Transition Metal Complexes with Sulfur Ligands, Part 119[◇]

Synthesis of Water Soluble Fe and Ru Complexes with Novel Multidentate Thioether Thiolate Ligands Containing Carboxylate Substituents

Dieter Sellmann*, Thomas Becker, and Falk Knoch

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg,
Egerlandstraße 1, D-91058 Erlangen, Germany
Telefax: (internat.) +49(0)9131/857367
E-mail: sellmann@anorganik.chemie.uni-erlangen.de

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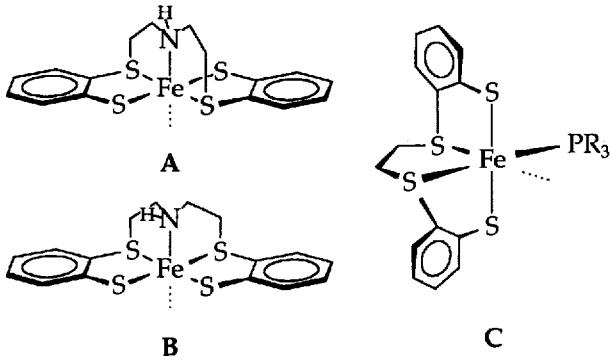
In search of water soluble transition metal complexes with sulfur dominated coordination spheres that model key reactions of nitrogenases, the benzenedithiol derivatives 'CO_2H-S_2'-H_2 (**1**) and 'CO_2Me-S_2'-H_2 (**2**) were synthesized as precursors for multidentate sulfur ligands. The template alkylation of **2** by $C_2H_4Br_2$ at $[Fe(CO)_2]$ fragments yielded a mixture of two diastereomeric C_2 symmetrical $[Fe(CO)_2('CO_2Me$-$S_4')]$ complexes (**4a** and **4b**), which were separated by crystallization. The hydrolysis of the mixture of the diastereomers **4a** and **4b** led to the isomerically pure tetradentate thioether thiol ligand 'CO_2Me-S_4'-H_2 (**5**) proving the regioselectivity of the template alkylation of the asymmetrical dithiol **2**. The C_i symmetrical $[Fe('CO_2Me$-$S_2')_2]^{2-}$ anion is an intermediate of the template alkylation and was isolated as $(AsPh_4)_2[Fe('CO_2Me$-$S_2')_2]$ (**11**). **4a**, **5** and **11** were characterized by X-ray structural analysis. Saponification of the methyl ester groups of **5** yielded 'CO_2H-S_4'-H_2 (**7**). Treatment of **7** with $FeCl_2 \cdot 4\ H_2O$ in the presence of CO and LiOMe gave a mixture of two C_2 symmetrical and water soluble diastereomers of $Li_2[Fe(CO)_2('CO_2$-$S_4')]$ (**8**). Upon treatment with $[RuCl_2(PPh_3)_3]$, **7** yielded isomerically pure $[Ru(PPh_3)_2('CO_2H$-$S_4')]$ (**9**). **9** also exhibits C_2 symmetry and could be reversibly deprotonated to form the water soluble complex $K_2[Ru(PPh_3)_2('CO_2$-$S_4')]$ (**10**). Treatment of $(NBu_4)_2('CO_2Me$-$S_2')$ with "$Ru(NO)Cl_3$" led to isomerically pure $(NBu_4)[Ru(NO)('CO_2Me$-$S_2')_2]$ (**12**).

Introduction

Iron is the prevalent metal in the active sites of Fe/Mo[1], Fe/V[2] and Fe/Fe nitrogenases[2,3]. Numerous investigations[4] and, in particular, the X-ray structural model for the FeMo cofactor of FeMo nitrogenases[5] prove that the Fe centers are surrounded predominantly by sulfur donors. In recognition of the fact that structure-function relationships exist which govern the reactions taking place at these active centers, the identity of the donor atoms is of particular importance. We therefore consider iron complexes with sulfur ligands (in particular complexes that bind N_2, N_2H_2, N_2H_4 or NH_3) to be promising functional models of nitrogenase. In previous work we showed that $[Fe('N_HS_4')]$ (**A** and **B**) and $[Fe(PR_3)('S_4')]$ (**C**) molecular fragments containing the multidentate sulfur ligands 'N_HS_4'$^{2-}$ [2,2′-bis(2-mercaptophenylthio)diethylamine(2−)][6] and 'S_4'$^{2-}$ [1,2-bis(2-mercaptophenylthio)ethane(2−)][7] do bind reduction intermediates of N_2 fixation. However, no corresponding complexes containing a dinitrogen ligand have been isolated as yet.

The isolated complexes are generally soluble only in organic solvents such as CH_2Cl_2, THF, DMSO or DMF. We are expecting complexes of this type to show different behaviour in aqueous media. For example, the hindered dimerization of coordinatively unsaturated fragments may be relevant to their catalytic potential and their ability to coordinate N_2. In order to render our complexes water soluble, we sought ways to introduce hydrophilic substituents into the dimercaptophenylene units of the sulfur ligands. We report here the synthesis of a new tetradentate ligand that contains carboxylic acid functions and is derived from 2,3-dimercaptobenzoic acid. Scheme 1 summarizes the ligands and their abbreviations. 'S_2'-H_2 and 'S_4'-H_2 denote the parent ligands 1,2-benzenedithiol and 1,2-bis(2-mercaptophenylthio)ethane. The addition of 'CO_2H' and 'CO_2Me' is intended to allow an easy description of the various states of deprotonation. These ligands yield complexes of Fe(II) and



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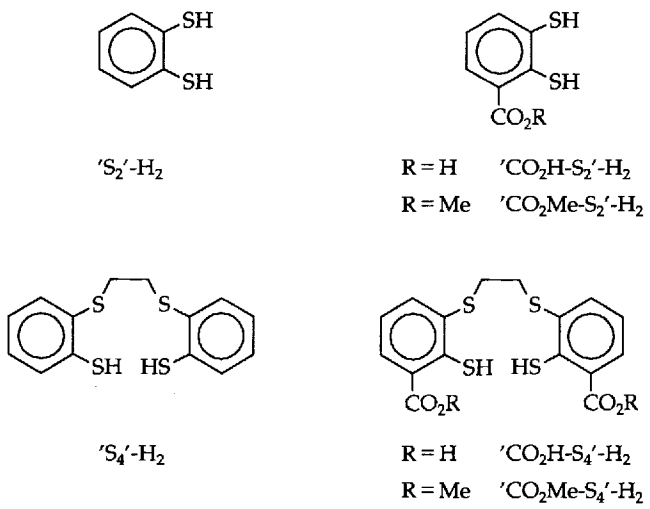
its group homologue Ru(II) that become water soluble when the carboxylic acid substituents are deprotonated.

Scheme 1. Abbreviations for the ligands



Results

Syntheses of Ligands

Scheme 2 shows the synthesis of 'CO_2H-S_4'-H_2 (**7**).

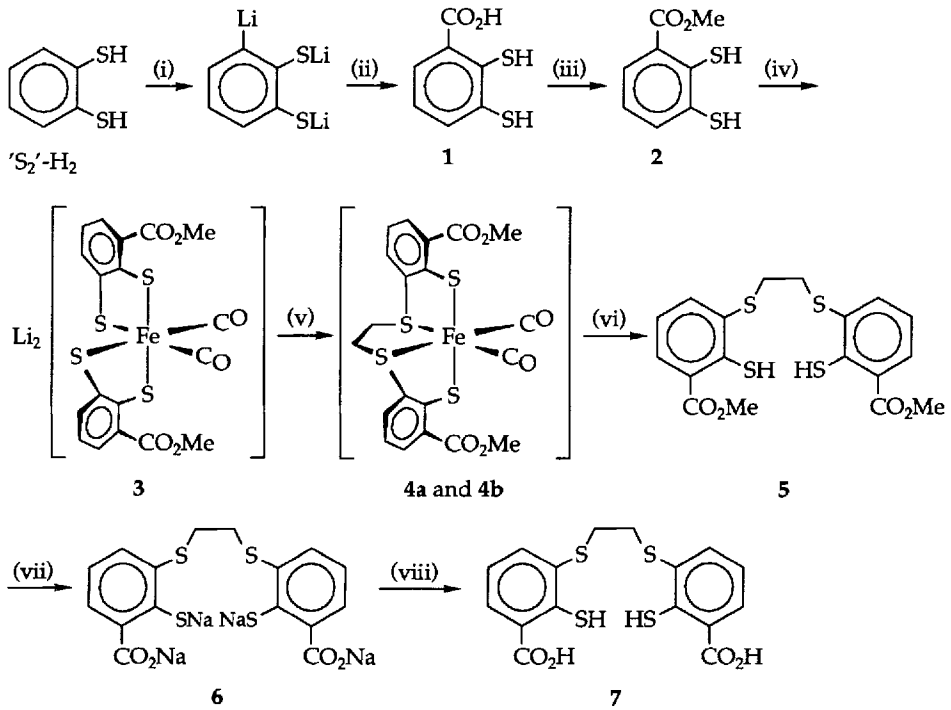
Lithiation of 1,2-benzenedithiol, 'S_2'-H_2, with three equivalents of *n*-BuLi in the presence of three equivalents of TMEDA yielded 'S_2'-Li_3, in which the thiolate sulfur atoms and one *ortho* C atom are metalated. Subsequent reaction with solid carbon dioxide and acidic work-up resulted in 2,3-dimercaptobenzoic acid, 'CO_2H-S_2'-H_2 (**1**). This procedure essentially follows the reports of J. Martin et al., E. Block et al., and K. Smith et al., who describe the ortho lithiation and subsequent carboxylation of thiophenol[8,9]. **1** proved to be soluble in MeOH, THF, Et_2O, MeCN, DMSO and DMF, but insoluble in aliphatic and chlorinated hydrocarbons. The EI mass spectrum of **1** gave a peak for the parent ion ['CO_2H-S_2'-H_2]$^+$ at m/z = 186. A doubly carboxylated product was not detected.

All attempts to link two units of **1** with a C_2H_4 or an $X(C_2H_4)_2$ (X = NH, S) bridge by the template alkylation at $[Fe(CO)_2]$ fragments to give regioselectively the corresponding tetra- or pentadentate ligands have been unsuccessful so far. This method, however, has proved very efficient in template alkylations of 'S_2'-H_2[10] or '$^{bu}S_2$'-H_2 (= 3,5-di-tertiary-butyl-1,2-dimercaptobenzene)[11].

Because of these initial difficulties, we tried to obtain such polydentate derivatives via the methyl ester 'CO_2Me-S_2'-H_2 (**2**). **2** was formed by refluxing **1** in MeOH in the presence of HCl and proved to be soluble in all common organic solvents. Deprotonation of **2** by LiOMe and subsequent treatment with $FeCl_2 \cdot 4\ H_2O$ and CO in MeOH yielded $Li_2[Fe(CO)_2('CO_2Me\text{-}S_2')_2]$ (**3**). **3** could not be isolated, but was observed in solution. As in the parent complex, $Na_2[Fe(CO)_2('S_2')_2]$[12], two strong ν(CO) absorptions in the solution IR spectrum at 2000 and 1942 cm^{-1} indicated the presence of the *cis*-$Fe(CO)_2$ entity and the anionic character of $[Fe(CO)_2('CO_2Me\text{-}S_2')_2]^{2-}$.

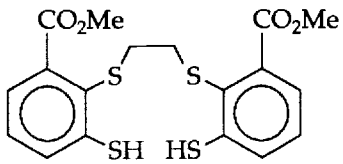
Alkylation of **3** by $C_2H_4Br_2$ led to the neutral complex $[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (**4**), which formed as a mixture of two diastereomeric, C_2 symmetrical complexes (**4a** and **4b**). This mixture could be separated by crystallization and both

Scheme 2. Synthesis of 'CO_2H-S_4'-H_2 (**7**). (i) 6 *n*-BuLi, 6 TMEDA, cyclohexane, 0°C → room temp.; (ii) 1. excess CO_2, 2. excess HCl/H_2O, 0°C; (iii) HCl gas, MeOH, reflux; (iv) 4 LiOMe, $FeCl_2 \cdot 4\ H_2O$, CO 1 bar, MeOH; (v) $C_2H_4Br_2$; (vi) HCl excess, THF, reflux; (vi) 4 NaOH, H_2O/THF; (vii) 4 HCl, H_2O



diastereomers were readily soluble in THF, CH_2Cl_2, $CHCl_3$, DMSO and DMF, but insoluble in H_2O and MeOH.

The diastereoisomerism of **4a, b** does not result from the two different thioether thiol ligands, such as **5** and the isomer **D**, that can potentially form if the thiolates either *meta* or *ortho* to the CO_2Me groups (in the 'CO_2Me-S_2'$^{2-}$ subunits of **3**) are symmetrically linked by a C_2H_4 bridge. This was proved by the acidic hydrolysis of a mixture of **4a**, **4b**. The reaction yielded the isomerically pure dithioether dithiol ligand 'CO_2Me-S_4'-H_2 (**5**), in addition to $FeCl_2$ and CO, and thus established the regioselectivity of the template alkylation. **5** is soluble in CH_2Cl_2, $CHCl_3$, THF, Et_2O, DMSO and DMF.

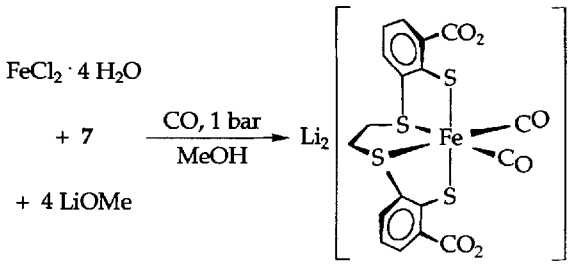


D

Saponification of the methyl esters in **5** by treating it with NaOH in H_2O/THF gave 'CO_2-S_4'-Na_4 (**6**). **6** dissolved in water and methanol and yielded 'CO_2H-S_4'-H_2 (**7**) as white powder upon treatment with aqueous HCl. **7** proved soluble in THF and DMF but insoluble in H_2O and MeOH.

Synthesis of Complexes

The isolation of the free dicarboxylic acid thioether thiol **7** allowed for the synthesis of water soluble complexes. $FeCl_2 \cdot 4\ H_2O$, **7** and CO in the presence of LiOMe yielded red Li_2['$Fe(CO)_2$('CO_2-S_4')] (**8**) according to eq. (1).

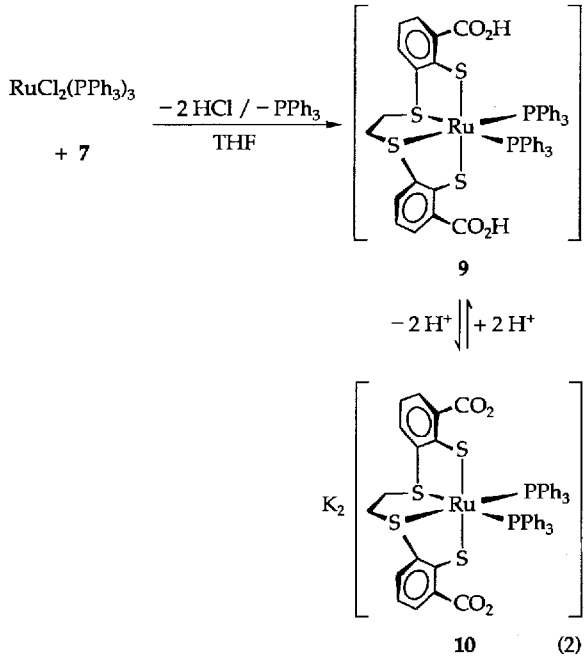


8

+ 2 LiCl + 4 H_2O + 4 MeOH (1)

8 was isolated as the MeOH solvate and is soluble in H_2O and MeOH, but insoluble in all common organic solvents. Like the methyl ester complex **4**, complex **8** also formed as a mixture of two diastereomeric, C_2 symmetrical species. **8** could be reversibly protonated with dilute hydrochloric acid, but so far it has not been possible to isolate the resulting carboxylic acid complex in pure form.

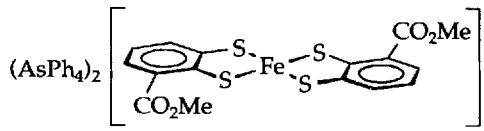
In the case of ruthenium, the isolation of a carboxylic acid complex in pure form was possible according to eq. (2).



Yellow [$Ru(PPh_3)_2$('CO_2H-S_4')] (**9**) was isolated as the THF solvate **9** · 2 THF. The THF is possibly hydrogen-bonded to the CO_2H functions and could not be removed even by prolonged drying in vacuo. In contrast to **4** or **8**, the synthesis of **9** yielded only one of the two theoretically possible diastereomers. Like the parent compound [$Ru(PPh_3)_2$('S_4')][13], **9** is insoluble in water and soluble in aprotic solvents such as acetone, CH_2Cl_2, $CHCl_3$, DMF and DMSO. In contrast to the parent complex, however, **9** dissolves in MeOH and becomes soluble in water when treated with bases such as KOH [eq. (2)]. The resulting potassium salt was isolated as K_2[$Ru(PPh_3)_2$('CO_2-S_4')] · 2 H_2O (**10** · 2 H_2O). This salt is insoluble in aprotic organic solvents and can be reversibly protonated to give **9** again.

In order to gain a better insight into the reactions leading from 'CO_2Me-S_2'-H_2 (**2**) to the template alkylation product, [$Fe(CO)_2$('CO_2Me-S_4')] (**4**), as shown in Scheme 1, the intermediate complex resulting from the reaction of $FeCl_2 \cdot 4\ H_2O$ with 'CO_2Me-S_2'-Li_2 was isolated as the $AsPh_4^+$ salt according to eq. (3).

$$Fe^{2+} + 2\ {}'CO_2Me\text{-}S_2{}'^{2-} + 2\ AsPh_4^+ \longrightarrow$$



11 (3)

Dark red crystals of the paramagnetic complex, $(AsPh_4)_2$[Fe('CO_2Me-S_2')$_2$] (**11**) formed and were fully characterized. The X-ray structure analysis confirmed the structure indicated in eq. (3). **11** exhibited a magnetic moment of μ_{eff} = 2.96 μ_B (298 K) indicating an S = 1 spin

state for the Fe(II) center. The ^{1}H-NMR spectrum showed, in addition to the $AsPh_4^+$ multiplet at $\delta = 7.83-7.73$, paramagnetically shifted singlets at $\delta = 6.32$, -3.27, -8.75 and -10.96 that were assigned to the methyl and the aromatic protons of the 'CO_2Me-S_2'$^{2-}$ ligands due to their intensities. The number of signals suggests that only one stereoisomer of **11** is present in solution.

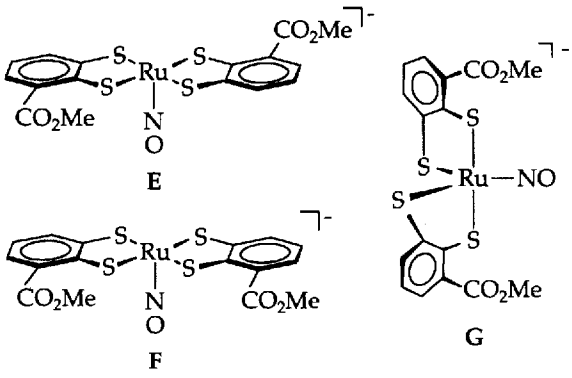
The [Ru(NO)('CO_2Me-S_2')$_2$]$^-$ anion had been of interest in order to attempt regioselective template alkylations of the 'CO_2Me-S_2' units by $NH(C_2H_4Br)_2$ or $S(C_2H_4Br)_2$ in hopes of leading to isomerically pure pentadentate ligands. All attempts to obtain these ligands through template alkylation of [Fe(CO)$_2$('CO_2Me-S_2')$_2$] (**3**) have failed to date.

The treatment of $(NBu_4)_2$('CO_2Me-S_2')$_2$ with "Ru(NO)Cl_3", which was obtained from the reaction of $RuCl_3 \cdot x\ H_2O$ and gaseous NO[14] in MeOH, yielded (NBu_4)[Ru(NO)('CO_2Me-S_2')$_2$] (**12**) as red-brown micro crystals according to eq. (4).

$$\text{"Ru(NO)Cl}_3\text{"} + 2\ (NBu_4)_2(\text{'CO}_2\text{Me-S}_2\text{'}) \xrightarrow[\text{MeOH}]{-3\ (NBu_4)Cl} (NBu_4)[\text{Ru(NO)('CO}_2\text{MeS}_2\text{')}_2] \quad (4)$$

12

12 is diamagnetic and soluble in CH_2Cl_2, $CHCl_3$, acetone, THF, DMSO and DMF. The number of ^{1}H and ^{13}C{^{1}H}-NMR signals indicated that the anion of **12** exhibits twofold symmetry in solution. This is compatible with several configurations that have been discussed previously for the related anion [Ru(NO)('$^{bu}S_2$')$_2$]$^-$[15] ('$^{bu}S_2$'-H_2 = 3,5-di-tertiary-butyl-1,2-dimercaptobenzene). A selection of the possible isomers is shown in formulas **E**–**G**.

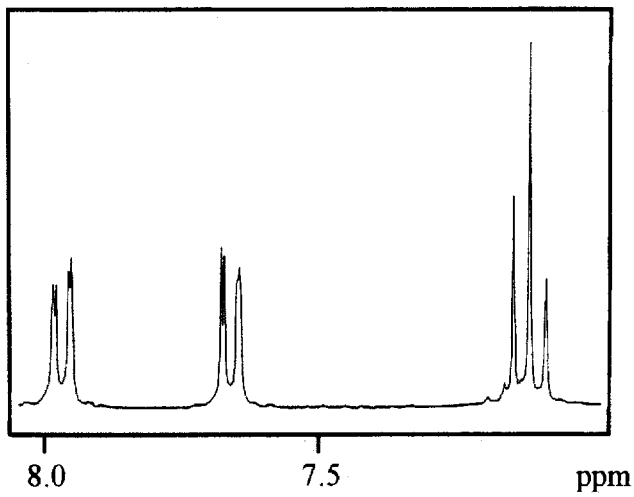


However, all attempts to obtain the pentadentate ligands by template alkylation of **12** were as yet unsuccessful.

Spectroscopic Characterization

All compounds containing 'CO_2R-S_2' entities displayed in their ^{1}H-NMR spectra a typical splitting pattern of one triplet and two doublets for the ABC spin system of the aromatic protons; this pattern resembles that of 2,3-dihydroxybenzoic acid[16]. Figure 1 displays the aromatic region of the ^{1}H-NMR spectrum of 'CO_2H-S_2'-H_2 (**1**) as an example.

Figure 1. Aromatic region of the ^{1}H-NMR spectrum of 'CO_2H-S_2'-H_2 (**1**) in [D$_6$]acetone



In our studies, this pattern served as a sensitive probe for monitoring the purity of compounds such as **1** or **2**. It also allowed for an analysis of the stereochemistry of compounds **4**–**12**, each of which contains two 'CO_2R-S_2' units. The ^{1}H-NMR spectra of isomerically pure **4a**, **4b**, **5**–**7**, **9**, **10** and **12** show only one such signal pattern proving the magnetic equivalence of the aromatic protons of the two 'CO_2R-S_2' entities and indicating the twofold symmetry of the respective compounds. In contrast, the ^{1}H-NMR spectra of Li_2[Fe(CO)$_2$('CO_2-S_4')] (**8**) and the diastereomeric mixture of [Fe(CO)$_2$('CO_2Me-S_4')] (**4a**, **b**) exhibit two sets of this signal pattern with different intensities. The δ(SH) shifts of 'CO_2Me-S_4'-H_2 (**5**) and 'CO_2H-S_4'-H_2 (**7**) (6.52 and 7.23) indicated that the S atoms in the position *meta* to the CO_2Me groups are bound to the ethylene bridge.

The IR (KBr) spectra of **8** and **10** exhibit two carboxylate bands at about 1590 and 1390 cm^{-1} indicating that the CO_2^- groups are not coordinated to the metal centers[17]. The IR (KBr) spectra of **4a**, **b** and **8** show two strong ν(CO) bands of nearly equal intensities and point to the *cis* coordination of the CO ligands. In conjunction with the IR spectroscopic results, the NMR spectra thus allowed for the assignment of C_2 symmetry for **4a**, **b** and **8**. The *cis* coordination of the two PPh_3 ligands in the [Ru(PPh_3)$_2$('CO_2R-S_4')] complexes **9** and **10** is assumed by analogy to the numerous [RuL_2('S_4')] complexes characterized by X-ray structural analysis[18].

The twofold symmetry, that was concluded from ^{1}H-NMR spectra, could be corroborated in all cases by ^{13}C{^{1}H} and ^{31}P{^{1}H}-NMR spectra. The ^{13}C{^{1}H}-NMR spectrum of **9** displays a complex splitting pattern resulting from the ^{13}C-^{31}P coupling. The C_2H_4 signal of the 'CO_2H-S_4'$^{2-}$ ligand and the C(*ortho*) and C(*meta*) signals of the PPh_3 ligands appear as pseudo triplets and the C(*ipso*) signal as pseudo quintet, because the C atoms each represent the X part of ABX spin systems in which the two P atoms are the A or B part[19].

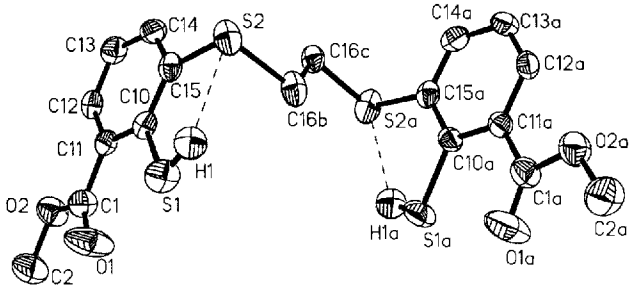
The signals of the aromatic H and C atoms of all diamagnetic compounds could be assigned by the use of the corresponding increment systems[20].

Noteworthy are the analogies and differences between $(NBu_4)[Ru(NO)('CO_2Me\text{-}S_2')_2]$ (**12**) and the parent complex $(NBu_4)[Ru(NO)('S_2')_2]$[21]. Both complexes yield green solutions in CH_2Cl_2 or $CHCl_3$ that showed one intense ν(NO) IR band at 1745 cm^{-1} and that contained, according to the NMR spectra, mononuclear anions, which exhibit twofold symmetry. In the solid state, however, **12** is brown, and its ν(NO) band is shifted to 1785 cm^{-1}; however the parent compound remains green, and its ν(NO) band is in the original position at 1740 cm^{-1}. This could suggest that the anion of **12** dimerizes in the solid state. Furthermore, the approximately identical ν(NO) frequencies of **12** and the parent compound in solution indicate that the CO_2Me substituents have no influence on the electron density at the Ru center.

X-ray Structural Analyses of $[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (4a), $'CO_2Me\text{-}S_4'\text{-}H_2$ (5) and $(AsPh_4)_2[Fe('CO_2Me\text{-}S_2')_2]$ (11)

The X-ray structural analysis of $[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (**4a**) and $'CO_2Me\text{-}S_4'\text{-}H_2$ (**5**) provided the final proof that the thiolate donors in the position *meta* to the CO_2Me groups are linked in the template alkylation of $[Fe(CO)_2('CO_2Me\text{-}S_2')_2]^{2-}$ by $C_2H_4Br_2$ [step (v) in Scheme 2].

Figure 2. ORTEP plot of $'CO_2Me\text{-}S_4'\text{-}H_2$ (**5**) drawn with 50% probability ellipsoids (H atoms bound to C atoms omitted). Selected distances (pm): S(1)–C(10) 176.7(4), S(2)–C(15) 178.2 (4), S(2)–C(16b) 194.0(8), C(16b)–C(16c) 151.6(13), C(11)–C(1) 148.1(6), C(1)–O(1) 118.5(5), C(1)–O(2) 132.9(5), O(2)–C(2) 144.5(6). Selected angles (°): C(15)–S(2)–C(16a) 99.4(3), S(2)–C(16b)–C(16c) 105.2(6), S(1)–C(10)–C(15) 121.3(3), C(15)–C(14)–C(13) 120.7(4), S(1)–C(10)–C(11) 120.5(3), C(11)–C(1)–O(2) 112.3(4), O(1)–C(1)–O(2) 122.0(4), C(1)–O(2)–C(2) 115.6(3)

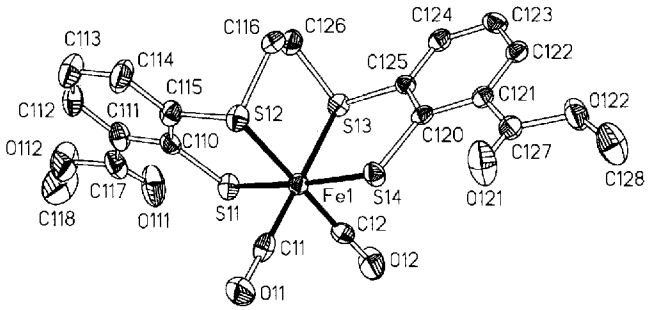


$'CO_2Me\text{-}S_4'\text{-}H_2$ (**5**) has crystallographically imposed C_2 symmetry (Figure 2). The C atoms of the ethylene bridge are disordered; Figure 2 shows only the ethylene carbon atoms that have the positions with the higher occupation of 53(1)%.

5 has an angular chain structure in which the benzene rings are arranged parallel to each other. This resembles the structure of the related molecules, $H_2\text{-}'S_2N_2Me_2'$ [$'S_2N_2Me_2'^{2-}$ = 1,2-ethanediamine-*N*,*N'*-dimethyl-*N*,*N'*-bis-(2-benzenethiolate)(2−)] and $H_2\text{-}'S_2N_2H_2'$ [$'S_2N_2H_2'^{2-}$ = 1,2-ethanediamine-*N*,*N'*-bis(2-benzenethiolate)(2−)][22]. Angles and distances of **5**, including the C–C distances in the benzene rings that range from 137.5(6) to 141.3(6) pm, show no anomalies[23]. The distances H(1)–S(2) and H(1a)–S(2a) (253.5 pm) are shorter than the sum of the van der Waals radii of hydrogen and sulfur (r_H = 100 pm, r_S = 180 pm[24]) and thus suggest intramolecular S–H···S bridges. We expected to find S–H···O bridges to the O atom of the methyl ester groups in the *ortho* position due to the the higher electronegativity of the O atom[24a,25].

Figure 3 shows the molecular structure of the isomer **4a** of $[Fe(CO)_2('CO_2Me\text{-}S_4')]$. **4a** crystallizes in red cubes and the asymmetric unit of **4a** contains two independent chiral molecules that are approximately enantiomeric; both isomers are identical within standard deviation.

Figure 3. ORTEP plot of $[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (**4a**) drawn with 50% probability ellipsoids (H atoms omitted). Selected distances (pm): Fe(1)–C(11) 175.9(8), Fe(1)–S(11) 229.0(3), Fe(1)–S(12) 226.3(3), Fe(1)–S(13) 228.8(3), Fe(1)–S(14) 229.6(3), C(11)–O(11) 117.7(10), S(11)–C(110) 173.6(8), S(12)–C(115) 178.1(7), S(12)–C(116) 184.3(8), C(116)–C(126) 147.9(13), C(115)–C(110) 141.5(13), C(111)–C(110) 142.3(9). Selected angles (°): C(11)–Fe(1)–C(12) 91.1(4), Fe(1)–C(11)–O(11) 179.4(6), C(11)–Fe(1)–S(11), 91.0(3), C(11)–Fe(1)–S(12) 88.6(3), S(11)–Fe(1)–S(12) 89.4(1), S(11)–Fe(1)–S(14) 176.7(1), Fe(1)–S(11)–C(110) 104.9(3), Fe(1)–S(12)–C(115) 104.4(3), Fe(1)–S(12)–C(116) 101.8(3), S(12)–C(116)–C(126) 111.7(6) S(11)–C(110)–C(111) 123.1(7), C(115)–C(110)–C(111) 116.0(7)



The Fe center of **4a** is pseudo octahedrally coordinated by four sulfur donors and two CO ligands. The thiolate atoms are *trans*, while the thioether and C donors are *cis* to each other; therefore **4a** can be considered to possess idealized C_2 symmetry. The Fe–S(thiolate) [229.0(3)/229.6(3) pm] and Fe–S(thioether) distances [226.3(3)/228.8(3) pm] lie in the same range and are identical within the 3σ criterion. This similarity can be traced back to the σ-donor-π-donor and σ-donor-π-acceptor characteristics of the respective Fe–S bonds[11,26]. Similar distances were found previously for the parent compound $[Fe(CO)_2('S_4')]$[27] and the tertiary butyl derivative $[Fe(CO)_2('^{bu}S_4')]$[11]; this showed that the CO_2Me or tertiary butyl substituents in the benzene rings do not influence the Fe–S bonds. It should also be noted that the distances and angles of the $'CO_2Me\text{-}S_4'^{2-}$ core in **4a** and the free ligand **5** are practically identical.

The exact stereochemistry of $(AsPh_4)_2[Fe('CO_2Me\text{-}S_2')_2]$ (**11**) was elucidated by X-ray structure analysis. **11** consists of discrete $AsPh_4^+$ cations and $[Fe('CO_2Me\text{-}S_2')_2]^{2-}$ anions (Figures 4 and 5).

The $AsPh_4^+$ cations reveal a nearly regular tetrahedral structure. The Fe center of the $[Fe('CO_2Me\text{-}S_2')_2]^{2-}$ anion lies on a crystallographic inversion center and is square planar coordinated by the four thiolate atoms. The C–C

Figure 4. Projection of the unit cell of $(AsPh_4)_2[Fe('CO_2Me\text{-}S_2')_2]$ (**11**)

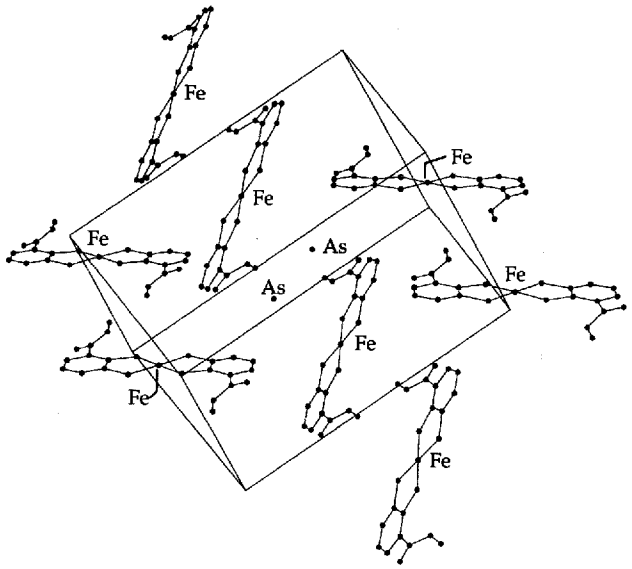
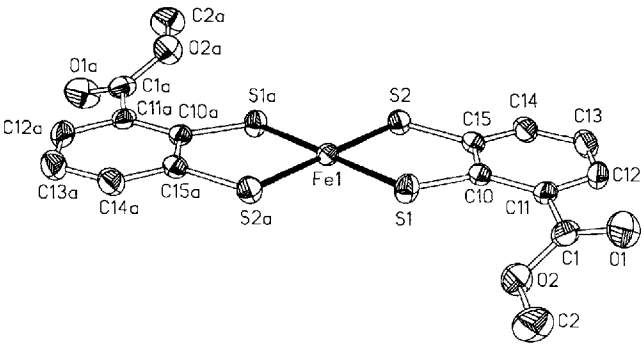


Figure 5. Molecular structure of $[Fe('CO_2Me\text{-}S_4')]^{2-}$ drawn with 50% probability ellipsoids (H atoms omitted). Selected distances [pm]: Fe(1)–S(1a) 220.55(8), Fe(1)–S(1) 220.55(8), Fe(1)–S(2) 220.72(8), Fe(1)–S(2a) 220.72(8), S(1)–C(10) 175.7(3), S(2)–C(15) 176.5(3), C(15)–C(14) 138.7(4), C(15)–C(10) 141.8(3), C(14)–C(13) 138.5(4), C(13)–C(12) 137.7(4). Selected angles (°): S(1a)–Fe(1)–S(1) 180.0, S(1a)–Fe(1)–S(2) 90.09(3), S(1)–Fe(1)–S(2) 89.91(3), S(1a)–Fe(1)–S(2a) 89.91(3), S(1)–Fe(1)–S(2a) 90.09(3), S(2)–Fe(1)–S(2a) 180.0, C(15)–S(2)–Fe(1) 105.60(9), C(15)–S(2)–Fe(1) 105.60(9), C(14)–C(15)–S(2) 120.0(2), C(10)–C(15)–S(2) 119.7(2)



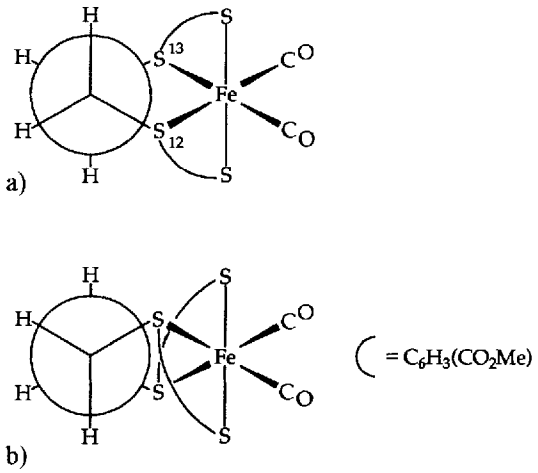
distances in the benzene rings range from 137.4(4) to 141.8(3) pm and do not suggest dithioketone character in the sulfur ligands. Figure 4 further shows that no direct S–Fe–S contacts exist between different anions. The Fe–S distances (220.55(8), 220.72(8) pm) are relatively short and nearly identical with those observed for the parent compound $(AsPh_4)_2[Fe('S_2')_2]$[28]. They are also in excellent agreement with the values expected from the correlation between the electron configuration and the Fe–S distances[29]. This correlation shows that short Fe–S distances in this type of complex result from the π donation of the sulfur *p*-electrons to empty iron *d* orbitals such that the Fe center can achieve the 18 valence electron configuration.

It should be noted that $[Fe('CO_2Me\text{-}S_2')_2]^{2-}$ is an example of a relatively rare class of square planar, monomeric d^6 iron(II) thiolate complex. These complexes have been compared and contrasted to tetrahedral Fe(II) complexes such as $[Fe(SPh)_4]^{2-}$[30] and related d^4, d^5 and d^6 complexes in detail elsewhere[28,29,31].

Discussion of the Isomerism of $[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (4) and the Regioselectivity of the Template Alkylation

In **4a**, the ethylene bridge of the chelate ligand exhibits the same gauche conformation as in $[Fe(CO)_2('S_4')]$[27] and $[Fe(CO)_2('^{bu}S_4')]$[11] and is indicated by the Newman type projection in Figure 6a. The diastereomer **4b** can be reasonably explained by assuming that the alkylation of the two *cis* thiolate donors for this isomer led to the conformation depicted in Figure 6b. This complex is related to the one shown in Figure 6a by an inversion of the two C atoms in the C_2 bridge.

Figure 6. a) Newman projection along the C116–C126 bond in **4a**, b) proposed structure for **4b**



Molecular models show that **4b** is sterically more strained than **4a**. Accordingly, **4a** and the diastereomer **4b** might be, respectively, the thermodynamically and kinetically controlled alkylation products. This proposal was supported by the varying ratios of **4a**:**4b** that resulted when the alkylations of the precursor anion **3** were carried out at different temperatures. The ratios of **4a**:**4b** decreased from 3:1 at ~20°C to 1:1 at 0°C and 1:11 at −20°C. Template alkylations at higher temperatures were impossible because of the thermal lability of the CO ligands of **3**.

The formation of only one stereoisomer for the precursor anion in $(AsPh_4)_2[Fe('CO_2Me\text{-}S_2')_2]$ (**11**) and the regioselectivity of the alkylation reactions of the corresponding $[Fe(CO)_2('CO_2Me\text{-}S_2')_2]^{2-}$ anion in **3** can both be traced back to the steric demands of the CO_2Me substituents. In the first case, repulsion of the CO_2Me groups favors the stereoisomer of C_i symmetry, which minimizes the interactions between the two substituents.

In the alkylation reactions, this repulsion may also play a role. An additional and possibly more important role of the CO_2Me groups may be to shield the *ortho* thiolate S atoms. Molecular models show that the CO_2Me substituents could effectively hinder the access of electrophilic alky-

lation reagents to the *ortho* thiolates. In particular, the methyl groups can come into close contact to the thiolate S atoms. This may explain why all attempts to template alkylate the carboxylate derivative 'CO_2-S_2'$^{3-}$ in a regioselective way have not been successful. It should also be noted that the coordination of two additional CO ligands to the anion of **11** is also required for the formation of the desired configuration of the two dithiolate ligands.

As outlined in Scheme 3, the coordination of CO can be assumed to proceed stepwise yielding a stereochemically non-rigid five coordinate intermediate, **H**, in the first step. It must be the coordination of the second CO that favors the formation of **I** instead of the alternatives such as **J**. **I** exhibits the proper configuration for the subsequent alkylation to yield **4**. Thus, in summary, the regioselective formation of 'CO_2Me-S_4'$^{2-}$ is due to steric repulsion of the two CO_2Me substituents *and* the shielding of the thiolate S atoms in their *ortho* position.

Concluding Discussion

The derivatization of metal ligands such that the resulting complexes are soluble in water is an important issue in catalysis[32]. For example, sulfonation of 2,2'-bis(diphenylphosphinomethyl)-1,1'-binaphthalene has led to rhodium catalysts that carry out hydroformylation in aqueous solution[33]. The synthesis of carboxylic acid derivatives of the tetradentate ligand 'S_4'-H_2 was the goal of this work.

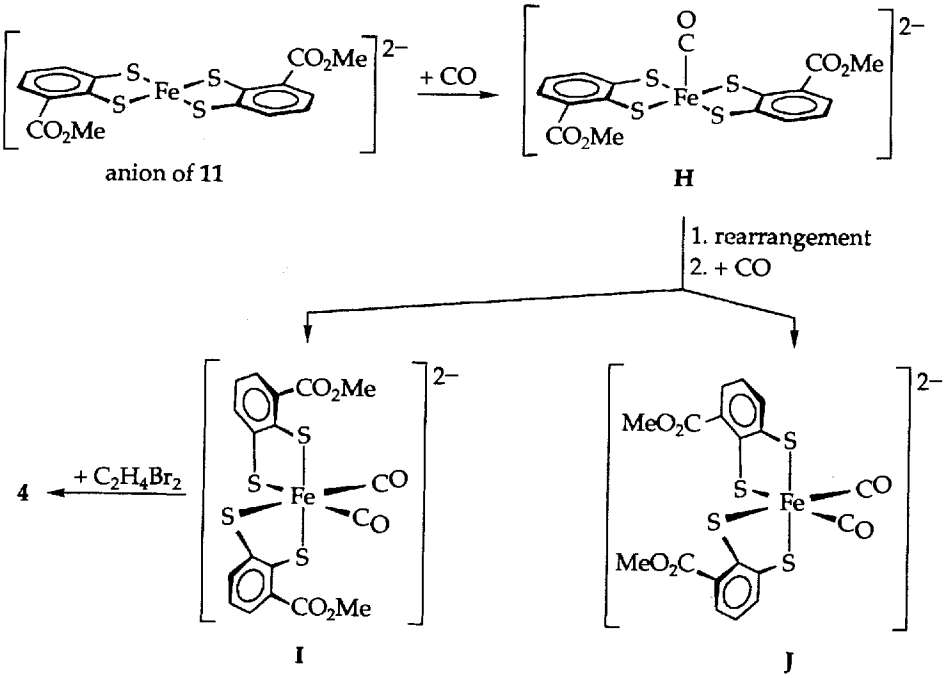
These ligands are important for the ultimate goal, which is to synthesize metal complexes that can coordinate and subsequently reduce molecular dinitrogen under mild reducing conditions in aqueous media. In the course of this work, 1,2-benzenedithiol could be converted into 2,3-dimercaptobenzoic acid **1**. The linkage of the two units of **1** to give the tetradentate dithioether dithiol ligand 'CO_2H-S_4'-H_2 (**7**) required the esterification of **1** yielding 'CO_2Me-S_2'-H_2 (**2**), because only **2** could be alkylated with 1,2-$C_2H_4Br_2$ in a regioselective way at [$Fe(CO)_2$] templates. Finally, the desired product, **7**, could be obtained from the saponification of 'CO_2Me-S_4'-H_2 (**5**).

The treatment of **7** with $FeCl_2$ in the presence of CO and LiOMe gave the water soluble complex Li_2[$Fe(CO)_2$('CO_2-S_4')] (**8**), which can be reversibly protonated to give the water insoluble product [$Fe(CO)_2$(CO_2H-S_4)]. In an analogous way, the treatment of [$RuCl_2(PPh_3)_3$] with neutral **7** led to [$Ru(PPh_3)_2$('CO_2H-S_4')] (**9**), and **9** can be reversibly deprotonated by KOH to form the water soluble complex K_2[$Ru(PPh_3)_2$('CO_2-S_4')] (**10**). Thus, the neutral complexes and their salts behave like fatty acids with respect to their solubility in aqueous and non-aqueous solvents. The same holds for the free ligand **7** and its sodium salt 'CO_2-S_4'-Na_4 (**6**).

While **8** and the corresponding methyl ester [$Fe(CO)_2$('CO_2Me-S_4')] (**4**) were obtained as mixtures of two diastereomers, **9** and **10** yielded only one stereoisomer. The molecular structures of the reaction intermediate $(AsPh_4)_2$[Fe('CO_2Me-S_2')$_2$] (**11**) and one of the diastereomers of [Fe($CO)_2$('CO_2Me-S_4')] (**4a**) could be elucidated by X-ray structural analysis. The structural data allowed for the rationalization of the diastereoisomerism of **4a** and **4b** which results from conformational differences in the C_2H_4 bridge. The X-ray structural analysis of **5** ultimately confirmed the regioselectivity of the template alkylation. This regioselectivity can be traced back to steric repulsion of the CO_2Me substituents *and* efficient shielding of the *ortho* thiolate S atoms.

The preparation of the free ligand 'CO_2H-S_4'-H_2 (**7**) now pave the way for investigations leading to the synthesis of

Scheme 3. Proposed reaction mechanism for the regioselective formation of [$Fe(CO)_2$('CO_2Me-S_4')] (**4**)



key intermediates of N_2 fixation such as N_2H_2 complexes in aqueous solution.

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Experimental

General Methods: Unless otherwise noted, all procedures were carried out under N_2 at room temp. using Schlenk techniques. Solvents were dried and distilled before use. As far as possible, the reactions were monitored by IR spectroscopy. Spectra were recorded on following instruments: – IR (CaF_2 cuvettes or KBr discs): Perkin Elmer 1620 FT IR or Perkin Elmer 16 PC FT-IR; solvent bands were compensated. – NMR: JNM-GX 270 and JNM-EX 270. – Mass spectra: Varian MAT 212. – Magnetic susceptibility: Johnson Matthey susceptibility balance. 'S_2'-H_2 = 1,2-benzenedithiol[34], $[RuCl_2(PPh_3)_3]$[35] and $RuCl_3(NO) \cdot x\ H_2O$[14] were prepared by literature methods.

Syntheses

'CO_2H-S_2'-H_2 (**1**): A solution of 'S_2'-H_2 (14.42 g, 11.5 ml, 100 mmol) in cyclohexane (40 ml) was added dropwise at 0°C to a mixture of TMEDA (tetramethylethylenediamine, 37.18 g, 48.3 ml, 320 mmol) and *n*-BuLi (320 mmol, 128 ml of a 2.5 M solution in *n*-hexane) in cyclohexane (125 ml). The reaction mixture was stirred for 30 min at 0°C, warmed up to room temp., and stirred for another 22 h. During this time, an off-white precipitate formed. The yellow suspension was poured on an excess of solid CO_2 (150 g, 3.4 mol). After the evaporation of the CO_2, concd. hydrochloric acid (240 ml, 2.88 mol) was added at 0°C and the resultant mixture was extracted with Et_2O (1 l). The organic phases were combined, dried with anhydrous Na_2SO_4 (30 g), filtered, and the yellow filtrate was reduced in volume to 100 ml. A yellow powder precipitated that was separated, washed with cyclohexane (300 ml), dried in vacuo, and purified by sublimation (0.2 mbar, 180°C oil bath temperature) yielding pure **1** as a light yellow powder. Yield: 11.9 g (64%) of 'CO_2H-S_2'. – $C_7H_6O_2S_2$ (186.2): calcd. C 45.14, H 3.25, S 34.44; found C 45.01, H 3.22, S 34.30. – IR (KBr): $\tilde{\nu}$ = 2985 cm^{-1} (OH), 2518 (SH), 1674 (CO_2H). – ^1H NMR ([D_6]acetone): δ = 10.90 (br., 1H, CO_2H), 7.96 (dd, 1H, C_6H_3, H ortho to CO_2H), 7.66 (dd, 1H, C_6H_3, para to CO_2H), 7.12 (t, 1H, C_6H_3, meta to CO_2H), 7.12 (br., 1H, S*H* ortho to CO_2H), 4.58 (s, 1H, S*H* meta to CO_2H). – $^{13}C\{^1H\}$ NMR ([D_6]acetone): δ = 169.4 (CO_2H), 137.9 [C_6H_3, C(CO_2Me)], 135.3 (C_6H_3, CH para to CO_2Me), 133.1 [C_6H_3, C(SH) ortho to CO_2Me], 130.5 (C_6H_3, CH ortho to CO_2Me), 127.6 [C_6H_3, C(SH) meta to CO_2Me], 125.0 (C_6H_3, CH meta to CO_2Me). – EI MS (70 eV), *m/z*: 186 ['CO_2H-S_2'-H_2]$^+$.

'CO_2Me-S_2'-H_2 (**2**): Gaseous HCl was bubbled through a yellow solution of 'CO_2H-S_2'-H_2 (**1**) (7.09 g, 38.1 mmol) in MeOH (70 ml) for 15 min at −78°C. The yellow solution was refluxed for 15 h and then the solvent was removed under vacuum yielding a viscous yellow residue. It was dissolved in 70 ml of cyclohexane and dried by addition of anhydrous Na_2SO_4 (5 g). After filtration and removal of the solvent, distillation of the residue (110−112°C/0.2 mbar) yielded a yellow oil that solidified at room temp. Yield: 4.4 g (57%) of 'CO_2Me-S_2'-H_2. – $C_8H_8O_2S_2$ (200.3): calcd. C 47.97, H 4.03, S 32.02; found C 48.13, H 4.03, S 31.79. – IR (KBr): $\tilde{\nu}$ = 2493 cm^{-1} (SH), 1703, 1287, 1250 (CO_2Me). – ^1H NMR ($CDCl_3$): δ = 7.89 (d, 1H, C_6H_3, ortho to CO_2Me), 7.54 (d, 1H, C_6H_3, para to CO_2Me), 7.04 (t, 1H, meta to CO_2Me), 6.57 (s, 1H, S*H*, ortho to CO_2Me), 3.81 (s, 3H, CH_3), 3.60 (s, 1H, S*H*, meta to CO_2Me). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 167.7 (CO_2Me), 138.3 [C_6H_3, C(SH) ortho to CO_2Me], 135.3 (C_6H_3, CH para to CO_2Me), 131.1 [C_6H_3, C(CO_2Me)], 130.0 (C_6H_3, CH ortho to CO_2Me), 127.2 [C_6H_3, C(SH) meta to CO_2Me], 124.0 (C_6H_3, CH meta to CO_2Me), 52.5 (CH_3). – FD MS (70 eV, CH_2Cl_2), *m/z*: 200 ['CO_2Me-S_2'-H_2]$^+$.

$Li_2[Fe(CO)_2('CO_2Me\text{-}S_2')_2]$ (**3**): LiOMe in MeOH (40 mmol, 40 ml of a 1 M solution) and $FeCl_2 \cdot 4\ H_2O$ (1.98 g, 10 mmol) were added to a solution of 'CO_2Me-S_2'-H_2 (**2**) (4.01 g, 20 mmol) in MeOH (60 ml). CO was bubbled through the reaction mixture for 2 h yielding a red solution of $Li_2[Fe(CO)_2('CO_2Me\text{-}S_2')_2]$ (**3**) (ca. 10 mmol in 100 ml of MeOH). – IR (MeOH): $\tilde{\nu}$ = 2000, 1942 cm^{-1} (CO), 1702 (CO_2Me).

$[Fe(CO)_2('CO_2Me\text{-}S_4')]$ (**4**): 1,2-Dibromoethane (0.86 ml, 1.88 g, 10 mmol) was added to 100 ml of the red MeOH solution of $Li_2[Fe(CO)_2('CO_2Me\text{-}S_2')_2]$ (**3**) (10 mmol). The reaction mixture was stirred under a CO atmosphere for 4 h. The bright red precipitate that formed was filtered off, washed with MeOH and Et_2O (50 ml each), dried in vacuo, and identified as a diastereomeric mixture of **4a** and **4b**. Yield: 3.5 g (65%) of [Fe(CO)$_2$('CO_2Me-S_4')]. – $C_{20}H_{16}FeO_6S_4$ (536.5): calcd. C 44.78, H 3.01, S 23.91; found C 44.54, H 3.01, S 23.92. – FD MS (70 eV, CH_2Cl_2), *m/z*: 536 [Fe(CO)$_2$('CO_2Me-S_4')]$^+$, 426 ['CO_2Me-S_4'-H_2]$^+$.

200 mg of the diastereomeric mixture of **4** were dissolved in CH_2Cl_2 (10 ml), and this mixture was layered with the equal volume of Et_2O. Dark red cubes of **4a** and bright red plates of **4b** crystallized. After decanting the solvent, the two crystal forms were separated manually, and the dark red cubes of **4a** proved suitable for X-ray structural analysis. **4a**: IR (KBr): $\tilde{\nu}$ = 2038, 1989 cm^{-1} (CO), 1717 (CO_2Me). – ^1H NMR ($CDCl_3$): δ = 7.82 (d, 2H, C_6H_3, ortho to CO_2Me), 7.57 (d, 2H, C_6H_3, para to CO_2Me), 7.02 (t, 2H, C_6H_3, meta to CO_2Me), 3.91 (s, 3H, CO_2CH_3), 3.25 (m, 2H, C_2H_4), 2.43 (m, 2H, C_2H_4). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 208.2 (*C*O), 167.6 (*C*O_2Me), 159.9 (C_6H_3, CS ortho to CO_2Me), 135.2 (C_6H_3, CH para to CO_2Me), 134.5 [C_6H_3, C(CO_2Me)], 133.8 (C_6H_3, CH ortho to CO_2Me), 133.2 (C_6H_3, CS meta to CO_2Me), 123.4 (C_6H_3, CH meta to CO_2Me), 52.9 (CO_2CH_3), 43.7 (C_2H_4). **4b**: IR (KBr): $\tilde{\nu}$ = 2044, 1996 cm^{-1} (CO), 1719 (CO_2Me). – ^1H NMR ($CDCl_3$): δ = 7.70 (d, 2H, C_6H_3, ortho to CO_2Me), 7.55 (d, 2H, C_6H_3, para to CO_2Me), 7.13 (t, 2H, C_6H_3, meta to CO_2Me), 3.91 (s, 3H, CO_2CH_3), 3.91 (m, 2H, C_2H_4, superimposed), 2.60 (m, 2H, C_2H_4). – $^{13}C\{^1H\}$ NMR: ($CDCl_3$): δ = 209.0 (*C*O), 167.3 (*C*O_2Me), 161.0 (C_6H_3, CS ortho to CO_2Me), 135.0 (C_6H_3, CH para to CO_2Me), 133.2 [C_6H_3, C(CO_2Me)], 130.0 (C_6H_3, CH ortho to CO_2Me), 129.8 (C_6H_3, CS meta to CO_2Me), 126.5 (C_6H_3, CH meta to CO_2Me), 53.4 (CO_2CH_3), 44.1 (C_2H_4).

'CO_2Me-S_4'-H_2 (**5**): Concd. hydrochloric acid (5 ml, 60 mmol of HCl) was added to a red solution of [Fe(CO)$_2$('CO_2Me-S_4')] (**4**) (4.95 g, 9.22 mmol) in THF (140 ml). The reaction mixture was heated under reflux for 3 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (40 ml). The yellow CH_2Cl_2 solution was chromatographed over 10 cm of SiO_2 (mesh 60), reduced in volume to 20 ml and layered with *n*-hexane (40 ml). After 2 d, colorless needles were filtered off, washed with *n*-hexane (40 ml) and dried in vacuo. Yield: 2.6 g (67%) of 'CO_2Me-S_4'-H_2. – $C_{18}H_{18}O_4S_4$ (426.6): calcd. C 50.68, H 4.25, S 30.07; found C 50.51, H 4.34, S 30.28. – IR (KBr): $\tilde{\nu}$ = 2454 cm^{-1} (SH), 1709, 1289, 1247 (CO_2Me). – ^1H NMR ($CDCl_3$): δ = 7.95 (dd, 2H, C_6H_3, para to CO_2Me), 7.60 (dd, 2H, C_6H_3, ortho to CO_2Me), 7.04 (t, 2H, C_6H_3, meta to CO_2Me), 6.52 (s, 2H, S*H*), 3.92 (s, 6H, CO_2CH_3), 2.99 (s, 4H, C_2H_4). – $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ = 168.0 (CO_2Me), 143.9 (C_6H_3, CS ortho to CO_2Me), 138.9 (C_6H_3,

CH para to CO_2Me), 133.8 [C_6H_3, C(CO_2Me)], 132.4 (C_6H_3, CH ortho to CO_2Me), 128.0 (C_6H_3, CS meta to CO_2Me), 124.5 (C_6H_3, CH meta to CO_2Me), 53.2 (CO_2CH_3), 34.6 (C_2H_4). – FD MS (70 eV, CH_2Cl_2), *m/z*: 426 ['CO_2Me-S_4'-H_2]$^+$.

'CO_2-S_4'-Na_4 (**6**): NaOH (10.2 mmol, 10.2 ml of a 1 M aqueous solution) was added to a solution of 'CO_2Me-S_4'-H_2 (**5**) (1.08 g, 2.53 mmol) in THF (10 ml). The reaction mixture was stirred for 15 h. Removal of the solvents in vacuo yielded a colorless powder, which was characterized as 'CO_2-S_4'-Na_4 (**6**) by ^{1}H-NMR and ^{13}C{^{1}H}-NMR spectroscopy. – ^{1}H NMR (D_2O): δ = 7.03 (dd, 2H, C_6H_3, para to CO_2), 6.97 (t, 2H, C_6H_3, meta to CO_2), 6.86 (d, 2H, C_6H_3, ortho to CO_2), 3.25 (s, 2H, C_2H_4). – ^{13}C{^{1}H} NMR (D_2O): δ = 182.8 (CO_2), 147.5 (C_6H_3, CS ortho to CO_2), 142.4 [C_6H_3, C(CO_2)], 141.4 (C_6H_3, CS meta to CO_2), 124.7, 124.3, 123.4 (C_6H_3, CH), 33.1 (C_2H_4).

'CO_2H-S_4'-H_2 (**7**): 'CO_2-S_4'-Na_4 (**6**) was dissolved in 10 ml of H_2O. After addition of hydrochloric acid (21 mmol, 21 ml of a 1 M aqueous solution), a colorless powder precipitated, which was filtered off, washed with H_2O (30 ml), and dried in vacuo. Yield: 710 mg (70%) of 'CO_2H-S_4'-H_2. – $C_{16}H_{14}O_4S_4$ (398.6): calcd. C 48.22, H 3.54; found C 48.55, H 3.58. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1} (OH), 2511 (SH), 1682 (CO_2H). – ^{1}H NMR ([D_8]THF): δ = 10.80 (br., 2H, CO_2H), 8.02 (dd, 2H, C_6H_3, para to CO_2H), 7.60 (dd, 2H, C_6H_3, ortho to CO_2H), 7.23 (s, 2H, S*H*), 7.07 (t, 2H, C_6H_3, meta to CO_2H), 3.09 (s, 4H, C_2H_4). – ^{13}C{^{1}H} NMR ([D_8]THF): δ = 169.1 (CO_2H), 144.2 (C_6H_3, CS ortho to CO_2H), 137.7 (C_6H_3, CH para to CO_2H), 134.8 (C_6H_3, C(CO_2H)), 132.4 (C_6H_3, CH ortho to CO_2H), 127.8 (C_6H_3, CS meta to CO_2H), 124.4 (C_6H_3, CH meta to CO_2Me), 34.5 (C_2H_4). – FD MS (70 eV, THF), *m/z*: 398 ['CO_2H-S_4'-H_2]$^+$.

Li_2[Fe(CO)$_2$('CO_2-S_4')] (**8**): LiOMe (3.72 mmol, 3.72 ml of a 1 M solution in MeOH) and $FeCl_2 \cdot 4\ H_2O$ (185 mg, 0.93 mmol) dissolved in 5 ml of MeOH were added successively to a suspension of 'CO_2H-S_4'-H_2 (**7**) (370 mg, 0.93 mmol) in MeOH (10 ml). The resultant solution was saturated with CO for 15 min, combined with THF (15 ml) and filtered over filter pulp. After removal of the solvents the red residue was suspended in THF (20 ml), stirred for 1 h, separated, washed with THF (10 ml), and dried in vacuo. Yield: 280 mg (55%) of Li_2[Fe(CO)$_2$('CO_2-S_4')] · MeOH. – $C_{19}H_{14}FeLi_2O_7S_4$ (552.3): calcd. C 41.32, H 2.56, S 23.23; found C 40.97, H 2.65, S 23.64. – IR (MeOH): $\tilde{\nu}$ = 2042, 1998 cm^{-1} (CO), 1585 (CO_2). – IR (KBr): $\tilde{\nu}$ = 2043, 1994 cm^{-1} (CO), 1588, 1391 (CO_2). The ^{1}H-NMR spectra indicated that **8** contained a mixture of two C_2 symmetrical diastereomers **8a** and **8b** in the approximate ratio of 4:1. ^{1}H NMR (D_2O): δ = 7.48 (d, 2H, C_6H_3, ortho to CO_2Me, **8a**), 7.36 (d, 2H, C_6H_3, ortho to CO_2Me, **8b**), 7.09 (d, 4H, C_6H_3, para to CO_2Me, **8a** and **8b**, superimposed), 6.97 (t, 4H, C_6H_3, meta to CO_2Me, **8a** and **8b**, superimposed), 3.56 (m, 2H, C_2H_4, **8b**), 3.37 (m, 4H, C_2H_4, **8a** and **8b**, superimposed), 2.28 (m, 2H, C_2H_4, **8a**).

[Ru(PPh$_3$)$_2$('CO_2H-S_4')] (**9**): 'CO_2H-S_4'-H_2 (**7**) (205 mg, 0.51 mmol) was added to a red brown solution of $RuCl_2(PPh_3)_3$ (495 mg, 0.51 mmol) in THF (15 ml). The color changed to green-brown and a yellow powder precipitated. This powder was filtered off after 3 h, washed with THF (10 ml), and dried in vacuo. Yield: 400 mg (67%) of [Ru(PPh$_3$)$_2$('CO_2H-S_4')] · 2 THF (**9** · 2 THF). – $C_{60}H_{58}P_2O_6RuS_4$ (1166.4): calcd. C 61.78, H 5.01, S 11.00; found C 61.60, H 5.05, S 10.83. – IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1} (OH), 1717 (CO_2H). – ^{1}H NMR ($CDCl_3$): δ = 12.59 (br., 2H, CO_2H), 7.95 (d, 2H, C_6H_3, para to CO_2H), 7.45 (m, 12H, C_6H_5), 7.15 (t, 6H, C_6H_5), 7.03 (t, 12H, C_6H_5), 6.85 (d, 2H, C_6H_3, ortho to CO_2H), 6.62 (t, 2H,C_6H_3, meta to CO_2H), 2.60 (m, 2H, C_2H_4), 1.97 (m, 2H, C_2H_4). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 168.4 (CO_2H), 157.6 (C_6H_3), 136.1 (C_6H_3), 135.6 (t, C_6H_5, C ortho), 135.3 (C_6H_3), 135.0 (C_6H_3), 133.9 (qu, C_6H_5, C ispo), 131.3 (C_6H_3), 130.6 (s, C_6H_5, C para), 127.7 (t, C_6H_5, C meta), 123.1 (C_6H_3), 42.9 (t, C_2H_4). – ^{31}P{^{1}H} NMR ($CDCl_3$): δ = 25.4.

K_2[Ru(PPh$_3$)$_2$('CO_2-S_4')] (**10**): KOH (0.16 mmol, 0.16 ml of a 1 M aqueous solution) was added to a yellow suspension of [Ru(PPh$_3$)$_2$('CO_2H-S_4')] (**9** · 2 THF) (95 mg, 0.08 mmol) in MeOH (10 ml) yielding a yellow solution that was filtered over filter pulp. After removal of the solvents the resultant yellow powder was dried in vacuo. Yield: 75 mg of K_2[Ru(PPh$_3$)$_2$('CO_2-S_4')] · 2 H_2O (83%). – $C_{52}H_{44}K_2P_2O_6RuS_4$ (1134.4): calcd. C 55.06, H 3.91, S 11.31; found C 55.28, H 4.17, S 11.45. – IR (KBr): $\tilde{\nu}$ = 1591, 1386 cm^{-1} (CO_2). – ^{1}H NMR (D_2O): δ = 7.37 (m, 12H, C_6H_5), 7.11 (t, 6H, C_6H_5), 6.97 (t, 12H, C_6H_5), 6.88 (d, 2H, C_6H_3, para to CO_2H), 6.75 (d, 2H, C_6H_3, ortho to CO_2H), 6.59 (t, 2H, C_6H_3, meta to CO_2H), 2.60 (m, 2H, C_2H_4), 1.92 (m, 2H, C_2H_4). – ^{31}P{^{1}H} NMR (CD_3OD): δ = 27.8.

(AsPh$_4$)$_2$[Fe('CO_2Me-S_2')$_2$] (**11**): LiOMe (5.40 mmol, 5.40 ml of a 1 M solution in MeOH) and $FeCl_2 \cdot 4\ H_2O$ (270 mg, 1.35 mmol) dissolved in 10 ml of THF were added successively to a solution of 'CO_2Me-S_2'-H_2 (**2**) (540 mg, 2.70 mmol) in MeOH (10 ml). The resultant bright red solution was filtered over filter pulp and layered with a solution of $AsPh_4Cl \cdot H_2O$ (1.18 g, 2.70 mmol) in MeOH (10 ml). Dark red crystals precipitated that were separated after 3 d, washed with MeOH and Et_2O (10 ml each), and dried in vacuo. Yield: 1.2 g (73%) of $(AsPh_4)_2$[Fe('CO_2Me-S_2')$_2$]. – $C_{64}H_{52}As_2FeO_4S_4$ (1219.0): calcd. C 63.06, H 4.30, S 10.52; found C 62.07, H 4.25, S 11.07. – IR (KBr): $\tilde{\nu}$ = 1709 cm^{-1} (CO_2Me). ^{1}H-NMR ([D_6]DMSO): δ = 7.83–7.73 (br., 40H, C_6H_5), 6.32 (s, 6H, CO_2CH_3), –3.27 (br., 2H, C_6H_3), –8.75 (br., 2H, C_6H_3), –10.96 (br., 2H, C_6H_3).

(NBu$_4$)[Ru(NO)('CO_2Me-S_2')$_2$] (**12**): NO was bubbled through a red-brown solution of $RuCl_3 \cdot x\ H_2O$ (1.22 g, 4.67 mmol) in MeOH (60 ml) for 7 h. The resultant clear red-violet solution was added rapidly to a solution of 'CO_2Me-S_2'-H_2 (**1**) (1.87 g, 9.34 mmol) and NBu_4OH (18.7 mmol, 18.7 ml of a 1 M solution in MeOH) in 40 ml of MeOH yielding a green solution. Brown microcrystals began precipitating, and these crystals were separated after 3 h, washed with MeOH and Et_2O (20 ml each), and dried in vacuo. Yield: 1.9 g (51%) of (NBu_4)[Ru(NO)('CO_2Me-S_2')$_2$]. – $C_{32}H_{48}N_2O_5RuS_4$ (770.1): calcd. C 49.91, H 6.28, N 3.64, S 16.66; found C 49.95, H 6.36, N 3.66, S 16.72. – IR (KBr): $\tilde{\nu}$ = 1785 cm^{-1} (NO), 1715, 1250 (CO_2Me). – ^{1}H NMR ($CDCl_3$): δ = 7.80 (d, 2H, C_6H_3, ortho to CO_2Me), 7.56 (d, 2H, C_6H_3, para to CO_2Me), 7.03 (t, 2H, C_6H_3, meta to CO_2Me), 3.92 (s, 3H, CO_2CH_3), 2.83 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.27 (m, 8H, $NCH_2CH_2CH_2CH_3$), 1.14 (m, 8H, $NCH_2CH_2CH_2CH_3$), 0.83 (m, 12H, $NCH_2CH_2CH_2CH_3$). – ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 169.1 (CO_2Me), 155.1 (C_6H_3, CS ortho to CO_2Me), 152.6 [C_6H_3, C(CO_2Me)], 132.9 (C_6H_3, CH para to CO_2Me), 130.9 (C_6H_3, CS meta to CO_2Me), 126.0 (C_6H_3, CH ortho to CO_2Me), 123.3 (C_6H_3, CH meta to CO_2Me), 59.2 ($NCH_2CH_2CH_2CH_3$), 52.6 (CO_2CH_3), 24.5 ($NCH_2CH_2CH_2CH_3$), 20.2 ($NCH_2CH_2CH_2CH_3$), 14.3 ($NCH_2CH_2CH_2CH_3$). – FD MS (70 eV, acetone), *m/z*: 770 [(NBu_4)(Ru(NO)('CO_2Me-S_2')$_2$)]$^+$, 528 [(Ru(NO)('CO_2Me-S_2')$_2$)]$^+$.

X-Ray Structural Analysis of [Fe(CO)$_2$('CO_2Me-S_4')] (**4a**), *'CO_2Me-S_4'-H_2* (**5**) *and (AsPh$_4$)$_2$[Fe('CO_2Me-S_2')$_2$]* (**11**): Red cubes of [Fe(CO)$_2$('CO_2Me-S_4')] (**4a**) were obtained by layering a saturated solution of the diastereomeric mixture of [Fe(CO)$_2$-('CO_2Me-S_4')] (**4**) in CH_2Cl_2 with Et_2O, colorless needles of 'CO_2Me-S_4'-H_2 (**5**) were formed by layering a saturated CH_2Cl_2

Table 1. Selected crystallographic data for [Fe(CO)$_2$('CO$_2$Me-S$_4$')] (**4a**), 'CO$_2$Me-S$_4$'-H$_2$ (**5**) and (AsPh$_4$)$_2$[Fe('CO$_2$Me-S$_2$')$_2$] (**11**)

Compound	[Fe(CO)$_2$('CO$_2$Me-S$_4$')] (4a)	'CO$_2$Me-S$_4$'-H$_2$ (5)	(AsPh$_4$)$_2$[Fe('CO$_2$Me-S$_2$')$_2$] (11)
Formula	$C_{20}H_{16}FeO_6S_4$	$C_{18}H_{18}O_4S_4$	$C_{64}H_{52}As_2FeO_4S_4$
M_r [g/mol]	536.4	426.6	1218.99
Crystal size. [mm]	0.7 x 0.5 x 0.4	0.4 x 0.4 x 0.3	0.7 x 0.6 x 0.5
F (000)	1096	888	1248
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$C2/c$	$P2_1/c$
a [pm]	784.1(8)	1267.0(2)	1018.4(3)
b [pm]	1660.5(15)	1534.3(3)	1915.7(5)
c [pm]	1892.0(2)	999.9(2)	1392.4(4)
α [°]	113.58(8)	-	-
β [°]	98.17(8)	100.23(1)	97.58(2)
γ [°]	94.58(8)	-	-
Cell volume [pm^3]	2209(4)·10^6	1913.0(5)	2692.8(13)
Z	4	4	2
$D_{calcd.}$ [g/cm^3]	1.613	1.481	1.503
μ [cm^{-1}]	10.96	5.18	17.05
Temperature [K]	200	200	200
Diffractometer	Siemens P4	Siemens P4	Siemens P4
Radiation [pm]	Mo-K$_\alpha$ (71.073)	Mo-K$_\alpha$ (71.073)	Mo-K$_\alpha$ (71.073)
Scan technique	ω-scan	ω-scan	ω-scan
2 θ - range [°]	3 - 54	3 - 54	3 - 54
Scan speed [°/min]	3 - 29.3	3 - 29.3	3 - 30
Measured reflections	10681	3609	10536
Independent reflections	9559	2101	5894
Observed reflections	6168	1321	4142
σ-Criterion	F > 4σ(F)	F > 4σ(F)	F > 4σ(F)
Refined parameters	559	128	340
R/R$_W$ bzw. R$_W$^{2}	0.054/0.049	0.045/0.042	0.0316/0.0767

solution with *n*-hexane, and black needles of (AsPh$_4$)$_2$[Fe('CO$_2$Me-S$_2$')$_2$] (**11**) were obtained by layering a solution of Li$_2$[Fe('CO$_2$Me-S$_2$')$_2$] in MeOH/THF (3:1) with a solution of AsPh$_4$Cl · H$_2$O in MeOH.

Suitable single crystals were sealed in glass capillaries and data were collected with a Siemens P4 diffractometer. The structures were solved by direct methods (SHELXTL-PLUS)[36]. Nonhydrogen atoms were refined anisotropically, and hydrogen atoms with isotropic thermal parameters. In the case of (AsPh$_4$)$_2$[Fe('CO$_2$Me-S$_2$')$_2$] (**11**), the anisotropic refinement was carried out with SHELXL93[37]. The hydrogen atoms were located in the difference Fourier synthesis and restricted during refinement.

The C$_2$H$_4$ bridge in 'CO$_2$Me-S$_4$'-H$_2$ (**5**) was disordered and was refined in two different positions with the occupation factors of 47(1) and 53(1)%. The hydrogen atoms of the C$_2$H$_4$ unit were not located. Selected crystallographic data are listed in Table 1[38].

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[38] Further details of the X-ray structure analyses are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD 404293 [$Fe(CO)_2$('CO_2Me-S_4')], CSD 404294 'CO_2Me-S_4'-H_2, CSD 404292 $(AsPh_4)_2$[Fe('CO_2Me-S_2')$_2$], the names of the authors, and the journal citation.

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