Functionalized 1,1-Ethenedithiolates as Ligands, III[1]

Palladium(II) and Platinum(II) Complexes with Ferrocenyl-Substituted 1,1-Ethenedithiolate Ligands. Crystal Structure Analyses of *cis*-$(Ph_3P)_2M[S_2C=CH-C(O)-(\eta^5$-$C_5H_4)Fe(\eta^5$-$C_5H_5)]$ (M = Pd, Pt)☆

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The ferrocenyl-substituted mono- (**3**) and 1,1′-bis-dithiocarboxylic acids (**4**) have been prepared. These acids react with L_2MCl_2 (M = Pd, Pt; L = PEt_3, PPh_3, and 1/2 dppe) in the presence of sodium acetate to give the *cis* heterodi- and heterotrimetallic complexes *cis*-$L_2M[S_2C=CH-C(O)-(\eta^5$-$C_5H_4)Fe(\eta_5$-$C_5H_5)]$ (**5a**: M = Pd, L = PPh_3; **5b**: M = Pt, L = PPh_3; **5c**: M = Pt, L = 1/2 dppe) and [*cis*-$L_2MS_2C=CH-C(O)-(\eta^5$-$C_5H_4)]_2Fe$ (**6a**: M = Pd, L = PPh_3; **6b**: M = Pt, L = PEt_3; **6c**: M = Pt, L = PPh_3; **6d**: M = Pt, L = 1/2 dppe). The structures of **5a** and **5b** have been determined by single-crystal X-ray diffraction.

The synthesis of heterodi- and heterotrimetallic compounds has received much attention in recent years[2]. The impetus stems from the observation that polynuclear complexes may play an important role in catalytic processes[3]. Furthermore, they may exhibit antiferromagnetic interactions [Mn(II)/Cu(II); Cr(III)/Fe(II)][4] and electrical conductivity[5].

In this paper we report on the synthesis, characterization, and X-ray analyses of heterodi- and heterotrimetallic complexes *cis*-$(R_3P)_2ML$ (M = Pd, Pt) containing ferrocenyl-substituted 1,1-ethenedithiolato ligand (L = $[(\eta^5$-$C_5H_5)$-$Fe(\eta^5$-$C_5H_4-C(O)-CH=CS_2)]^{2-}$ and 1/2 $[Fe(\eta^5C_5H_4-C(O)-CH=CS_2)_2]^{4-}$).

Results and Discussion

We have recently prepared 1,1-ethenedithiolate complexes of Ni(II), Pd(II), and Pt(II) from *para*-substituted β-hydroxydithiocinnamic acids *p*-$R-H_4C_6-C(OH)=CH-CSSH$ (R = H, C_nH_{2n+1}, OC_nH_{2n+1}) and L_2MCl_2 (L = phosphane, phenanthroline)[1,6]. Moreover, ferrocenyl-substituted mono- (**3**) and bisdithiocarboxylic acids (**4**) have been prepared in a one-step synthesis by treating THF solutions of acetyl- (**1**) or 1,1′-diacetylferrocene (**2**) with potassium *tert*-butoxide at 0°C, adding carbon disulfide and protonating the red di- or tetraanion, respectively, with a diluted hydrogen chloride solution. The resulting acids **3** and **4** are deep violet microcrystalline solids. The IR absorptions of the SH group (2465/2540 cm^{-1}) are in accordance with other data reported in ref.[7]. Also, the strong UV absorptions [λ_{max} = 400 (4.28)/382 (4.39) nm] as well as the very intensive thiocarbonyl IR absorption at 1244/1246 cm^{-1} are typical of thiocarbonyl compounds[7].

The heterodi- and the heterotrimetallic complexes **5a**–**6d** have been prepared by the reaction of L_2MCl_2 (M = Pd, Pt; L = PEt_3, PPh_3, and 1/2 dppe) with **3** or **4** in CH_2Cl_2 in the presence of sodium acetate. The products are air-stable orange-red compounds which can be recrystallized from dichloromethane/hexane.

The IR spectra (experimental) show medium ν(C=O) vibrations in the range of 1610–1616 cm^{-1}. The very strong band at about 1480 cm^{-1} can be assigned to a coupling of the C=C and C=O vibration; these values are comparable to those observed for other 1,1-ethenedithiolates[1,6,8]. SH and C=S bands are not observed in accordance with the 1,1-ethenedithiolato structure.

The ^1H-NMR data of the complexes **6a**–**d** (see Experimental) are typical of 1,1′-disubstituted ferrocene systems[9]. Two pseudotriplets are observed for the cyclopentadienyl ring protons, which are slightly deshielded in comparison with those of the unsubstituted ring of **5a**–**c**. The resonances of the vinylic protons in **3** and **4** are found at about δ = 7; these signals are shifted upfield in **5a**–**c** and **6a**–**d** by 0.7–1 ppm.

The ^{13}C-NMR spectrum (see Experimental) of **3** shows signals at δ = 105.50 for the –CH= fragment, at δ = 182.98 for C–OH, and at 202.45 for the CSS group. In the 1,1-ethenedithiolato complexes **5a**–**c**, **6b** the resonances for the vinylic carbons are shifted downfield (Δδ ≈ 15). The

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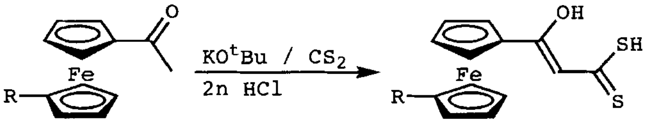
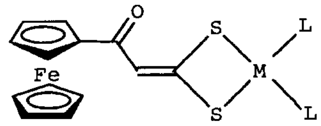
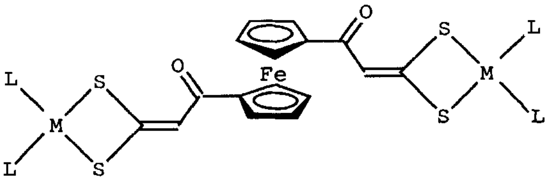


1: R = H
2: R = C(O)CH$_3$

3: R = H
4: R = C(OH)CHCSSH



5a: M = Pd, L = PPh$_3$
5b: M = Pt, L = PPh$_3$
5c: M = Pt, L = 1/2 dppe



6a: M = Pd, L = PPh$_3$
6b: M = Pt, L = PEt$_3$
6c: M = Pt, L = PPh$_3$
6d: M = Pt, L = 1/2 dppe

resonance for the dithiocarboxylic carbon (C=CSS), which is found at about δ = 182, is significantly shielded as compared to the corresponding signals of **3** and other substituted β-hydroxy dithiocinnamic acids[1,6]. However, the signal due to the carbonyl carbon is shifted downfield by 2–7 ppm.

The ^{31}P-NMR spectra (see Experimental) indicate that the two phosphorus atoms are non-equivalent (AB spin pattern).

Crystal Structures of *cis*-(Ph$_3$P)$_2$M[S$_2$C=CH−C(O)−(η^5-C$_5$H$_4$)Fe(η^5-C$_5$H$_5$)] · S (M = Pd, S = CH$_2$Cl$_2$; M = Pt, S = CHCl$_3$) in the Solid State

The molecular structures of **5a** and **5b** are depicted in Figures 1 and 2. In these complexes the palladium and platinum atoms are in a square-planar environment (mean deviation from plane 0.17 pm) with two *cis*-positioned phosphorus and two sulfur atoms. The two cyclopentadienyl rings are eclipsed. The cyclopentadienyl ring C(40)−C(44) and the plane Pt,S(1),S(2),P(1),P(2) are tilted in **5b** with respect to each other, the interplanar angle being 21.9°. The Pt−S bond lengths are 235.1(3) and 234.0(3) pm in **5b**, comparable values are found in *cis*-(Ph$_3$P)$_2$Pt-[S$_2$C=CH−C(O)−C$_6$H$_5$][1]. The C(1)−C(2), C(2)−C(3), C(3)−O, C(3)−C(4), and C(37)−C(38), C(38)−C(39), C(39)−O, C(39)−C(40) bond distances, respectively, are similar to those in *cis*-(Ph$_3$P)$_2$Pt[S$_2$C=CH−C(O)−C$_6$H$_5$][1].

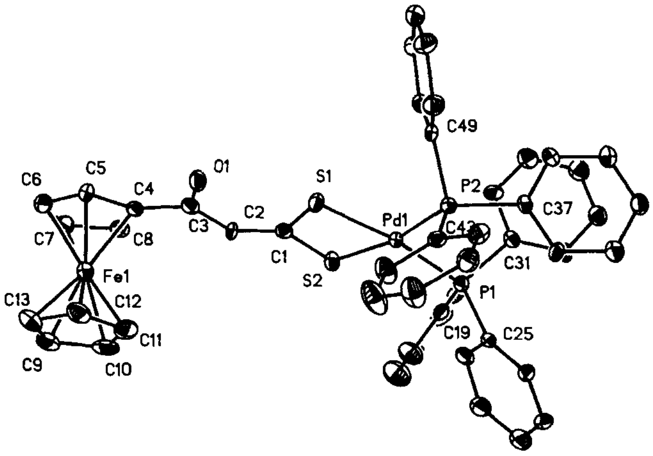


Figure 1. A view of the molecular structure of **5a** in the crystal. Selected bond lengths [pm] and angles [°]: Pd−P(1) 231.5(2), Pd−P(2) 232.5(1), Pd−S(1) 232.7(1), Pd−S(2) 231.5(1), S(1)−C(1) 173.2(4), S(2)−C(1) 175.7(6), C(1)−C(2) 136.1(5), C(2)−C(3) 144.3(8), C(3)−C(4) 149.4(5), O−C(3) 123.3(6). P(1)−Pd−P(2) 97.7(1), S(1)−Pd−S(2) 74.4(1), Pd−S(1)−C(1) 89.3(2), Pd−S(2)−C(1) 89.0(1), S(1)−C(1)−S(2) 107.1(2)

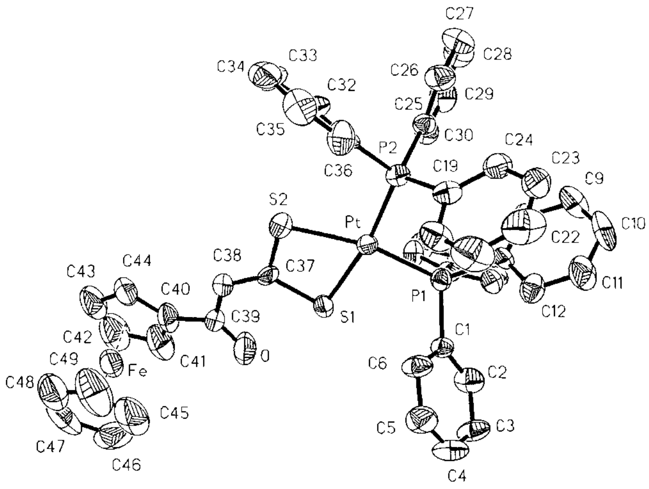


Figure 2. A view of the molecular structure of **5b** in the crystal. Selected bond lengths [pm] and angles [°]: Pt−P(1) 228.5(3), Pt−P(2) 228.6(3), Pt−S(1) 235.1(3), Pt−S(2) 234.0(3), S(1)−C(37) 174.3(11), S(2)−C(37) 175.5(10), C(37)−C(38) 137.2(14), C(38)−C(39) 145.4(16), C(39)−C(40) 149.1(15), O−C(39) 121.6(15). P(1)−Pt−P(2) 99.1(1), S(1)−Pt−S(2) 74.3(1), Pt−S(1)−C(37) 88.5(3), Pt−S(2)−C(37) 88.6(4), S(1)−C(37)−S(2) 108.1(5)

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Experimental

All experiments were performed under dry, oxygen-free nitrogen in distilled solvents using Schlenk technique. Compounds **5b**, **c**, **6b**, **c** were dried in vacuo (<10^{-3} Torr), **5a**, **6a**, **d** in a vacuum desiccator. – IR (KBr): (a): Nicolet ZDX 5, (b): Bruker IFS 45. – UV/Vis: Zeiss DMR 10. – ^{1}H NMR (internal standard TMS), ^{13}C NMR (internal standard TMS), ^{31}P NMR (external standard 85% aqueous H$_3$PO$_4$): (c) Bruker WP 80, (d) Bruker AC 200, (e) Jeol GSX 270, (f) Jeol EX 400. – Cyclic voltammetry: Bioanalytical

Systems, CV-1B. All measurements were performed in dichloromethane solutions ($c = 10^{-3}$ mol/l) with $(Bu_4N)PF_6$ ($c = 10^{-1}$ mol/l) as supporting electrolyte. A platinum electrode was used as the working electrode, and values were recorded relative to a standard Ag/AgCl/NaCl (c = 3 mol/l). Sweep rates varied from 150, 250 to 350 mV/s.

3-Ferrocenyl-3-hydroxydithioacrylic Acid (**3**): Acetylferrocene (**1**)[10] (2.71 g, 11.8 mmol) was added to a suspension of potassium *tert*-butoxide in 100 ml of THF. After stirring for 1 h at 0°C, 0.90 ml (12 mmol) of carbon disulfide was added dropwise. The deep red mixture was stirred for 4 h at room temp., then poured into ice-cold water, and acidified (pH = 2) with a diluted hydrogen chloride solution (c = 2 mol/l). The emulsion was mixed with 100 ml of chloroform and the aqueous phase extracted with chloroform (2 × 50 ml). The combined organic phases were dried with $MgSO_4$. The filtrate was concentrated, and **3** was isolated as a deep-violet microcrystalline powder, which was recrystallized from chloroform/hexane yielding 2.71 g (75.4%), m.p. 101–104°C. – IR (b): $\tilde{\nu}$ = 2465 (m) cm^{-1} (SH), 1244 (vs) (C=S). – UV ($CHCl_3$): λ_{max} (lg ε) = 323 nm (4.11), 400 (4.28), 539 (3.68). – ^1H NMR (c, $CDCl_3$): δ = 4.20 (s, 5H, C_5H_5), 4.60/4.84 (m, 4H, C_5H_4), 6.55 (s, 1H, SH), 7.00 (s, 1H, –CH=). – ^{13}C NMR (d, $CDCl_3$): δ = 69.03 (s, C_5H_5), 70.21/71.15 (s, C-2,5/C-3,4), 73.97 (s, C-1), 105.50 (s, –CH=), 182.28 (s, C–OH), 202.45 (s, CSSH). – CV (g): E = +0.70 V (quasireversible). – $C_{13}H_{12}FeOS_2$ (304.2): calcd. C 51.33, H 3.98, S 21.08; found C 50.76, H 3.79, S 20.75.

3,3'-(Ferrocene-1,1'-diyl)bis(3-hydroxydithioacrylic Acid) (**4**): **4** was prepared in a manner similar to that described above for **3**. 4.49 g (40.0 mmol) of potassium *tert*-butoxide in 50 ml of THF, 2.70 g (10.0 mmol) of 1,1'-diacetylferrocene[10], 1.21 ml (20.0 mmol) of carbon disulfide; dark-violet solid, yield: 2.72 g (64%), m.p. 138–140°C. – IR (b): $\tilde{\nu}$ = 2540 (w) cm^{-1} (SH), 1246 (vs) (C=S). – UV ($CHCl_3$): λ_{max} (lg ε) = 325 nm (4.32), 382 (4.39), 543 (3.69). – CV (g): E = 0.88 V (quasireversible). – $C_{16}H_{14}FeO_2S_2$ (422.4): calcd. C 45.50, H 3.34, S 30.26; found C 45.41, H 3.62, S 30.21.

Preparation of the Palladium(II) and Platinum(II) Complexes **5a–c** *and* **6a–d**: A solution of **3** (0.20–0.43 mmol) or **4** (0.10–0.22 mmol) in dichloromethane was added dropwise to a solution of L_2MCl_2 (M = Pd, Pt; L = PEt_3[11], PPh_3[12], 1/2 dppe[13]) (0.20–0.43 mmol) in dichloromethane in the presence of sodium acetate. After stirring for 3 d at room temp., the mixture was filtered over Celite. The solvent was removed, and the remaining bright brownish crude product was recrystallized from dichloromethane/hexane to afford an orange-red crystalline solid.

cis-$(Ph_3P)_2Pd[S_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (**5a**): 0.30 g (0.43 mmol) of $(Ph_3P)_2PdCl_2$, 0.07 g (0.86 mmol) of NaOAc in 5 ml of dichloromethane, 0.13 g (0.43 mmol) of **3** in 20 ml of dichloromethane; yield 0.30 g (75%) of **5a**, m.p. 220°C. – IR (b): $\tilde{\nu}$ = 1610 (m) cm^{-1} (C=O), 1480 (vs) (C=C). – UV ($CHCl_3$): λ_{max} (lg ε) = 330 nm (4.39), 364 (4.44), 455 (3.60). – ^1H NMR (c) ($CDCl_3$): δ = 4.19 (s, 5H, C_5H_5), 4.42/4.96 (m, 4H, C_5H_4), 6.31 (s, 1H, –CH=), 7.48 (m_c, 30H, C_6H_5). – ^{13}C NMR (d) ($CDCl_3$): δ = 68.89 (s, C_5H_5), 69.57/70.62 (s, C-2,5/C-3,4), 83.22 (s, C-1), 120.09 [d, $^4J(^{31}P^{13}C)$ = 4.7 Hz, –CH=], 182.21 (s, S_2C=C), 184.75 (s, C=O). – ^{31}P NMR (e) ($CHCl_3$): δ = 29.45/29.89 (AB spin system, J = 48.4 Hz). – CV (g): E = +0.57 V (reversible). – $C_{49}H_{40}FeOP_2PdS_2 \cdot 0.5\,CH_2Cl_2$ (975.5): calcd. C 60.32, H 4.23, S 6.56; found C 60.34, H 4.24, S 6.14.

cis-$(Ph_3P)_2Pt[S_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (**5b**): 0.237 g (0.30 mmol) of $(Ph_3P)_2PtCl_2$, 49 mg (0.60 mmol) of NaOAc in 5 ml of dichloromethane, 91 mg (0.30 mmol) of **3** in 7 ml of dichloromethane; orange-red plates, yield 0.24 g (79%) of **5b**. – IR (a): $\tilde{\nu}$ = 1617 (m) cm^{-1} (C=O), 1482/1491 (vs) (C=C). – UV (CH_2Cl_2): λ_{max} (lg ε) = 372 nm (4.42), 457 (3.65). – ^1H NMR (e) (CD_2Cl_2): δ = 4.14 (s, 5H, C_5H_5), 4.32/4.61 (t, N = 3.7, 4H, C_5H_4), 5.94 [s with ^{195}Pt satellites, $^4J(^{195}Pt^1H)$ = 4.0 Hz, 1H, –CH=], 7.20–7.50 (m, 30H, C_6H_5). – ^{13}C NMR (e) (CD_2Cl_2): δ = 69.56 (s, C_5H_5), 68.72/70.86 (s, C-2,5/C-3,4), 83.80 (s, C-1), 120.10 [d, $^4J(^{31}P^{13}C)$ = 7.1 Hz, –CH=], 178.18 (s, S_2C=C), 188.86 (s, C=O). – ^{31}P NMR (e) ($CHCl_3$): δ = 29.45/29.89 [AB spin system with ^{195}Pt satellites, J = 22.8 Hz, $J(^{195}Pt^{31}P)$ = 2900/3126 Hz]. – CV (g): E = +0.57 V (reversible). – $C_{49}H_{40}FeOP_2PtS_2$ (1021.8): calcd. C 57.59, H 3.94, S 6.26; found C 57.07, H 4.13, S 6.04.

cis-dppePt$[S_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)]$ (**5c**): 0.20 g (0.30 mmol) of $dppePtCl_2$, 0.05 g (0.6 mmol) of NaOAc in 5 ml of dichloromethane, 0.09 g (0.3 mmol) **3** in 15 ml of dichloromethane; small orange-red plates, yield 0.16 g (60.0%) of **5c**, m.p. 255–258°C. – IR (b): $\tilde{\nu}$ = 1616 (m) cm^{-1} (C=O), 1487 (vs) (C=C). – UV ($CHCl_3$): λ_{max} (lg ε) = 366 nm (4.35), 383 (4.31), 454 (3.44). – ^1H NMR (c) ($CDCl_3$): δ = 2.24/2.70 (m, 4H, CH_2CH_2), 4.13 (s, 5H, C_5H_5), 4.30/4.70 (m, 4H, C_5H_4), 6.08 (s, 1H, –CH=), 7.64 (m_c, 24H, C_6H_5). – ^{13}C NMR (d) ($CDCl_3$): δ = 68.9 (s, C_5H_5), 69.7/70.8 (s, C-2,5/C-3,4), 83.8 (s, C-1), 122.0 (s, –CH=), 182.3 (s, S_2C=C), 189.4 (s, C=O). – CV (g): E = +0.57 V (reversible). – $C_{39}H_{34}FeOP_2PtS_2$ (895.7): calcd. C 52.30, H 3.83, S 7.16; found C 51.95, H 3.91, S 7.16.

$[cis\text{-}(Ph_3P)_2PdS_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)]_2Fe$ (**6a**): 0.20 g (0.28 mmol) of $(Ph_3P)_2PdCl_2$, 0.05 g (0.6 mmol) of NaOAc in 5 ml of dichloromethane, 0.06 g (0.14 mmol) of **4** in 15 ml of dichloromethane, orange-yellow powder, yield 0.22 g (33.8%) of **6a**, m.p. 225–228°C. – IR (b): $\tilde{\nu}$ = 1610 (m) cm^{-1} (C=O), 1480 (vs) (C=C). – UV (DMSO): λ_{max} (lg ε) = 389 nm (4.66). – ^1H NMR (c) ($CDCl_3$): δ = 4.23/4.58 (m, 4H, C_5H_4), 6.04 (s, 1H, –CH=), 7.48 (m_c, 30H, C_6H_5). – $C_{88}H_{70}FeO_2P_4Pd_2S_4 \cdot 0.5\,CH_2Cl_2$ (1723): calcd. C 61.69, H 4.25, S 7.45; found C 61.46, H 4.45, S 7.43.

$[cis\text{-}(Et_3P)_2PtS_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)]_2Fe$ (**6b**): 0.10 g (0.2 mmol) of $(Et_3P)_2PtCl_2$, 33 mg (0.4 mmol) of NaOAc in 5 ml of dichloromethane, 40 mg (0.1 mmol) of **4** in 7 ml of dichloromethane; orange-red powder, yield 79 mg (31.0%) of **6b**. – IR (a): $\tilde{\nu}$ = 1614 (s) cm^{-1} (C=O), 1485/1454 (vs) (C=C). – UV (CH_2Cl_2): λ_{max} (lg ε) = 278 nm sh (4.50), 390 (4.62), 492 sh (3.57). – ^1H NMR (f) (CD_2Cl_2): δ = 1.12–1.19 (m, 18H, PCH_2CH_3), 1.81–1.90 (m, 12H, PCH_2CH_3), 4.34/4.70 (m, 4H, C_5H_4), 6.01 (s, 1H, –CH=). – ^{13}C NMR (f) (CD_2Cl_2, int. standard CD_2Cl_2): δ = 69.82/73.44 (s, C-2,5/C-3,4), 84.67 (s, C-1), 121.09 [d, $^4J(^{31}P^{13}C)$ = 4.7 Hz, –CH=], 182.47 (s, S_2C=C), 188.02 (s, C=O). – ^{31}P NMR (e) (CH_2Cl_2): δ = 3.76/4.30 [AB spin system with ^{195}Pt satellites, J = 21.5, $J(^{195}Pt^{31}P)$ = 2802/2980 Hz]. – $C_{40}H_{70}FeO_2P_4Pt_2S_4$ (1281): calcd. C 37.50, H 5.51, S 10.01; found C 37.12, H 5.80, S 9.85.

$[cis\text{-}(Ph_3P)_2PtS_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)]_2Fe$ (**6c**): 158 mg (0.2 mmol) of $(Ph_3P)_2PtCl_2$, 33 mg (0.4 mmol) of NaOAc in 10 ml of dichloromethane, 40 mg (0.1 mmol) of **4** in 5 ml of dichloromethane; red powder, yield 124 mg (33.4%) of **6c**. – IR (a): $\tilde{\nu}$ = 1617 (m) cm^{-1} (C=O), 1482 (vs) (C=C). – UV (CH_2Cl_2): λ_{max} (lg ε) = 395 nm (4.64), 490 (3.73). – ^1H NMR (e) ($CDCl_3$): δ = 4.27/4.64 (t, N = 3.6 Hz, 4H, C_5H_4), 5.95 (s, 1H, –CH=), 7.14–7.52 (m, 30H, C_6H_5). – ^{31}P NMR (e) ($CHCl_3$): δ = 18.80/20.54 [AB spin system with ^{195}Pt satellites, J = 22.2, $J(^{195}Pt^{31}P)$ = 2897/3118 Hz]. – $C_{88}H_{70}FeO_2P_4Pt_2S_4$ (1858): calcd. C 56.88, H 3.81, S 6.89; found C 55.97, H 3.56, S 6.47.

$[cis\text{-}dppePtS_2C{=}CH{-}C(O){-}(\eta^5\text{-}C_5H_4)]_2Fe$ (**6d**): 0.20 g (0.30 mmol) of $dppePtCl_2$, 50 mg (0.60 mmol) of NaOAc in 5 ml of

dichloromethane, 60 mg (0.15 mmol) of **4** in 15 ml of dichloromethane; orange-red powder, yield 90 mg (36.4%) of **6d**. – IR (b): $\tilde{\nu}$ = 1616 (s) cm^{-1} (C=O), 1485 (vs) (C=C). – UV (DMSO): λ_{max} (lg ε) = 383 nm (4.53). – $C_{68}H_{58}FeO_2P_4Pt_2S_4 \cdot CH_2Cl_2$ (1605): calcd. C 49.03, H 3.58, S 7.59; found C 49.06, H 3.57, S 7.68.

Crystal Structure Determination **5a**[14]: Plates from a dichloromethane/hexane solution. $C_{50}H_{40}Fe_2OP_2PdS_2 \cdot CH_2Cl_2$, M_r = 1018.0, crystal size: 0.15 × 0.2 × 0.25 mm, space group $P\bar{1}$ (Nr. 2); Z = 2, a = 13.761(3), b = 14.137(4), c = 14.676(4) Å; α = 104.68(2), β = 103.63(2), γ = 115.60(2)°; V = 2287.4(4) Å^3, d_{calcd} = 1.478 g/cm^3, diffractometer: Siemens R3m/V, radiation: graphite-monochromated Mo-K_α (λ = 0.71073 Å), T = 294 K, 2Θ range: 4–46°, variable scan speed in the range of 1.00 to 3.00°/min., scan mode: ω, reflections collected: 4470, independent reflections: 4067, observed reflections: 3785 with $|F| > 4.0\sigma_{|F|}$, R_{int} = 0.0075, index ranges: $-13 \leq h \leq 12$, $-13 \leq k \leq 13$, $0 \leq l \leq 14$, program system used: SHELXTL-PLUS. Direct methods, weighting scheme: $w^{-1} = \sigma^2_{|F|}$, hydrogen atoms: U_{iso}, nonhydrogen atoms were refined anisotropically, R = 0.0252, R_w = 0.0233, R_g = 0.0253, extremes of a final difference Fourier synthesis: +0.54/−0.34 e · 10^{-6} pm^{-3}.

Crystal Structure Determination **5b**[14]: Brown-orange plates from chloroform/hexane. $C_{50}H_{40}Fe_2OP_2PtS_2 \cdot CHCl_3$, M_r = 1141.2, crystal size: 0.22 × 0.16 × 0.04 mm, space group $P\bar{1}$ (Nr. 2); Z = 2, a = 11.135(4), b = 14.346(6), c = 15.144(5) Å; α = 77.09(3), β = 86.80(3), γ = 83.14(3)°; V = 2340.2(15) Å^3, d_{calcd} = 1.619 g/cm^3, diffractometer: Siemens R3m/V, radiation: graphite-monochromated Mo-K_α (λ = 0.71073 Å), temperature 295 K, 2Θ range: 5–50°, variable scan speed in the range of 1.20 to 14.65°/min, scan mode: ω, reflections collected: 8794, independent reflections: 8139, observed reflections: 6282 with $|F| > 3.0\sigma_{|F|}$, R_{int} = 0.0185, index ranges: $0 \leq h \leq 13$, $-16 \leq k \leq 17$, $-18 \leq l \leq 18$, absorption correction: face-indexed numerical, min./max. transmission: 0.5750/0.8668; program system used: SHELXTL-PLUS. Direct methods, weighting scheme: $w^{-1} = \sigma^2_{|F|}$ hydrogen atoms: U_{iso}, nonhydrogen atoms were refined anisotropically, final residuals (observed data): R = 0.0658, R_w = 0.0483, R_g = 0.0420, extremes of the final difference Fourier synthesis: +1.66/−1.41 e · 10^{-6} pm^{-3}.

☆ Dedicated to Professor Dr. Dr. h. c. mult. *E. O. Fischer* on the occasion of his 75th birthday.

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[14] Further details concerning the crystal structure analysis are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57761, the names of the authors, and the journal citation.

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