2$ (1979 vs. 1965 cm$^{-1}$)[9] shows that the iron centres have a lower electron density in the [Fe(‘tpS$_4$’)] species than in [Fe(‘S$_4$’)], disfavouring the bonding of the π-acceptor CO.

Dinuclear [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**) could also be cleaved by PMe$_3$ to give mononuclear [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**). Complex **4** and the homologous compounds [Fe(CO)(PR$_3$)(‘tpS$_4$’)] with R = Et (**5**), Pr (**6**) and Bu (**7**) were similarly accessible directly from [Fe(‘tpS$_4$’)] (**1**) and equivalent amounts of CO and the corresponding PR$_3$. The series of complexes **4**−**7** revealed another difference between [Fe(‘tpS$_4$’)] and [Fe(‘S$_4$’)] complexes. While [Fe(CO)(PR$_3$)(‘S$_4$’)] species could be obtained with practically every phosphane, ranging from PMe$_3$ over PBu$_3$ up to bulky PPh$_3$ and PCy$_3$,[10] [Fe(CO)(PR$_3$)(‘tpS$_4$’)] complexes were accessible only with alkylphosphanes with relatively small cone angles.[11] No evidence could be found for the coordination of PPh$_3$ or PCy$_3$ to [Fe(CO)(‘tpS$_4$’)] fragments.

As judged by their NMR spectra, all complexes **4**−**7** are diamagnetic. They each show a characteristic ν(CO) band in the 1959−1955 cm$^{-1}$ range. The influence of the size of the PR$_3$ moiety for coordination of phosphanes to [Fe(‘tpS$_4$’)] fragments became even more apparent with bis(phosphane) complexes [Fe(PR$_3$)$_2$(‘tpS$_4$’)]. Isolable complexes could be obtained only with PMe$_3$ and the chelating dppe. Treatment of **1** with an excess of PMe$_3$ or equivalent amounts of dppe gave [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**) and [Fe(dppe)(‘tpS$_4$’)] (**11**), respectively, which could be completely characterised. Treatment of [Fe(‘tpS$_4$’)] (**1**) with PPr$_3$ or PBu$_3$, however, yielded very labile [Fe(PR$_3$)$_2$(‘tpS$_4$’)] with R = Pr (**9**) or Bu (**10**), which could be identified only by their molecular ions in their FD mass spectra and by $^{31}$P NMR spectroscopy in solution in the presence of excess phosphane. Attempts to isolate **9** or **10** in the solid state resulted in phosphane dissociation and products that gave unsatisfactory elemental analyses. The lability of the bis(phosphane) complexes [Fe(PR$_3$)$_2$(‘tpS$_4$’)] **9** (Pr) and **10** (Bu), which prevents their isolation in the solid state, however, has considerable synthetic value and explains the hitherto unexplained decisive influence of the R substituents for trapping diazene, N$_2$H$_2$, from solution and the stabilisation of the diazene complexes [μ-N$_2$H$_2${Fe(PR$_3$)(‘tpS$_4$’)}$_2$] with R = Pr, Bu.

As evidenced by the diamagnetism of complexes **4**−**8** or **11**, binding of σ−π ligands to [Fe(‘tpS$_4$’)] fragments produces a low-spin state in the Fe$^{\mathrm{II}}$ centres. The NMR spectra and chemical behaviour of **9** and **10**, on the other hand, indicate that their lability is due to an equilibrium according to Equation (1).

$$[\mathrm{Fe(PR_3)_2(\text{'tpS}_4\text{'})}] \rightleftharpoons [\mathrm{Fe(PR_3)(\text{'tpS}_4\text{'})}] + \mathrm{PR_3} \qquad (1)$$

The resulting five-coordinate [Fe(PR$_3$)(‘tpS$_4$’)] fragment has a vacant coordination site and a low-spin (diamagnetic) Fe$^{\mathrm{II}}$ centre, both of which are necessary to enable the coordination and stabilisation of N$_2$H$_2$. (In molecular orbital theory terms, the diamagnetism of [Fe(PR$_3$)(‘tpS$_4$’)] means that no electrons occupy antibonding orbitals.)

In concluding experiments, the coordination of NO and NO$^+$ to [Fe(‘tpS$_4$’)] fragments was examined. The same complex was formed in all cases, its elemental analysis and spectroscopic data being compatible with the formula [Fe(NO)$_2$(‘tpS$_4$’)] (**12**). In CH$_2$Cl$_2$ solution, complex **12** shows two strong ν(NO) bands at 1779 and 1750 cm$^{-1}$, indicative of a *cis*-Fe(NO)$_2$ entity. The strong tendency towards the formation of **12** became evident from the various reactions in which it was formed. For example, complex **12** was produced when [Fe(‘tpS$_4$’)] (**1**) in CH$_2$Cl$_2$ was treated with 2 equiv. of NO gas. The two ν(NO) bands of **12** became visible in the IR spectrum of the solution even after injection of only the first equivalent. Injection of the second equivalent increased the ν(NO) band intensity. Likewise, successive treatment of [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**) in CH$_2$Cl$_2$ with 2 equiv. of NO gas instantaneously gave rise to the formation of [Fe(NO)$_2$(‘tpS$_4$’)] (**12**). No intermediates such as the 19-VE species [Fe(CO)(NO)(‘tpS$_4$’)] or [Fe(NO)(‘tpS$_4$’)]$_2$ could be observed by IR spectroscopy. That 19-VE complexes such as [Fe(CO)(NO)(‘tpS$_4$’)], which may be expected to be labile, may occur can be concluded from the fact that [Fe(CO)$_2$(‘tpS$_4$’)] was formed as the second product in the reaction between [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**) and NO gas (Figure 1).

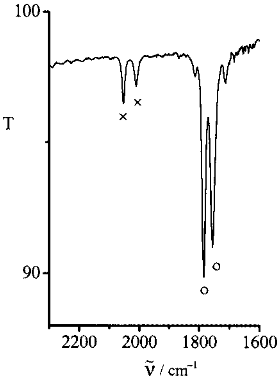
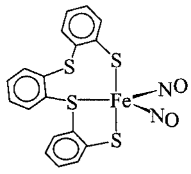


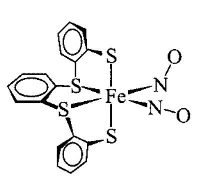
Figure 1. ν(CO)/ν(NO) region of the reaction solution (CH$_2$Cl$_2$) when [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**) is treated with 2 equiv. of NO gas {× = [Fe(CO)$_2$(‘tpS$_4$’)] (**2**), o = [Fe(NO)$_2$(‘tpS$_4$’)] (**12**)}

The formation of [Fe(CO)$_2$(‘tpS$_4$’)] can be explained by CO dissociation and transfer reactions between the labile [Fe(CO)(NO)(‘tpS$_4$’)] and dinuclear **3**. Treatment of **1** or **3** with NOBF$_4$ also yielded [Fe(NO)$_2$(‘tpS$_4$’)]. No other nitrosyl complexes were observed, and the reducing agent necessary for the NO$^+$ → NO conversion was not identified.

The $^1$H NMR spectrum of **12** shows only a multiplet for the aromatic protons of the [Fe(‘tpS$_4$’)] fragment and indicates diamagnetism of **12**, but is inconclusive in any other respect. The insufficient solubility of **12** prevented the recording of $^{13}$C NMR spectra. The FD mass spectra showed a minor peak for the molecular ion at $m/z$ = 472 and strong peaks at $m/z$ = 442 as well as at 412, 824 and 1236, assignable to [Fe(NO)(‘tpS$_4$’)] and [Fe(‘tpS$_4$’)]$_x$ species with $x$ = 1, 2 and 3. The diamagnetism of **12**, the fact that all [Fe(‘tpS$_4$’)] complexes with σ−π co-ligands obey the 18-valence-electron rule and the other data are compatible with the alternative structures **I** and **II**.



**I**



**II**

In formula **I**, the two [FeNO] groups are linear and one sulfur donor atom of ‘tpS$_4$’$^{2-}$ is decoordinated. In formula **II**, the ‘tpS$_4$’$^{2-}$ ligand stays tetradentate, but one NO ligand acts as a 1e$^-$ donor, the other one as a 3e$^-$ donor, and both types of NO possibly isomerise quickly as in, for example, [Ru(NO)$_2$Cl(PPh$_3$)$_2$]$^+$.[12]

In order to examine the stability of [Fe(‘tpS$_4$’)] fragments towards photolysis, solutions of [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**), [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**) and [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**) were UV-irradiated for prolonged periods of time. The CO ligands of **3** and **4** dissociated, but in no case could decomposition of

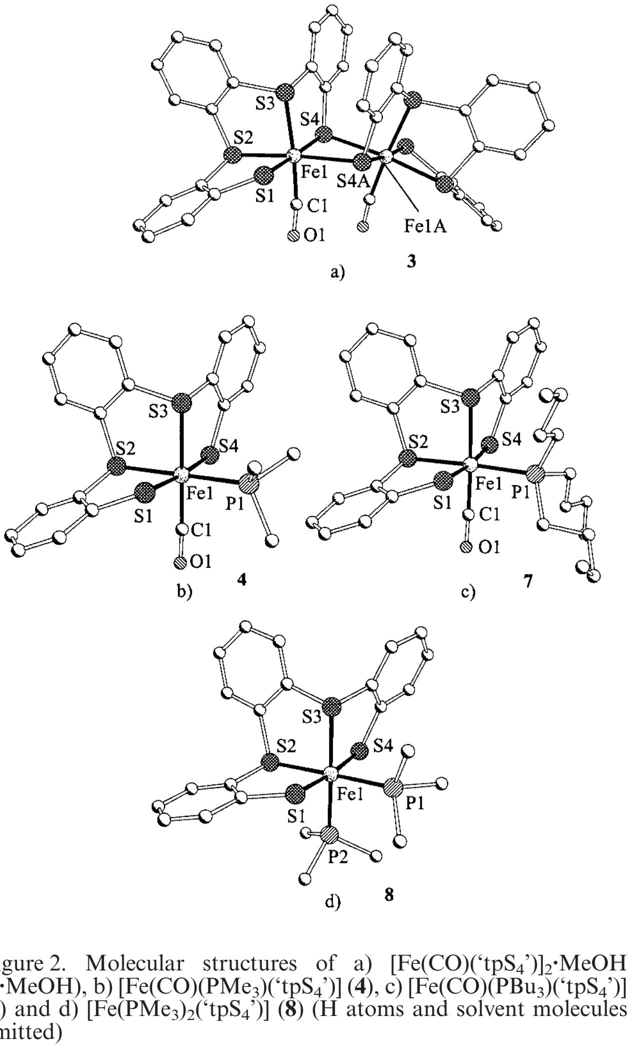


Figure 2. Molecular structures of a) [Fe(CO)(‘tpS$_4$’)]$_2$·MeOH (**3**·MeOH), b) [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**), c) [Fe(CO)(PBu$_3$)(‘tpS$_4$’)] (**7**) and d) [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**) (H atoms and solvent molecules omitted)

Table 1. Selected distances [pm] and angles [°] of [Fe(CO)(‘tpS$_4$’)]$_2$·MeOH (**3**·MeOH), [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**), [Fe(CO)(PBu$_3$)(‘tpS$_4$’)] (**7**) and [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**)

| | **3**·MeOH | | **4** | **7** | | **8** |
|---|---|---|---|---|---|---|
| Fe1−S1 | 228.9(3) | Fe1−S1 | 230.9(2) | 230.5(2) | Fe1−S1 | 231.7(2) |
| Fe1−S2 | 224.1(3) | Fe1−S2 | 227.6(3) | 225.7(2) | Fe1−S2 | 224.9(2) |
| Fe1−S3 | 228.5(3) | Fe1−S3 | 226.2(3) | 227.1(2) | Fe1−S3 | 224.8(2) |
| Fe1−S4 | 228.5(3) | Fe1−S4 | 229.8(3) | 231.0(2) | Fe1−S4 | 230.3(2) |
| Fe1−S4A | 234.5(3) | Fe1−P1 | 225.0(3) | 225.2(2) | Fe1−P1 | 225.1(2) |
| Fe1−C1 | 176.4(9) | Fe1−C1 | 177(1) | 175.2(6) | Fe1−P2 | 224.7(2) |
| C1−O1 | 113.2(9) | C1−O1 | 113(2) | 114.8(7) | | |
| Fe1−Fe1A | 341.0(2) | | | | | |
| S1−Fe1−S4 | 174.6(2) | S1−Fe1−S4 | 175.5(2) | 173.71(7) | S1−Fe1−S4 | 174.94(9) |
| S2−Fe1−S4A | 174.0(2) | S2−Fe1−P1 | 176.0(1) | 177.38(6) | S2−Fe1−P1 | 173.81(8) |
| S3−Fe1−C1 | 174.7(4) | S3−Fe1−C1 | 178.5(4) | 177.8(2) | S3−Fe1−P2 | 174.71(8) |
| S1−Fe1−S4A | 93.6(2) | S1−Fe1−P1 | 89.6(1) | 91.54(6) | S1−Fe1−P1 | 87.60(7) |
| S1−Fe1−C1 | 87.9(4) | S1−Fe1−C1 | 90.4(3) | 90.1(2) | S1−Fe1−P2 | 95.56(8) |
| C1−Fe1−S4A | 87.1(3) | P1−Fe1−C1 | 89.6(4) | 89.2(2) | P1−Fe1−P2 | 93.15(8) |
| Fe1−C1−O1 | 172(2) | Fe1−C1−O1 | 177(1) | 178.1(5) | | |

the [Fe(‘tpS$_4$’)] fragments by C−S cleavage reactions be observed.

### X-ray Structure Analyses

The molecular structures of [Fe(CO)(‘tpS$_4$’)]$_2$·MeOH (**3**·MeOH), [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**), [Fe(CO)(PBu$_3$)(‘tpS$_4$’)] (**7**) and [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**) were determined by X-ray crystallography and are shown in Figure 2. Table 1 lists selected distances and angles.

All complexes exhibit six-coordinate Fe centres and helical coordination of the ‘tpS$_4$’$^{2-}$ ligands, resulting in chiral [Fe(‘tpS$_4$’)] fragments with *trans*-thiolate and *cis*-thioether donors. Figure 1 shows the respective (*R*) enantiomers of **4**, **7** and **8**. In [Fe(CO)(‘tpS$_4$’)]$_2$ (**3**), two such homochiral (*R*)-[Fe(‘tpS$_4$’)] fragments are bridged through thiolate donors to give $C_2$-symmetrical **3**. The structure of **3** is noteworthy because it appears to be favoured in spite of the strikingly different spatial filling of the coordination sphere and the evident resulting steric strain. While the top “half” of **3** is heavily overloaded, the bottom “half” is occupied only by the two CO ligands. The electronic inequivalence of the thiolate donors in $C_1$-symmetrical [Fe(CO)(‘tpS$_4$’)] fragments is a potential factor in favour of this type of structure. A precedent has been observed with [Fe(CO)(‘S$_4$’)][9] and, according to the classification introduced then, the structure shown in Figure 1 (part a) is the αα-*Z*(*RR*) isomer of **3**.

The bond lengths of all four compounds lie in the ranges characteristic for this type of diamagnetic Fe$^{II}$ complexes.[10] For example, terminal Fe−S distances are found in the 224−230 pm range, and Fe−S−Fe bridging distances can be elongated up to 234 pm, indicating the tendency of dinuclear complexes to dissociate into mononuclear species. As also observed for [Fe(‘S$_4$’)] complexes, no marked *trans* influence of such different donors as S(thiolate), CO or PR$_3$ upon the respective *trans* bonds can be recognised in any of the [Fe(‘tpS$_4$’)] complexes. The following structural differences between [Fe(L$^1$)(L$^2$)(‘tpS$_4$’)] and the corresponding [Fe(L$^1$)(L$^2$)(‘S$_4$’)] complexes are to be noted.

In [Fe(L$^1$)(L$^2$)(‘S$_4$’)] complexes, the Fe−S(thioether) and Fe−S(thiolate) distances tend to be equivalent, frequently identical.[3] In [Fe(L$^1$)(L$^2$)(‘tpS$_4$’)] complexes, however, the Fe−S(thioether) distances are usually distinctly shorter than the Fe−S(thiolate) distances. This is certainly not due to a better donor capability of the thioether donors but rather results from the bite angle of the *o*-phenylenebis(thioether) entity, which is smaller than that of the [SC$_2$H$_4$S] bridge in the ‘S$_4$’$^{2-}$ ligand. Another major difference is the conformation of the central five-membered chelate ring in [Fe(‘S$_4$’)] and [Fe(‘tpS$_4$’)] fragments. Figure 3 shows that this [FeS(2)S(3)] ring adopts a puckered (envelope) conformation in [Fe(‘S$_4$’)], whereas the chelate ring is virtually planar (coplanar to within 20 pm with the benzene ring) in [Fe(‘tpS$_4$’)].

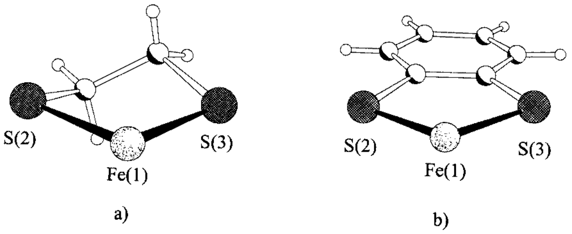


Figure 3. Comparison of the central five-membered [FeS$_2$C$_2$] rings in a) [Fe(‘S$_4$’)] and b) [Fe(‘tpS$_4$’)] complexes

Thus, the small but significantly different reactivities of [Fe(‘S$_4$’)] and [Fe(‘tpS$_4$’)] fragments with regard to the coordination of co-ligands such as CO and phosphanes can be traced back to slightly different electron densities at the Fe centres [cf. the ν(CO) frequencies] as well as to the structural flexibility or rigidity of the central [FeS$_2$C$_2$] chelate rings in these complexes.

## Conclusion

Optimised synthesis and purification steps have now made ‘tpS$_4$’-H$_2$ available in the preparative amounts needed for thorough investigation of its coordination properties. Comparison of the [Fe($L^1$)($L^2$)('tp$S_4$')] complexes described in this work with the [Fe($L^1$)($L^2$)('$S_4$')] complexes obtained in previous studies shows that [Fe('tp$S_4$')] and [Fe('$S_4$')] complex fragments exhibit both close similarities and distinctive differences. While the similarities can be traced back to the identical coordination of $Fe^{II}$ centres by two *trans*-thiolate and two *cis*-thioether donors, the differences result from a slightly lower electron density at the Fe centres and the more rigid core structure of [Fe('tp$S_4$')] vs. [Fe('$S_4$')] fragments. These differences are illustrated by, for example, the [Fe(CO)($PR_3$)('tp$S_4$')] and [Fe(CO)($PR_3$)('$S_4$')] complexes. While the [Fe(CO)('tp$S_4$')] fragment binds only small alkylphosphanes, the [Fe(CO)('$S_4$')] fragment can also coordinate bulky phosphanes such as $PPh_3$ and $PCy_3$. The lability of [Fe$(PR_3)_2$('tp$S_4$')] with R = Pr (**9**), Bu (**10**), resulting in the reversible dissociation of one $PR_3$ ligand, explains the decisive influence of $PPr_3$ and $PBu_3$ ligands for the stabilisation of $N_2H_2$ in the diazene complexes [μ-$N_2H_2$\{Fe($PR_3$)('tp$S_4$')\}$_2$] with R = Pr, Bu. While $PMe_3$ gives stable [Fe$(PMe_3)_2$('tp$S_4$')] (**8**) and $PPh_3$ or $PCy_3$ do not coordinate at all to [Fe('tp$S_4$')] fragments, the medium-sized phosphanes $PPr_3$ and $PBu_3$ in solution give rise to five-coordinate [Fe($PR_3$)('tp$S_4$')] species that are diamagnetic and have a vacant site. Diamagnetism and a vacant site are both necessary requirements for the binding and stabilisation of unstable $N_2H_2$ to [Fe($PR_3$)('tp$S_4$')] fragments. The previously inexplicable stabilisation effect of $PPr_3$ and $PBu_3$ in the iron diazene complexes is thus in the end due neither to pronounced electronic nor steric effects, but to a simple dissociation equilibrium between [Fe$(PR_3)_2$('tp$S_4$')], [Fe($PR_3$)('tp$S_4$')] and $PR_3$.

## Experimental Section

**General Methods:** Unless noted otherwise, all reactions and operations were carried out at room temperature under nitrogen by use of standard Schlenk techniques. Solvents were dried and distilled before use. As far as possible, reactions were monitored by IR or NMR spectroscopy. Spectra were recorded with the following instruments: IR (KBr disks or $CaF_2$ cuvettes, solvent bands were compensated): Perkin−Elmer 16 PC FT-IR; NMR: Jeol FT-JNM-GX 270, EX 270 and Lambda LA 400, with the protio solvent signals used as a reference, chemical shifts are quoted on the δ scale (downfield shifts are positive) relative to tetramethylsilane ($^1H$, $^{13}C\{^1H\}$ NMR) or 85% $H_3PO_4$ ($^{31}P\{^1H\}$ NMR). Spectra were recorded at 25 °C; MS: JEOL MSTATION 700 spectrometer; elemental analyses: Carlo Erba EA 1106 and 1108 analyser. Magnetic moments were determined with a Johnson−Matthey susceptibility balance. 'tp$S_4$'-$Li_2$,[5] $PMe_3$, $PEt_3$, P*n*$Pr_3$ and P*n*$Bu_3$ [13] were prepared as described in the literature, dppe was purchased from Aldrich.

**'tp$S_2(NO_2)_2$':** o-$C_6H_4(SH)_2$ (15.1 mL, 118.8 mmol) and 2-fluoronitrobenzene (35.1 mL, 332.6 mmol) were added to a solution of NaOMe (13.16 g, 243.6 mmol) in MeOH (400 mL). The solution was heated to reflux for 12 h, in the course of which a bright yellow precipitate formed. After the suspension had cooled to room temperature, the precipitate was separated, washed with MeOH (80 mL), $H_2O$ (120 mL), and again MeOH (30 mL) and dried in vacuo. Yield: 39.64 g (95%). The product was identified by $^1H$ NMR spectroscopy and mass spectrometry.

**'tp$S_2(NH_2)_2$':** Zinc powder (67.4 g, 1.031 mol) and $NH_4Cl$ (55.2 g, 1.031 mol) were added to a yellow suspension of 'tp$S_2(NO_2)_2$' (39.64 g, 103.1 mmol) in THF (600 mL). The resulting grey suspension was heated to reflux for 3 h and filtered while hot. The solid residue was thoroughly extracted with hot THF (400 mL). The filtrate and combined THF washing solutions were concentrated under reduced pressure, yielding a colourless oily residue. This residue was treated with hot EtOH (50 mL) to give a white powder, which was separated, washed with EtOH (50 mL) and dried in vacuo. Additional product precipitated from the combined EtOH filtrates overnight. Yield: 32.79 g (98%). The product was identified by IR and $^1H$ NMR spectroscopy and mass spectrometry.

**'tp$S_4$'-$H_2$ (Crude Product):** Whilst stirring, a white suspension of powdered 'tp$S_2(NH_2)_2$' (21.64 g, 66.7 mmol) in $H_2O$ (200 mL) was cooled to 0 °C. In order to keep the suspension at 0 °C, ice (90 g) was added. After addition of a solution of $H_2SO_4$ (15.9 g, 161.9 mmol) in $H_2O$ (100 mL), an aqueous solution of $NaNO_2$ (9.67 g, 140.1 mmol, 100 mL) was added dropwise. The resulting yellow orange suspension was stirred at 0 °C for another hour and subsequently added dropwise to a hot solution (85 °C) of potassium *O*-ethylxanthogenate (86.5 g, 539.9 mmol) in $H_2O$ (200 mL), yielding a red-brown oil. The reaction mixture was stirred for another 30 min at 85 °C, cooled to room temperature and extracted with $CH_2Cl_2$ (600 mL). The combined $CH_2Cl_2$ extracts were dried with $Na_2SO_4$ and filtered, and the solvents were evaporated to give a dark red oil as residue. EtOH (250 mL) and powdered KOH (42.9 g, 764.6 mmol) were added, and the resulting suspension was heated to reflux for 19 h to give a dark red solution. EtOH was removed in vacuo, the remaining orange-brown residue was dissolved in $H_2O$ (250 mL), and the resulting aqueous solution was extracted with $CH_2Cl_2$ (300 mL) in a separating funnel. The aqueous solution was separated and acidified with concentrated hydrochloric acid to pH = 0.5, whereupon a red oil separated. The oil/water mixture was extracted several times with $CH_2Cl_2$ (400 mL), the combined $CH_2Cl_2$ extracts were dried with $Na_2SO_4$ and filtered, and the solvents were evaporated to yield an orange-red oily residue, which was dried in vacuo for 12 h. Yield: 18.5 g (77%) of crude product, which contained approximately 62% of 'tp$S_4$'-$H_2$ according to the $^1H$ NMR spectrum in $CD_2Cl_2$.

**'tp$S_4$'-$Na_2$:** A dark red solution of the crude product [12.33 g, containing ca. 62% (21 mmol) of 'tp$S_4$'-$H_2$] in THF (50 mL) was combined with an MeOH solution (80 mL) of NaOMe (2.30 g, 42.6 mmol). Volatile components were removed, and the brown-red residue was dried in vacuo for 12 h and subsequently suspended in THF (200 mL). Stirring of the suspension for 1 h resulted in a white solid, which was separated, washed with THF (120 mL) and dried in vacuo for 12 h. Yield: 6.39 g (74%, referred to 'tp$S_4$'-$H_2$ contained in the crude product). The product contained traces of THF, which could not be removed by drying in vacuo for 48 h. $^1H$ NMR ([$D_4$]MeOH, 269.72 MHz): δ = 7.52−7.40 (m, 2 H), 7.30−7.18 (m, 2 H), 7.14−7.03 (m, 2 H), 6.82−6.57 (m, 6 H, $C_6H_4$), 3.70 (m, 4 H), 1.84 (m, 4 H, THF) ppm. $^{13}C\{^1H\}$ NMR ([$D_4$]MeOH, 100.40 MHz): δ = 149.25, 139.63, 137.98, 134.05, 132.91, 128.42, 126.82, 124.69, 120.90 [C (aryl)], 67.52, 25.16 (THF) ppm. IR (KBr): ṽ = 1565 m, 1437 s, 1422 s [ν(C=C)], 739 $cm^{-1}$ vs [δ(C−H)].

**[Fe('tp$S_4$')] (1):** $FeCl_2·4H_2O$ (68 mg, 0.34 mmol) was added to a light yellow solution of 'tp$S_4$'-$Li_2$ (126 mg, 0.34 mmol) in MeOH (30 mL). After stirring for 1 h, the reaction mixture was filtered and concentrated to dryness. The resulting yellow-brown residue was dried in vacuo overnight and redissolved in $CH_2Cl_2$ (25 mL) to remove LiCl. The resulting suspension was filtered and the brown-red filtrate was evaporated to dryness. Stirring of the residue with $Et_2O$ (20 mL) yielded brown microcrystals, which were separated, washed with $Et_2O$ (30 mL) and dried in vacuo. Yield: 102 mg (**1**·0.25 $CH_2Cl_2$) (69%). IR (KBr): $\tilde{\nu}$ = 1566 m [ν(C=C)], 746 cm$^{-1}$ vs [δ(C−H)]. MS (FD, THF, $^{56}$Fe): *m/z*: 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$; $\mu_{eff}$ (295 K) = 3.13 $\mu_B$. $C_{18.25}H_{12.5}Cl_{0.5}FeS_4$ (**1**·0.25$CH_2Cl_2$) (433.63): calcd. C 50.55, H 2.91, S 29.58; found C 50.52, H 3.06, S 29.68.

**[Fe(CO)(‘tpS$_4$’)]$_2$ (3):** $FeCl_2\cdot4H_2O$ (126 mg, 0.64 mmol) was added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (236 mg, 0.64 mmol) in MeOH (50 mL). The orange-red reaction mixture was stirred for 1 h and filtered, and CO gas (14.3 mL, 0.64 mmol) was injected into the filtrate by syringe. A brick-red precipitate formed; after 6 h this was separated, washed with MeOH (45 mL) and $Et_2O$ (30 mL), and dried in vacuo. Yield: 234 mg (**3**·MeOH) (81%). IR (KBr): $\tilde{\nu}$ = 1979 cm$^{-1}$ vs [ν(CO)]. MS (FD, THF, $^{56}$Fe): *m/z*: 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{39}H_{28}Fe_2O_3S_8$ (**3**·MeOH) (912.87): calcd. C 51.32, H 3.09, S 28.10; found C 51.13, H 3.08, S 28.13. Because of the low solubility of **3**, no NMR spectra could be recorded.

**[Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (4):** $FeCl_2\cdot4H_2O$ (59 mg, 0.30 mmol) and PMe$_3$ (59 μL, 0.30 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (110 mg, 0.30 mmol) in THF (20 mL) and MeOH (10 mL) to give an olive-green reaction mixture, into which CO gas (16.8 mL, 0.30 mmol) was injected by syringe. A red solution resulted, and this was filtered, reduced in volume to 2 mL and combined with MeOH (20 mL). A light green precipitate formed and was separated, washed with MeOH (20 mL) and $Et_2O$ (20 mL) and dried in vacuo. Yield: 80 mg (**4**·0.5MeOH) (51%). $^1$H NMR ($CD_2Cl_2$, 269.72 MHz): δ = 8.25−6.70 (m, 12 H, $C_6H_4$), 1.44 (br. s, 9 H, $CH_3$) ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 100.40 MHz): δ = 217.25 (d, $J_{PC}$ = 31.1 Hz, *C*O), 157.59, 156.44 (d, $J_{PC}$ = 2.7 Hz), 139.13, 138.97, 137.57, 136.01, 132.23, 132.11, 131.18, 131.04, 130.74, 130.69, 130.33, 129.78, 129.67, 129.40, 122.60, 122.53 [*C* (aryl)], 16.44 (d, $J_{PC}$ = 29.2 Hz, $CH_3$) ppm. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 161.70 MHz): δ = 21.50 (s, *P*Me$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1966, 1957 vs [ν(CO)], 952 cm$^{-1}$ m [δ(PCH)]. IR (THF): $\tilde{\nu}$ = 1959 cm$^{-1}$ vs [ν(CO)]. MS (FD, THF, $^{56}$Fe): *m/z*: 516 [Fe(CO)(PMe$_3$)(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{22.5}H_{23}FeO_{1.5}PS_4$ (**4**·0.5MeOH) (532.51): calcd. C 50.75, H 4.35, S 24.09; found C 50.76, H 4.43, S 23.92.

**[Fe(CO)(PEt$_3$)(‘tpS$_4$’)] (5):** $FeCl_2\cdot4H_2O$ (99 mg, 0.50 mmol) and PEt$_3$ (158 μL, 0.50 mmol) were added to a light yellow solution of ‘tpS$_4$’-Na$_2$ (200 mg, 0.50 mmol) in MeOH (10 mL) and THF (20 mL). An olive-green solution resulted, into which CO gas (11.2 mL, 0.50 mmol) was injected by syringe. The reaction mixture was stirred for 2.5 h and filtered, and the dark red filtrate was reduced in volume to 2 mL. Upon addition of MeOH (20 mL), light brown microcrystals formed, and were separated, washed with MeOH (20 mL) and dried in vacuo. Yield: 53 mg (19%). $^1$H NMR ($CD_2Cl_2$, 269.72 MHz): δ = 8.07−7.73 (m, 4 H), 7.44−7.25 (m, 4 H), 7.00−6.81 (m, 4 H, $C_6H_4$), 1.96−1.63 (m, 6 H), 1.28−1.10 [m, 9 H, P($C_2H_5$)$_3$] ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 67.83 MHz): δ = 217.79 (d, $J_{PC}$ = 30.1 Hz, *C*O), 157.73, 156.83 (d, $J_{PC}$ = 7.3 Hz), 139.11 (d, $J_{PC}$ = 11.9 Hz), 137.11, 136.29, 132.27, 131.97, 131.07, 130.90, 130.66, 130.63, 130.19, 129.74, 129.64, 129.42, 122.48 [*C* (aryl), partly superimposed], 17.83 (d, $J_{PC}$ = 24.9 Hz), 7.99 [d, $J_{PC}$ = 4.7 Hz, P($C_2H_5$)$_3$] ppm. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 161.70 MHz): δ = 42.56 (s, *P*Et$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1951 cm$^{-1}$ vs [ν(CO)]. IR (THF): $\tilde{\nu}$ = 1955 cm$^{-1}$ vs [ν(CO)]. MS (FD, THF, $^{56}$Fe): *m/z*: 558 [Fe(CO)(PEt$_3$)(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{25}H_{27}FeOPS_4$ (558.57): calcd. C 53.76, H 4.87, S 22.96; found C 53.62, H 5.14, S 22.93.

**[Fe(CO)(P*n*Pr$_3$)(‘tpS$_4$’)] (6):** $FeCl_2\cdot4H_2O$ (157 mg, 0.79 mmol) and P*n*Pr$_3$ (158 μL, 0.79 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (292 mg, 0.79 mmol) in THF (25 mL) and MeOH (10 mL). CO gas (17.7 mL, 0.79 mmol) was injected by syringe into the olive-green mixture, which turned into a dark-red solution within 3 h. The solution was filtered, reduced in volume to 5 mL and combined with MeOH (20 mL). Grey microcrystals formed, and were separated, washed with MeOH (30 mL) and $Et_2O$ (20 mL) and dried in vacuo. Yield: 314 mg (**6**·MeOH) (63%). $^1$H NMR ($CD_2Cl_2$, 269.72 MHz): δ = 8.08−7.69 (m, 4 H), 7.46−7.23 (m, 4 H), 7.02−6.79 (m, 4 H, $C_6H_4$), 1.88−1.42 (m, 12 H), 1.01 [t, 9 H, P($C_3H_7$)$_3$] ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 100.40 MHz): δ = 217.78 (d, $J_{PC}$ = 30.2 Hz, *C*O), 158.01, 156.81 (d, $J_{PC}$ = 7.3 Hz), 139.15, 138.98, 138.84 (d, $J_{PC}$ = 0.9 Hz), 137.02, 136.43, 132.24, 131.98, 131.13, 130.91, 130.64, 130.59, 130.22, 129.70, 129.62, 129.48, 122.49 [*C* (aryl)], 27.98 (d, $J_{PC}$ = 23.8 Hz), 17.52 (d, $J_{PC}$ = 2.0 Hz), 15.99 [d, $J_{PC}$ = 12.9 Hz, P($C_3H_7$)$_3$] ppm. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 161.70 MHz): δ = 35.88 (s, *Pn*Pr$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1957, 1953 cm$^{-1}$ vs [ν(CO)]. IR (THF): $\tilde{\nu}$ = 1955 cm$^{-1}$ vs [ν(CO)]. MS (FD, THF, $^{56}$Fe): *m/z*: 600 [Fe(CO)(P*n*Pr$_3$)(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{29}H_{37}FeO_2PS_4$ (**6**·MeOH) (632.69): calcd. C 55.05, H 5.89, S 20.27; found C 54.56, H 5.78, S 20.57.

**[Fe(CO)(P*n*Bu$_3$)(‘tpS$_4$’)] (7):** $FeCl_2\cdot4H_2O$ (257 mg, 1.29 mmol) and P*n*Bu$_3$ (257 μL, 1.29 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (479 mg, 1.29 mmol) in THF (45 mL) and MeOH (20 mL). CO gas (28.9 mL, 1.29 mmol) was injected into the resulting olive-green solution by syringe. The reaction mixture was stirred for 3 h and filtered, and the dark red filtrate was reduced in volume to 5 mL. After addition of MeOH (20 mL), grey-brown microcrystals precipitated and were separated, washed with MeOH (45 mL) and $Et_2O$ (20 mL) and dried in vacuo. Yield: 482 mg (58%). $^1$H NMR ($CD_2Cl_2$, 269.72 MHz): δ = 8.08−7.68 (m, 4 H), 7.47−7.20 (m, 4 H), 7.03−6.79 (m, 4 H, $C_6H_4$), 1.89−1.31 (m, 18 H), 0.94 [t, 9 H, P($C_4H_9$)$_3$] ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 67.83 MHz): δ = 217.49 (d, $J_{PC}$ = 30.5 Hz, *C*O), 157.78, 156.59 (d, $J_{PC}$ = 7.5 Hz), 138.87, 138.75, 138.56, 136.74, 136.17, 131.93, 131.67, 130.78, 130.58, 130.29, 130.26, 129.89, 129.40, 129.29, 129.13, 122.14 [*C* (aryl)], 25.45 (d, $J_{PC}$ = 3.7 Hz), 25.14 (d, $J_{PC}$ = 23.6 Hz), 24.38 (d, $J_{PC}$ = 12.4 Hz), 13.51 [s, P($C_4H_9$)$_3$] ppm. $^{31}$P{$^1$H} NMR ($CD_2Cl_2$, 161.70 MHz): δ = 34.80 (s, *Pn*Bu$_3$) ppm. IR (KBr): $\tilde{\nu}$ = 1956, 1953 cm$^{-1}$ vs [ν(CO)]. IR (THF): $\tilde{\nu}$ = 1955 cm$^{-1}$ vs [ν(CO)]. MS (FD, THF, $^{56}$Fe): *m/z* = 642 [Fe(CO)(P*n*Bu$_3$)(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{31}H_{39}FeOPS_4$ (642.73): calcd. C 57.93, H 6.12, S 19.96; found C 57.90, H 6.34, S 19.84.

**[Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (8):** $FeCl_2\cdot4H_2O$ (62 mg, 0.31 mmol) and PMe$_3$ (0.65 mL, 6.21 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (115 mg, 0.31 mmol) in THF (30 mL) and MeOH (5 mL). The resulting dark green solution was stirred for 17 h, filtered and reduced in volume nearly to dryness. Upon addition of MeOH (20 mL), olive-green microcrystals precipitated, and were separated, washed with MeOH (30 mL) and $Et_2O$ (12 mL) and dried in vacuo. Yield: 108 mg (62%). $^1$H NMR ($CD_2Cl_2$, 269.72 MHz): δ = 7.99−7.93 (m, 2 H), 7.86−7.81 (vdd, 2 H), 7.31−7.24 (m, 4 H), 6.88−6.77 (m, 4 H, $C_6H_4$), 1.38 (vt, 18 H, P($CH_3$)$_3$] ppm. $^{13}$C{$^1$H} NMR ($CD_2Cl_2$, 100.40 MHz): δ = 160.17, 140.85, 138.74, 131.22, 130.82, 129.87, 129.65, 128.58, 121.49 [*C* (aryl)], 18.14 (t, $J_{PC}$ = 12.0 Hz, P($C$H$_3$)$_3$] ppm. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 161.70 MHz): δ = 22.09 (s, $P$Me$_3$) ppm. IR (KBr): ṽ = 956, 944 cm$^{-1}$ vs [δ(PCH)]. MS (FD, CH$_2$Cl$_2$, $^{56}$Fe): *m*/*z*: 564 [Fe(PMe$_3$)$_2$(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$. $C_{24}H_{30}FeP_2S_4$ (564.56): calcd. C 51.06, H 5.36, S 22.72; found C 50.51, H 5.64, S 22.96.

**[Fe(P*n*Pr$_3$)$_2$(‘tpS$_4$’)] (9):** FeCl$_2$·4H$_2$O (17 mg, 0.08 mmol) and P*n*Pr$_3$ (0.17 mL, 0.8 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (31 mg, 0.08 mmol) in THF (6 mL) and MeOH (1 mL). The resulting solution was stirred for 14 h and concentrated to dryness. A dark green residue resulted, and was dried in vacuo for 20 min and dissolved in CD$_2$Cl$_2$ (0.7 mL) to which a few drops of P*n*Pr$_3$ had been added, in order to record NMR spectra. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 161.70 MHz): δ = 29.1 (s, $P$*n*Pr$_3$), −33.4 (s, exc. $P$*n*Pr$_3$) ppm. MS (FD, CH$_2$Cl$_2$, $^{56}$Fe): *m*/*z*: 732 [Fe(P*n*Pr$_3$)$_2$(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$.

**[Fe(P*n*Bu$_3$)$_2$(‘tpS$_4$’)] (10):** FeCl$_2$·4H$_2$O (23 mg, 0.12 mmol) and P*n*Bu$_3$ (0.23 mL, 1.2 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (43 mg, 0.12 mmol) in THF (10 mL) and MeOH (2 mL). The resulting solution was stirred for 15 h and concentrated to dryness. The resulting dark green residue was dried in vacuo for 15 min and dissolved in CD$_2$Cl$_2$ (0.7 mL) to which a few drops of P*n*Bu$_3$ had been added in order to record NMR spectra. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 161.70 MHz): δ = 30.3 (s, $P$*n*Bu$_3$), −30.2 (s, exc. $P$*n*Bu$_3$) ppm. MS (FD, CH$_2$Cl$_2$, $^{56}$Fe): *m*/*z*: 816 [Fe(P*n*Bu$_3$)$_2$(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236 [Fe(‘tpS$_4$’)]$_3{}^+$.

**[Fe(dppe)(‘tpS$_4$’)] (11):** FeCl$_2$·4H$_2$O (98 mg, 0.49 mmol) and dppe (196 mg, 0.49 mmol) were added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (183 mg, 0.49 mmol) in THF (20 mL) and MeOH (8 mL). The resulting dark green solution was stirred for 90 min, filtered, reduced in volume to 5 mL and combined with MeOH (30 mL). A light green precipitate formed, and this was separated, washed with MeOH (30 mL) and Et$_2$O (10 mL) and dried in vacuo. Yield: 274 mg (**11**·2MeOH) (63%). $^1$H NMR (CD$_2$Cl$_2$, 269.72 MHz): δ = 8.15−7.97 (m, 6 H), 7.61−7.43 (m, 8 H), 7.34−7.23 (m, 2 H), 7.05 (vt, 4 H), 6.89−6.66 (m, 6 H), 6.59−6.43 (m, 4 H), 6.30 (vdt, 2 H, C$_6$$H_4$, C$_6$$H_5$), 3.27−2.76 (m, 4 H, Ph$_2$PC$_2$$H_4$PPh$_2$) ppm. $^{13}$C{$^1$H} NMR (CD$_2$Cl$_2$, 100.40 MHz): δ = 157.90 (t, $J_{PC}$ = 4.1 Hz), 140.79 (t, $J_{PC}$ = 6.0 Hz), 138.41, 134.33, 134.15, 134.13, 134.00, 133.97, 133.83, 133.36 (t, $J_{PC}$ = 4.2 Hz), 131.70 (t, $J_{PC}$ = 4.1 Hz), 131.24, 130.42, 130.17, 130.02, 129.70, 128.43 (t, $J_{PC}$ = 3.6 Hz), 127.95, 126.50 (t, $J_{PC}$ = 4.6 Hz), 121.10 ($C_6$H$_4$, $C_6$H$_5$, partly covered), 26.23 (t, $J_{PC}$ = 21.0 Hz, Ph$_2$P$C_2$H$_4$PPh$_2$) ppm. $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$, 161.70 MHz): δ = 74.01 (s, Ph$_2$$P$C$_2$H$_4$$P$Ph$_2$) ppm. IR (KBr): ṽ = 735, 695 cm$^{-1}$ vs [δ(PCH)]. MS (FD, CH$_2$Cl$_2$, $^{56}$Fe): *m*/*z*: 810 [Fe(dppe)(‘tpS$_4$’)]$_3{}^+$. $C_{46}H_{44}FeO_2P_2S_4$ (**11**·2MeOH) (874.91): calcd. C 63.15, H 5.07, S 14.66; found C 63.39, H 4.87, S 14.65.

**[Fe(NO)$_2$(‘tpS$_4$’)] (12):** FeCl$_2$·4H$_2$O (52 mg, 0.25 mmol) was added to a light yellow solution of ‘tpS$_4$’-Li$_2$ (93 mg, 0.25 mmol) in CH$_2$Cl$_2$ (30 mL) and MeOH (10 mL). The reaction mixture was filtered, and NO gas (11.4 mL, 0.50 mmol) was injected into the dark orange filtrate by syringe. After stirring for 1 h, the solution was reduced in volume to 4 mL. A red-brown solid precipitated, and this was separated, washed with MeOH (20 mL) and Et$_2$O (20 mL) and dried in vacuo. Yield: 50 mg (**12**·1.5MeOH) (38%). $^1$H NMR (CD$_2$Cl$_2$, 269.72 MHz): δ = 7.85−6.45 (m, C$_6$H$_4$) ppm. MS (FD, CH$_2$Cl$_2$, $^{56}$Fe): *m*/*z*: 472 [Fe(NO)$_2$(‘tpS$_4$’)]$^+$, 442 [Fe(NO)(‘tpS$_4$’)]$^+$, 412 [Fe(‘tpS$_4$’)]$^+$, 824 [Fe(‘tpS$_4$’)]$_2{}^+$, 1236

Table 2. Selected crystallographic data of [Fe(CO)(‘tpS$_4$’)]$_2$·MeOH (**3**·MeOH), [Fe(CO)(PMe$_3$)(‘tpS$_4$’)] (**4**), [Fe(CO)(PBu$_3$)(‘tpS$_4$’)] (**7**) and [Fe(PMe$_3$)$_2$(‘tpS$_4$’)] (**8**)

| | **3**·MeOH | **4** | **7** | **8** |
|---|---|---|---|---|
| Empirical formula | $C_{39}H_{28}Fe_2O_3S_8$ | $C_{22}H_{21}FeOPS_4$ | $C_{31}H_{39}FeOPS_4$ | $C_{24}H_{30}FeP_2S_4$ |
| $M_r$ [g mol$^{-1}$] | 912.79 | 516.45 | 642.68 | 564.51 |
| $T$ [K] | 298 | 294 | 200 | 298 |
| Crystal size [mm] | 0.30 × 0.18 × 0.12 | 0.62 × 0.40 × 0.04 | 0.50 × 0.42 × 0.30 | 0.55 × 0.45 × 0.18 |
| Crystal system | tetragonal | monoclinic | monoclinic | monoclinic |
| Space group | $I4_1/a$ | $C2/c$ | $P2_1/c$ | $Cc$ |
| $F$(000) | 3728 | 2128 | 1352 | 2352 |
| $a$ [pm] | 1484.7(2) | 2979.0(7) | 2081.8(5) | 1993.1(7) |
| $b$ [pm] | 1484.7(2) | 1128.1(6) | 1109.5(3) | 1895.6(6) |
| $c$ [pm] | 3551.0(10) | 1419.0(4) | 1435.2(3) | 1505.0(6) |
| β [°] | 90 | 106.88(1) | 108.86(1) | 110.17(3) |
| $V$ [nm$^3$] | 7.83(1) | 4.563(3) | 3.137(2) | 5.34(1) |
| Z | 8 | 8 | 4 | 8 |
| $\rho_{calcd.}$ [g cm$^{-3}$] | 1.549 | 1.503 | 1.361 | 1.405 |
| μ [mm$^{-1}$] | 1.206 | 1.109 | 0.821 | 1.009 |
| Diffractometer | Nicolet R3m/V | Siemens P4 | Siemens P4 | Nicolet R3m/V |
| Radiation [pm] | Mo-$K_\alpha$ (λ = 71.073) | Mo-$K_\alpha$ (λ = 71.073) | Mo-$K_\alpha$ (λ = 71.073) | Mo-$K_\alpha$ (λ = 71.073) |
| Scan technique | ω-scan | ω-scan | ω-scan | ω-scan |
| 2Θ range [°] | 4.4−54.0 | 3.8−50.0 | 4.0−54.0 | 3.6−54.0 |
| Scan speed [° min$^{-1}$] | 5 | 2 | 8 | 5 |
| Measured refl. | 5503 | 4959 | 8456 | 7285 |
| Unique refl. | 4284 | 3805 | 6839 | 6498 |
| $R_{int}$ [%] | 8.39 | 8.35 | 5.28 | 2.75 |
| Observed refl. | 764 | 1973 | 4403 | 3795 |
| σ criterion | $F_o \geq 4.0\sigma(F)$ | $F_o \geq 4.0\sigma(F)$ | $F_o \geq 4.0\sigma(F)$ | $F_o \geq 4.0\sigma(F)$ |
| Parameters | 240 | 265 | 431 | 559 |
| $R1$; $wR2$ [%] | 4.80; 9.62 | 6.90; 15.71 | 7.18; 17.86 | 3.78; 7.13 |
| Abs. structure parameter | − | − | − | −0.02(2) |

[Fe('tpS$_4$')]$_3$$^+$. IR (KBr): $\tilde{\nu}$ = 1812 w, 1779 vs, 1750 cm$^{-1}$ vs [ν(NO)]. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ = 1814 w, 1784 vs, 1756 cm$^{-1}$ vs [ν(NO)]. $C_{19.5}H_{18}FeN_2O_{3.5}S_4$ (**12**·1.5MeOH) (520.48): calcd. C 45.00, H 3.49, N 5.38, S 24.64; found C 44.09, H 2.95, N 5.23, S 24.71.

**X-ray Structure Analyses of [Fe(CO)('tpS$_4$')]$_2$·MeOH (3·MeOH), [Fe(CO)(PMe$_3$)('tpS$_4$')] (4), [Fe(CO)(PBu$_3$)('tpS$_4$')] (7) and [Fe(PMe$_3$)$_2$('tpS$_4$')] (8):** Dark red single crystals of **3**·MeOH were formed by layering a saturated THF solution of **3** with MeOH. Green platelets of **4** and brown crystals of **7** were grown by layering saturated CH$_2$Cl$_2$ solutions of **4** and **7** with MeOH. Black single crystals of **8** were obtained by layering a saturated THF solution of **8** with Et$_2$O. Suitable single crystals were either embedded in protective perfluoro polyalkyl ether oil or sealed in a glass capillary under N$_2$. The structures were solved by direct methods, and full-matrix, least-squares refinement was carried out on $F^2$ values.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms are geometrically positioned. The MeOH solvate molecule in **3**·MeOH is disordered on a crystallographic $4_1$ axis, no hydrogen atoms have been taken into account for this molecule. The PBu$_3$ ligand in **7** is strongly disordered. Selected crystallographic data are summarised in Table 2.[15]

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[15] CCDC-187351 (**3**·MeOH), -187352 (**4**), -187353 (**7**), and -187354 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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