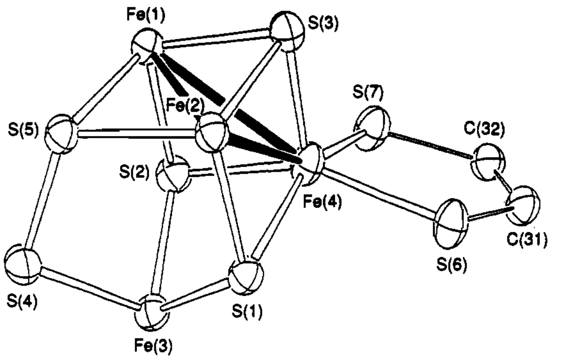

Figure 2. ORTEP drawing of the Fe_4S_5 core of $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^+$ (3) with a dithiolene chelate ring. Thermal ellipsoids are plotted at the 30% probability level. Selected distances (Å): Fe(1)–Fe(2), 2.736 (2); Fe(1)···Fe(3), 3.760 (2); Fe(1)–Fe(4), 2.783 (1); Fe(2)···Fe(3), 3.765 (2); Fe(2)–Fe(4), 2.767 (2), Fe(3)···Fe(4), 3.047 (2).

crystals used for the X-ray structural analysis were grown by means of layering hexane on a solution of 2 in THF.[10]

The structure of the Fe_4S_5 core of 2 with the dithiolene chelate ring is shown in Figure 1. Three (η-C_5Me_5) ligands coordinate to Fe(1), Fe(2), and Fe(3), while one dithiolene ligand coordinates to Fe(4). The Fe_4S_5 core of 2 consists of four Fe atoms, three μ_3-S ligands, and one μ_3-S_2 ligand. The μ_3-S_2 ligand is located on the opposite side of the core from the dithiolene ligand. It was found that the interatomic separations Fe(1)–Fe(4) (2.716 (1) Å) and Fe(2)–Fe(4) (2.725 (1) Å) were significantly smaller than the other four Fe–Fe distances (3.300 (1)–3.769 (1) Å). The former values are in the range expected for an Fe–Fe single bond. The plane of the dithiolene–Fe(4) chelate ring is nearly coplanar with that containing two Fe–Fe bonds. This phenomenon is also observed in both 1[4] and the monocation salt of 2, $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5](PF_6)$ (3) (vide infra). Three Fe atoms are arranged in a V-shaped configuration with the Fe atom having the dithiolene ligand, on Fe(4), at the apex. The coordination mode of μ_3-S_2 to the three iron atoms of 2 and 3 (see Figure 2) is different from that found in $[Cp_4Fe_4S_5]^+$[11] and $[Cp_4Fe_4S_5]^{2+}$.[12] In the former complexes, one of the S_2 sulfur atoms is bonded to two iron atoms, and the other is bonded to the third iron atom. In the latter complexes, the S_2 ligand is bonded to an iron atom in a "side-on" manner, with each of its sulfur atoms bonded to one other iron atom.

The ^1H NMR spectrum of 2 shows characteristically broad signals at δ 7.5 and 6.8 (Ph), 2.8 (two η-C_5Me_5's), and –0.5 ppm (one η-C_5Me_5). These line broadenings and shifts of signals are consistent with the paramagnetic nature of 2 as predicted from the skeletal electron counting[13] (2 has 19 skeletal electrons).

The cyclic voltammogram of 2 exhibits four reversible one-electron redox waves at +1.19, +0.58, –0.14, and –0.90 V vs SCE in CH_2Cl_2 solution containing 0.1 M n-Bu_4NBF_4 as supporting electrolyte. The resting potential was around –0.20 V vs SCE. These results indicate the existence of five discrete species $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^n$ for which n = 3+, 2+, 1+, 0, and 1–.

The reaction of 2 with 1 equiv of $[Cp_2Fe](PF_6)$ in CH_2Cl_2 afforded the monocation salt 3 in 77% yield.[14] The ORTEP drawing of the Fe_4S_5 core of 3[15] with the dithiolene chelate ring is shown in Figure 2. In the Fe_4S_5 core of 3, there are three Fe–Fe bonds, which combine three iron atoms (Fe(1), Fe(2), and Fe(4)). The remaining three Fe···Fe distances are longer than 3.0 Å, suggesting the absence of Fe–Fe bonds. The structural change of the Fe_4S_5 core of 2 which accompanies one-electron oxidation, in particular the increase in the total Fe–Fe bond order resulting from bond formation between Fe(1) and Fe(2), strongly suggests that the electron was removed from a metal-based antibonding orbital.

Supplementary Material Available: Tables of crystal data, atomic positional and thermal parameters, and bond distances and bond angles and ORTEP diagrams for 2 and 3 (32 pages); listings of observed and calculated structure factors for 2 and 3 (84 pages). Ordering information is given on any current masthead page.

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(9) Anal. Calcd for $C_{44}H_{55}Fe_4S_7$: C, 51.22; H, 5.37. Found: C, 51.27; H, 5.34. MS (FAB, m-nitrobenzylalcohol matrix, Xe): m/z 1031 (M^+). ^1H NMR (200 MHz, $CDCl_3$): δ 7.5 (6 H, br, $W_{1/2}$ = 9 Hz, Ph), 6.8 (4 H, br, $W_{1/2}$ = 10 Hz, Ph), 2.8 (30 H, br, $W_{1/2}$ = 21 Hz, Me), –0.5 (15 H, br, $W_{1/2}$ = 46 Hz, Me).

(10) Crystal data for 2·THF: $C_{48}H_{63}Fe_4OS_7$, F_w = 1103.9, monoclinic, space group $P2_1/c$, a = 17.302 (3) Å, b = 17.639 (2) Å, c = 17.099 (3) Å, β = 102.99 (3)°, V = 5085 (1) Å^3, Z = 4, D_c = 1.44, D_m = 1.44 g cm^{-3}, μ (Mo Kα) = 14.56 cm^{-1}. Diffraction data were collected with the ω–2θ scan mode, at 21 °C. The structure was solved by the standard heavy atom method. Block-diagonal least-squares refinement led to convergence with a final R value of 0.058 for 8164 reflections $[|F_o| > 3\sigma(F_o)]$ out of 15 293 measured (3 ° < 2θ < 60°).

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(14) Anal. Calcd for $C_{50}H_{67}F_6Fe_4O_2PS_7$ (3·2$(CH_3)_2CO$): C, 46.45; H, 5.22. Found: C, 46.27; H, 5.01. MS (FAB, m-nitrobenzylalcohol matrix, Xe): m/z 1031 (M^+). ^1H NMR (200 MHz, $CDCl_3$): δ 7.8–7.5, 7.2–6.7 (10 H, m, Ph), 3.6 (30 H, br, $W_{1/2}$ = 52 Hz, Me), –1.7 (15 H, br, $W_{1/2}$ = 67 Hz, Me).

(15) Crystal data for 3·2$(CH_3)_2CO$: $C_{50}H_{67}F_6Fe_4O_2PS_7$, F_w = 1292.9, triclinic, space group $P\bar{1}$. a = 14.112 (4) Å, b = 17.712 (3) Å, c = 13.325 (4) Å, α = 108.08 (2)°, β = 114.74 (3)°, γ = 84.00 (2)°, V = 2874 (1) Å^3, Z = 2, D_c = 1.49, D_m = 1.49 g cm^{-3}, μ (Mo Kα) = 13.44 cm^{-1}. Diffraction data were collected with the ω–2θ scan method, at 21 °C. The structure was solved by direct methods. Block-diagonal least-squares refinement led to convergence with a final R value of 0.066 for 9747 reflections $[|F_o| > 6\sigma(F_o)]$ out of 16 771 measured (3° < 2θ < 60°).

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Synthesis of Cationic Ruthenium Thiobenzaldehyde Complexes through β-Hydride Abstraction[1]

The heteroaldehydes RHC═E (E = S, Se, Te) are classical examples of the instability of π bonds involving heavier elements.[2] Their pronounced tendency to oligomerize can be suppressed either by introducing sterically demanding groups R[3] or by coordinating to a transition metal.[4-8] Complexes of thioaldehydes are particularly interesting since they offer the opportunity to selectively tailor the reactivity of the C═S function.[5] Two fairly general syntheses of heteroaldehyde complexes have been developed in

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(1) Communication 9 of the series The Coordination Chemistry of the C═S Function. Communication 8: Schenk, W. A.; Kuemmerle, D.; Burschka, C. *J. Organomet. Chem.* **1988**, *349*, 183.

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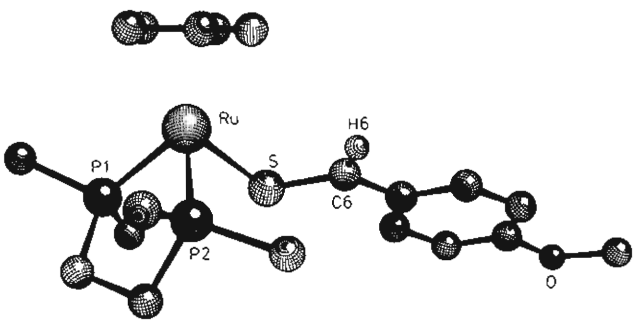
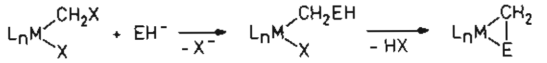
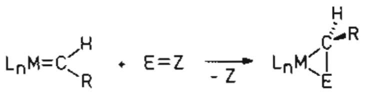


Figure 1. Structure of the cation of [cpRu(dppe) (S = CHC_6H_4OMe)]PF_6·$0.5Et_2O$ (**4c**) in the crystal. For reasons of clarity only C(ipso) of the phenyl groups on phosphorus is shown. Selected bond distances (in Å) and angles (in deg) (standard deviations in parentheses): Ru–P1 = 2.296 (1), Ru–P2 = 2.301 (1), Ru–S = 2.314 (1), Ru–ring centroid = 1.882 (1), S–C6 = 1.632 (5); P1–Ru–P2 = 83.78 (4), P1–Ru–S = 89.71 (5), P2–Ru–S = 89.30 (4), Ru–S–C6 = 112.0 (2), S–C6–C61 = 126.2 (4).

the past, both involving nucleophilic reactions: (i) substitution of X^- on halomethyl metal compounds (eq 1)[6] and (ii) E-transfer to electrophilic carbene complexes (eq 2).[7,8]

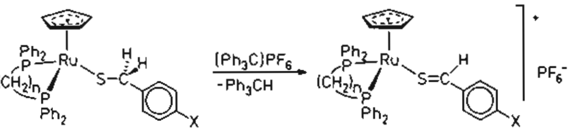


(1)



(2)

Here we report on a new and very simple access to thiobenzaldehyde complexes which is initiated by an electrophilic attack on a coordinated thiolate, similar to the synthesis of alkene complexes via β-hydride abstraction from transition metal alkyls.[9] Reaction of ruthenium thiolates **1** or **2** with $[Ph_3C]PF_6$ in dichloromethane at −70 °C (eq 3) is accompanied by an immediate color change to deep red. After chromatography over silica with 20:1 dichloromethane/acetone and crystallization from dichloromethane/ether, complexes **3** and **4** are isolated in 60–85% yield (all new compounds gave satisfactory elemental analyses). Triphenylmethane was detected by its ^1H-NMR signal at 5.46 ppm.



(3)

n\X	H	Cl	OMe
1	**1a**	**1b**	**1c**
2	**2a**	**2b**	**2c**

n\X	H	Cl	OMe
1	**3a**	**3b**	**3c**
2	**4a**	**4b**	**4c**

The new compounds contain η^1(S)-coordinated thioaldehyde ligands as evidenced by the low-field shift of both the ^1H- and ^{13}C-NMR signals of the CHS group (8.8 to 9.3 ppm and 193 to 213 ppm, respectively). Similar resonances have been found for $W(CO)_5(\eta^1\text{-}S{=}CHPh)$[8] whereas particularly the ^{13}C-NMR signals of η^2-thioaldehyde complexes appear at much higher field, e.g. at 30.5 ppm in $[cpRe(NO)(PPh_3)(\eta^2\text{-}CH_2S)]^+$.[7] Although there is the possibility that η^1- and η^2-isomers coexist in solution,[8] we have so far found no evidence supporting this. While the electron density on ruthenium might be sufficient to stabilize the side-on bonding mode, this would be disfavored by the bulkiness of the Cp and phosphine ligands surrounding the ruthenium atom.

Final proof of the η^1(S)-coordination comes from a crystal structure determination of **4c** (Figure 1).[11] The aryl group, the CHS unit, and the ruthenium atom are essentially coplanar with the bulky substituents at the C=S double bond occupying trans positions as expected. At 1.632 Å the C–S distance equals that in free thioformaldehyde (1.611 Å[12]) and is much shorter than in $[cpRe(NO)(PPh_3)(\eta^2\text{-}CH_2S)]^+$ (1.742 Å[7]).

The new thiobenzaldehyde complexes readily form [2 + 4] cycloadducts when treated with a large excess of cyclopentadiene in acetone at 35 °C (eq 4). Compounds **5** were purified by chromatography over silica with 20:1 dichloromethane/acetone. After crystallization from dichloromethane/ether they were isolated as yellow crystalline solids in 60–75% yield (satisfactory elemental analyses). The structure assignment of adducts **5** is based on comparison of their NMR data with those of the closely related pentacarbonyltungsten complexes.[5] Both phosphorus nuclei at ruthenium are diastereotopic since the addition of cyclopentadiene creates a stereocenter at the thioaldehyde carbon. The resonance of the proton at this carbon occurs around 3.8 ppm in all three cases, which seems to indicate that proton and aryl group of the former thioaldehyde occupy endo and exo positions, respectively, on the bicyclic ligand.[5] A final proof of this assignment, however, will have to await a crystal structure determination of one of these compounds.

(4)

5a–c

The rate of reaction 4 increases within the series with X = OMe < H < Cl. This would be expected for a Diels–Alder addition with "normal" electron demand and has been found also for the related pentacarbonyltungsten complexes.[13] The reaction of the dppe derivatives **4** with cyclopentadiene is much slower. We attribute this to steric effects: In dppm complexes the P–Ru–P angle is considerably smaller (cf. 70.4° in $[cpRu(dppm)(HS^tBu)]PF_6$[14]) than in their dppe analogues, which causes the phenyl groups on both phosphorus atoms to bend back and expose the thiocarbonyl function. Such a kind of steric interaction between the phenyl groups of a phosphorus ligand and the substrate is the predominant mechanism of chirality transfer in asymmetric syntheses and catalyses involving transition metal complexes.[15] Compounds similar to those described in this Communication but bearing chiral chelating diphosphines might therefore be suitable substrates for asymmetric Diels–Alder additions.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (SFB 347 "Selektive Reaktionen Metallaktivierter Moleküle") and the Fonds der Chemischen Industrie.

Supplementary Material Available: A table of selected NMR data for compounds **3–5** and an ORTEP plot and lists of atomic coordinates, bond distances, and bond angles for **4c** (11 pages). Ordering information is given on any current masthead page.

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(11) Dark red single crystals of **4c**·$0.5Et_2O$ were grown from dichloromethane/ether. Crystallographic data: triclinic, space group $P\bar{1}$, Z = 2 (2 formula units of **4c** and one molecule of ether per unit cell), a = 11.372 (4) Å, b = 12.782 (5) Å, c = 14.548 (4) Å, α = 70.33 (1)°, β = 80.61 (2)°, γ = 81.91 (2)°, V = 1945 Å^3, ρ_{calc} = 1.535 g/cm^3, Enraf Nonius CAD4 diffractometer, Mo Kα radiation (λ = 0.71073 Å), 5503 independent reflections with $2° < \theta < 23.5°$ collected, 5126 reflections with $I > 3\sigma(I)$ used in refinement, R = 0.042, R_w = 0.045.

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