Compound 2 crystallized in the monoclinic crystal system. The systematic absences observed during the collection of data (hkl, $h + k = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $h = 2n + 1$; $hk0$, $h + k = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) are consistent with either the centrosymmetric space group $C2/c$ or the noncentrosymmetric space group Cc. The successful solution and refinement of the structure confirmed the crystal belonged to the centrosymmetric space group $C2/c$. The coordination of metal atoms was obtained by direct methods (MULTAN), and remaining non-hydrogen atoms were subsequently obtained from difference electron density syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2).

Compound 5 crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2).

Compound 8 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2). The molecular structures with atomic labeling schemes, the bond lengths and angles are given in Figure 1 and Tables II and III for 2, Figure 2 and Tables IV and V for 5, and Figure 3, and Tables VI and VII for 8.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan.

Registry No. 1a, 61097-65-2; 1b, 111278-37-6; 2, 138061-90-2; 3, 138061-91-3; 4, 81740-70-7; 5, 138061-92-4; 6, 1000-86-8; 7, 32338-54-8; 8, 138061-93-5; 13, 138061-89-9; Ru, 7440-18-8; *tert*-butylthioketene, 54191-76-3.

Supplementary Material Available: For 2, 5, and 8, a textual presentation of experimental procedures and tables of experimental details, positional and thermal parameters, temperature factor expressions, root-mean-square amplitudes, and bond distances and angles (45 pages); listings of intensity data (31 pages). Ordering information is given on any current masthead page.

Thiolato Ligands Derived from Chiral Ferrocenylphosphines: Synthesis and Structure of the Trimeric Copper(I) Complex $[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-C}_5\text{H}_3(1\text{-PPh}_2)(2\text{-CH}(\text{CH}_3)\text{S}))\}\text{Cu}]_3$†

Antonio Togni* and Grety Rihs

Central Research Laboratories, CIBA-GEIGY Ltd., R-1060, P.O. Box, CH-4002 Basel, Switzerland

Ruth E. Blumer

Laboratorium für Anorganische Chemie, ETH-Zentrum, Universitätsstrasse 6, CH-8092 Zürich, Switzerland

Received August 28, 1991

The reaction of (R)-1-[(S)-(diphenylphosphino)ferrocenyl]ethyl acetate (**1a**) with KSAc in acetic acid leads to the corresponding thioacetate **4a** in 60% yield. This S_N1-type transformation occurs cleanly with retention of configuration. The use of other polar solvents was found to give (R)-1-[(S)-(diphenylthiophosphinyl)ferrocenyl]ethyl acetate (**6**) and only traces of the substitution product. The novel chelating, optically active ligand (R)-1-[(S)-(diphenylphosphino)ferrocenyl]ethyl mercaptan (**5a**) is obtained by treating **4a** with $LiAlH_4$ in Et_2O. The reaction of **5a** with $[CuOBu^t]_4$ (**10**) give the metathesis product $[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-C}_5\text{H}_3(1\text{-PPh}_2)(2\text{-CH}(\text{CH}_3)\text{S}))\}\text{Cu}]$ (**11**) in high yield. **11** was found to be very stable and rather unreactive. It is *trimeric* both in solution and in the solid state. Yellow-orange crystals of **11** are monoclinic, space group $P2_1$, with two molecules in a unit cell of dimensions $a = 13.206$ (1) Å, $b = 18.221$ (2) Å, $c = 16.028$ (1) Å, and $\beta = 113.13$ (1)°. The core of the trimeric complex is constituted by a Cu_3S_3 ring, which adopts a chairlike conformation. The substituents attached to this ring are pseudoequatorially arranged.

Introduction

Chiral ferrocenylphosphines of type 2 bearing a heteroatom-functionalized side chain have been shown, mainly by Hayashi, Kumada, and Ito, to be very effective ligands in numerous asymmetric homogeneous catalytic reactions.[1] The nature of the heteroatom substituent has been so far restricted to dialkylamino groups, mainly because of their ease of introduction starting from the acetate derivatives 1.[2] The reaction of 1 with an excess of a secondary amine occurs via an S_N1 mechanism, but with complete retention of configuration at the α-carbon atom of the side chain, due to the involvement of the configurationally stable

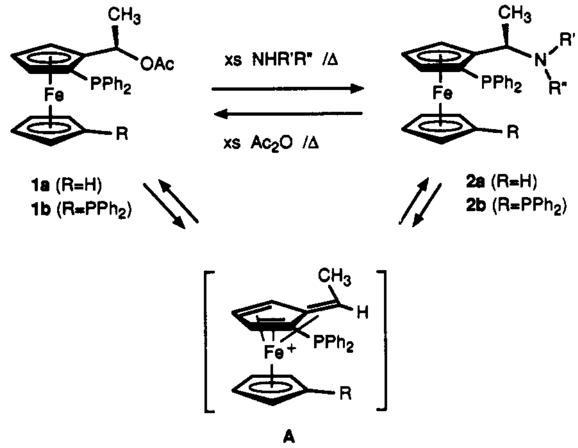
---

† Dedicated to Professor Luigi M. Venanzi on the occasion of his 65th birthday.

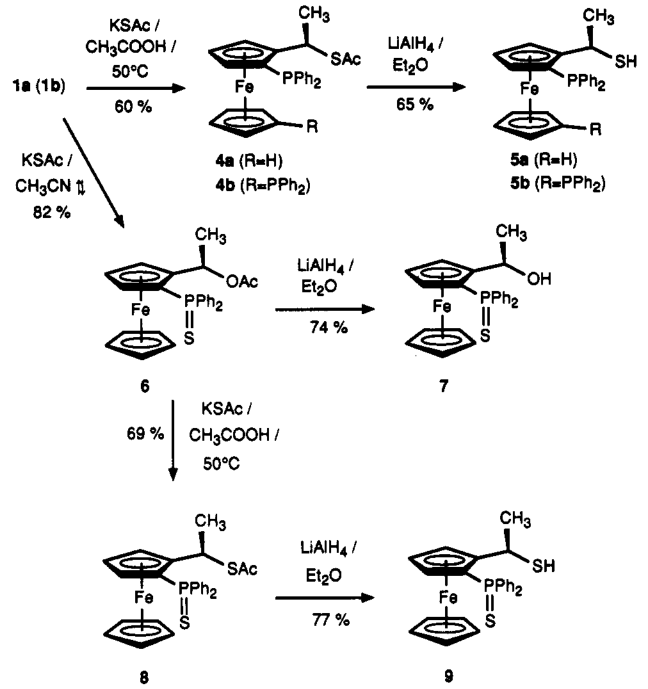
[1] For reviews see: (a) Hayashi, T. In *Organic Synthesis: an interdisciplinary challenge*; Streith, J., Prinzbach, H., Schill, G. Eds.; Blackwell: Oxford, U.K., 1985; pp 35–42. (b) Hayashi, T. *Pure Appl. Chem.* 1988, *60*, 7–12. (c) Hayashi, T.; Kumada, M. *Acc. Chem. Res.* 1982, *15*, 395–401. (d) Hayashi, T.; Kumada, M. In *Asymmetric Synthesis*: Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1985; Vol. 5, pp 147–169. For more recent examples see: (e) Hayashi, T.; Uozumi, Y.; Yamazaki, A.; Sawamura, M.; Hamashima, H.; Ito, Y. *Tetrahedron Lett.* 1991, *32*, 2799–2802. (f) Hayashi, T.; Matsumoto, Y.; Morikawa, I.; Ito, Y. *Tetrahedron: Asymmetry* 1990, *1*, 151–154. (g) Yamamoto, A.; Ito, Y.; Hayashi, T. *Tetrahedron Lett.* 1989, *30*, 375–378. (h) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* 1988, *29*, 99–102. (i) Hayashi, T.; Yamamoto, A.; Ito, Y. *Tetrahedron Lett.* 1988, *29*, 669–672.

0276-7333/92/2311-0613$03.00/0 © 1992 American Chemical Society

Scheme I



Scheme II



α-ferrocenylethyl carbonium ion A as an intermediate (see Scheme I).[3]

Derivatives of ferrocene containing the elements of group 16 directly bonded to the cyclopentadienyl rings have already been extensively studied[4] and include, among others, the simple chalcogenides,[5] chalcogenoethers,[6] and ferrocenophanes.[7] Compounds containing sulfur not directly attached to the ferrocene moiety are also known,[4] but, to our knowledge, no such optically active derivatives have yet been prepared and studied from the point of view of their coordination chemistry. Thioethers and thiolates display a rich coordination chemistry with transition metals[8] and are known for their propensity to act as bridging ligands in polynuclear compounds.[9] Disparate nuclearities have been reported in particular for copper(I) complexes containing thiolato ligands.[10] To our knowledge only very few thiolates containing an intramolecularly coordinating ligand (not a second thiolate or a thioether) have been described.[11] It can be speculated that the incorporation of an extra coordinating functionality should help in controlling the nuclearity of the complexes formed. In the context of the following discussion, the most prominent examples of copper complexes of thiolates which contain an intramolecularly coordinating dialkylamino group are those designed by van Koten and coworkers,[12] the most relevant derivative being the chiral compound **3**.

We describe herein the synthesis of novel, optically active, chelating thiols derived from the acetates **1** and the preparation and properties of an unusual trimeric copper(I) complex containing one such ligand.

Results and Discussion

Synthesis of Ligands. We previously communicated that the acetates **1a**,**b** react with potassium thioacetate in acetic acid at 50 °C to give the analogous sulfur-containing

---

(2) Hayashi, T.; Mise, T.; Fukushima, M.; Kagotani, M.; Nagashima, M.; Hamada, Y.; Matsumoto, A.; Kawakami, S.; Konishi, M.; Yamamoto, K.; Kumada, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1138–1151.

(3) (a) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Org. Chem.* **1972**, *20*, 3052–3058. (b) Marquarding, D.; Klusacek, H.; Gokel, G.; Hoffmann, P.; Ugi, I. *J. Am. Chem. Soc.* **1970**, *92*, 5389–5393. See also: (c) Dannenberg, J. J.; Levenberg, M. K.; Richards, J. H. *Tetrahedron* **1973**, *29*, 1575–1584.

(4) For a review see: *Gmelin Handbuch der Anorganischem Chemie*, 8th ed.; Springer-Verlag: Berlin, 1981; Organoiron Compounds, Part A, Ferrocene 5, pp 1–88.

(5) For recent examples see: (a) Seyferth, D.; Hames, B. W.; Rucker, T. G.; Cowie, M.; Dickson, R. S. *Organometallics* **1983**, *2*, 472–474. (b) Akabori, S.; Kumagai, T.; Shirahige, T.; Sato, S.; Kawazoe, K.; Tamura, C.; Sato, M. *Organometallics* **1987**, *6*, 526–531. (c) Herberhold, M.; Leitner, P.; Dörnhöfer, C.; Ott-Lastic, J. *J. Organomet. Chem.* **1989**, *377*, 281–289.

(6) For recent examples see: (a) Pastor, S. D. *Tetrahedron* **1988**, *44*, 2883, 2886. (b) Lai, C.-K.; Naiini, A. A.; Brubaker, C. H., Jr. *Inorg. Chim. Acta* **1989**, *164*, 205–210. (c) Herrmann, R.; Hübener, G.; Ugi, I. *Tetrahedron* **1985**, *41*, 941–947. (d) Deus, N.; Hübener, G.; Herrmann, R. *J. Organomet. Chem.* **1990**, *384*, 155–163. (e) Orrell, K. G.; Šik, V.; Brubaker, C. H., Jr.; McCulloch, B. *J. Organomet. Chem.* **1984**, *276*, 267–279.

(7) For recent examples see: (a) Sato, M.; Suzuki, K.; Akabori, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3611–3615. (b) Sato, M.; Sekino, M.; Akabori, S. *J. Organomet. Chem.* **1988**, *344*, C31–C34. (c) Butler, I. R.; Cullen, W. R. *Can. J. Chem.* **1989**, *67*, 1851–1858.

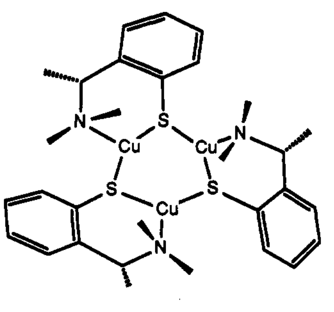
(8) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1986; Vol. 2, pp 516–555. For applications of complexes containing thiolato ligands in catalytic reactions, see: Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1–9.

(9) For reviews see: (a) Krebs, B.; Henkel, G. *Angew. Chem.* **1991**, *103*, 785–804. (b) Dance, I. G. *Polyhedron* **1986**, *5*, 1037–1104. (c) Omae, I. *Coord. Chem. Rev.* **1979**, *28*, 97–115. (d) Vergamini, P. J.; Kubas, G. J. *Prog. Inorg. Chem.* **1976**, *21*, 261–282. For recent examples see: (e) Jessop, P. G.; Rettig, S. J.; James, B. R. *J. Chem. Soc., Chem. Commun.* **1991**, 773–774. (f) Padill, E. M.; Jensen, C. M. *Polyhedron* **1991**, *10*, 89–93. (g) Birnbaum, J.; Haltiwanger, R. C.; Bernatis, P.; Teachout, C.; Parker, K.; Rakowski DuBois, M. *Organometallics* **1991**, *10*, 1779–1786. (h) Stephan, D. W. *Organometallics* **1991**, *10*, 2037–2045. (i) Padilla, E. M.; Golen, J. A.; Richmann, P. N.; Jensen, C. M. *Polyhedron* **1991**, *10*, 1343–1352. (j) Matsuzaka, H.; Mizobe, Y.; Nishio, M.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1011–1012.

(10) See e.g.: (a) Matsubayashi, G.; Yokozawa, A. *J. Chem. Soc., Chem. Commun* **1991**, 68–69. (b) Schröter-Schmid, I.; Strähle, J. *Z. Naturforsch.* **1990**, *45B*, 1537–1542. (c) Block, E.; Kang, H.; Ofori-Okai, G.; Zubieta, J. *Inorg. Chim. Acta* **1990**, *167*, 147–148. (d) Karagiannidis, P.; Hadjikakou, S. K.; Aslanidis, P.; Hountas, A. *Inorg. Chim. Acta* **1990**, *178*, 27–34. (e) Becker, B.; Wojnowski, W.; Peters, K.; Peters, E.-M.; Von Schnering, H. G. *Polyhedron* **1990**, *9*, 1659–1666. (f) Dance, I. G.; Scudder, M. L.; Fitzpatrick, L. J. *Inorg. Chem.* **1985**, *24*, 2547–2550. (g) Nicholson, J. R.; Abrahams, J. L.; Clegg, W.; Garner, C. D. *Inorg. Chem.* **1985**, *24*, 1092–1096. (h) Dance, I. G.; Guerney, P. J.; Rae, A. D.; Scudder, M. L. *Inorg. Chem.* **1983**, *22*, 2883–2887. (i) Dance, I. G.; Bowmaker, G. A.; Clark, G. R.; Seadon, J. K. *Polyhedron* **1983**, *2*, 1031–1043. (j) Dance, I. G.; Fitzpatrick, L. J.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1983**, 546–548. (k) Pope, L.; Laing, M.; Caira, M. R.; Nassimbeni, L. R. *Acta Crystallogr.* **1976**, *B32*, 612–613.

(11) Kitagawa, S.; Munataka, M.; Shimono, H.; Matsuyama, S. *J. Chem. Soc. Dalton Trans.* **1990**, 2105–2109.

(12) (a) Knotter, D. M.; van Koten, G.; van Maanen, H. L.; Grove, D. M.; Spek, A. L. *Angew. Chem.* **1989**, *101*, 351–352; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 341–342. (b) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309–3317. (c) Knotter, D. M.; Spek, A. L.; van Koten, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1738–1740. (d) Knotter, D. M.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1990**, *112*, 5895–5896. For a personal account see also: (e) van Koten, G. *J. Organomet. Chem.* **1990**, *400*, 283–301.



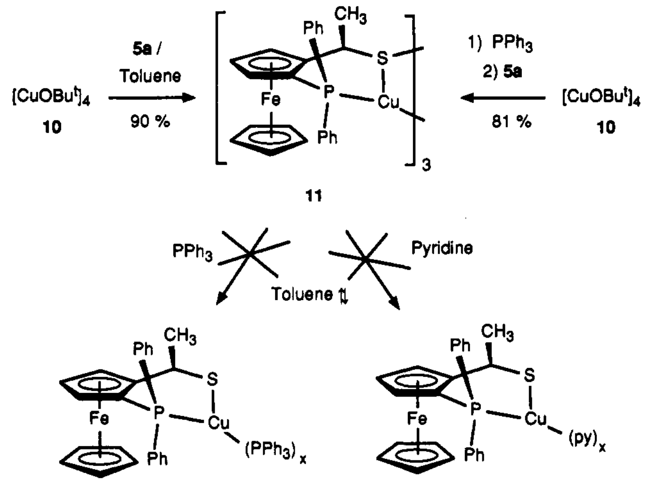
3

derivatives **4a,b** (see Scheme II).[13,14] The choice of acetic acid as a solvent in this preparation is crucial. We first reasoned that, in order to ensure S_N1 conditions, simply a polar solvent is needed. Nevertheless, attempts to carry out this substitution reaction in, for example, acetonitrile did not lead to the desired products. A remarkable oxidation reaction took place instead. When the synthesis was started with **1a**, the phosphine sulfide **6** was isolated in 82% yield after recrystallization and was accompanied by **4a** only in traces. It was also observed that, depending on the quality of the potassium thioacetate used, relevant amounts of **6** were formed in acetic acid solvent. The presence of traces of sulfur, contaminating old samples of KSAc, alone cannot account for this reaction, since **6** was formed in similar yields in acetonitrile using recrystallized thioacetate. The fate of the desulfurated thioacetate in the course of the reaction is not known and was not pursued any further. Upon treatment with $LiAlH_4$ in diethyl ether the thiols **5a,b** could be obtained in moderate to good yields. The phosphine sulfide **6** could not be reduced to the corresponding phosphine under these conditions. It was instead converted to the analogous thioacetate **8**, under the proper conditions noted above. Subsequently **8** was transformed into the mercaptan **9**.

The thiol functionality in compound **5b** has been previously exploited as a nucleophile for the purpose of extending the alkyl side chain in derivatives that could be used as suitable ligands for the gold(I)-catalyzed aldol reaction.[13,15] With the derivative **5a** in hand, we decided to study its coordination ability with copper(I) and to look at the potential catalytic properties of the complexes thus obtained in, for example, asymmetric cyclopropanation and conjugate-addition reactions.

Preparation and Properties of $[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-}C_5H_3(1\text{-}PPh_2)(2\text{-}CH(CH_3)S))\}Cu]_3$ (11). Despite its sensitivity toward oxygen and moisture, we chose to use the simple alkoxylate $[CuOBu^t]_4$ (**10**),[16] as a starting material for the preparation of Cu(I) complexes containing the anion of **5a**. As recently reported by Caulton and co-workers,[17] **10** is best suited for reactions involving acidic functionalities (in this case the thiol). The alcohol elimination reaction leads to the formation of *tert*-butyl alcohol, which is reasonably assumed to be an inert leaving group. Thus, **10** reacts cleanly with stoichiometric amounts of **5a** (Cu:Fe ratio 1:1) in toluene at 0 °C to give the metathesis product $[\{CpFe(\eta^5\text{-}C_5H_3(1\text{-}PPh_2)(2\text{-}CH(CH_3)\text{-}S))\}Cu]$ (**11**). The latter can be isolated in high yields as an orange microcrystalline material upon addition of

Scheme III



pentane to the reaction mixture. The product is recrystallized from CH_2Cl_2/toluene to give thin, transparent, yellow-orange needles. The complex is indefinitely stable in air in the solid state, and it decomposes only slowly in solution when exposed to oxygen. It can be flash-chromatographed on silica gel, and no particular precautions need be taken. These qualitative properties are quite remarkable for a Cu(I) thiolato complex. **11** is moderately soluble in ordinary polar organic solvents but only sparingly soluble at room temperature in common aromatic hydrocarbon solvents. A molecular weight determination in CH_2Cl_2 solution, using the method of isothermal distillation,[18] showed the complex to be *trimeric* (M_r found 1375, calcd 1478.6). By ^{31}P NMR spectroscopy no evidence for the formation of detectable amounts of different species (e.g., other oligomers) could be found. We take this observation as indicative of the high stabilization of the trimeric structure due to the presence of the intramolecularly coordinating diphenylphosphino group. A similar stabilizing effect of a six-membered cyclic Cu_3S_3 core of the cluster, due to a chelating dimethylamino group, has been suggested by van Koten for compound **3**.[12a,b] The trimeric species is also detected in the FAB MS spectrum. Interestingly, under the conditions of fast atom bombardment, a recombination of the trimer with copper generates the adduct $(11\cdot Cu)^+$. The intensity of the signal of the latter ion is comparable to that of the M^+ peak (see Figure 1). This observation could be a hint that **11** may be suited for the addition of organocopper fragments, generating neutral, tetranuclear species.

Simple reactivity studies evidenced complex **11** as very stable and inert. Thus, exposure to an excess of triphenylphosphine or pyridine, respectively, in refluxing toluene left compound **11** essentially unchanged and did not afford any monomeric species (e.g., **12** or **13**, respectively; see Scheme III). This is not too surprising in view of the fact that mononuclear copper(I) thiolato complexes are so far unprecedented. An attempt to circumvent the trimer formation by using $[^tBuOCuPPh_3]_2$[17] as a starting material was also unsuccessful. Thus, addition of **5a** to $[^tBuOCuPPh_3]_2$ (formed in situ from equimolar amounts of **10** and PPh_3) gave **11** in only slightly lower yields, thereby supporting the idea of the high stability of **11**.

---

[13] Togni, A.; Häusel, R. *Synlett* **1990**, 633–635.

[14] Reference deleted on revision.

[15] (a) Togni, A.; Pastor, S. D. *Chirality* **1991**, *3*, 331–340. (b) Togni, A.; Pastor, S. D. *J. Org. Chem.* **1990**, *55*, 1649–1664.

[16] (a) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658–659. (b) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142–3146.

[17] Lemmen, T. H.; Goeden, G. V.; Huffman, J. C.; Geerts, R. L.; Caulton, K. G. *Inorg. Chem.* **1990**, *29*, 3680–3685.

[18] (a) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 79–98. (b) Zoellner, R. W. *J. Chem. Educ.* **1990**, *67*, 714–715.

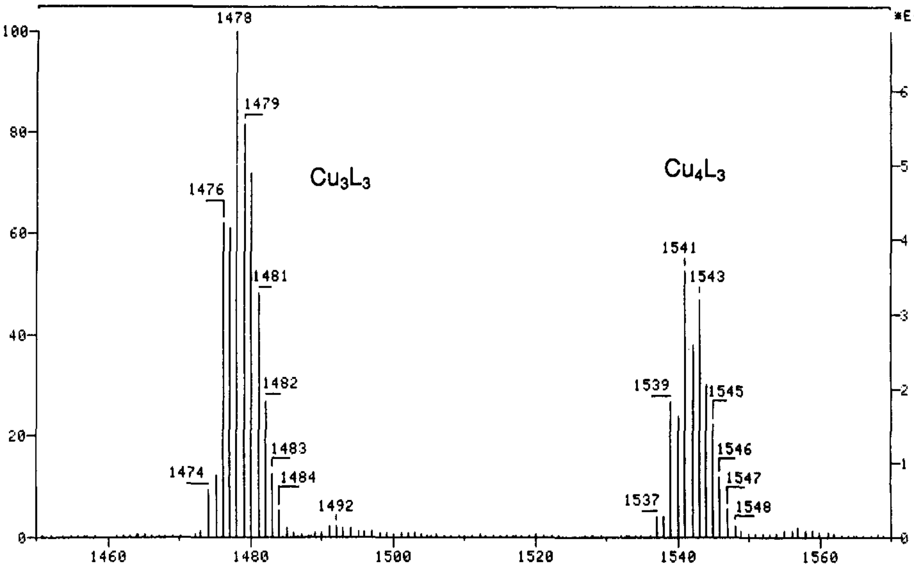


Figure 1. Section of the FAB MS spectrum (*o*-nitrobenzyl alcohol matrix, Xe, 8 keV) of **11**, showing the molecular peak at *m/z* 1476 and the peak due to (**11** + Cu)$^+$ at *m/z 1539 (based on* $^{56}Fe_3{}^{63}Cu_3$ *and* $^{56}Fe_3{}^{63}Cu_4$*, respectively). The distributions of the isotopomers* are in good agreement with the calculated ones.

Table I. Selected Interatomic Distances (Å),[a] Angles (deg),[a] and Torsion Angles (deg)[b] for 11

Cu(1)–S(7)	2.204 (5)	Cu(1)–S(8)	2.251 (4)
Cu(1)–P(10)	2.222 (5)	Cu(2)–S(8)	2.178 (6)
Cu(2)–S(9)	2.251 (6)	Cu(2)–P(11)	2.250 (6)
Cu(3)–S(7)	2.251 (6)	Cu(3)–S(9)	2.207 (5)
Cu(3)–P(12)	2.202 (5)	Cu(1)–Cu(2)	3.194 (3)
Cu(2)–Cu(3)	3.372 (4)	Cu(1)–Cu(3)	3.341 (4)
S(7)–S(8)	3.795 (7)	S(8)–S(9)	3.761 (8)
S(7)–S(9)	3.791 (7)	S(7)–C(32)	1.83 (1)
S(8)–C(18)	1.89 (2)	S(9)–C(25)	1.85 (2)
P(10)–C(13)	1.79 (2)	P(11)–C(20)	1.85 (2)
P(12)–C(27)	1.83 (2)		
S(7)–Cu(1)–S(8)	116.8 (2)	S(7)–Cu(1)–P(10)	137.8 (2)
S(8)–Cu(1)–P(10)	104.4 (1)	S(8)–Cu(2)–S(9)	116.2 (2)
S(8)–Cu(2)–P(11)	139.5 (2)	S(9)–Cu(2)–P(11)	103.7 (3)
S(7)–Cu(3)–S(9)	116.5 (1)	S(7)–Cu(3)–P(12)	107.1 (2)
S(9)–Cu(3)–P(12)	133.5 (2)	Cu(1)–S(7)–Cu(3)	97.2 (2)
Cu(1)–S(7)–C(32)	114.5 (5)	Cu(3)–S(7)–C(32)	108.2 (6)
Cu(1)–S(8)–Cu(2)	92.3 (2)	Cu(1)–S(8)–C(18)	111.7 (6)
Cu(2)–S(8)–C(18)	110.5 (7)	Cu(2)–S(9)–Cu(3)	98.3 (2)
Cu(2)–S(9)–C(25)	111.9 (6)	Cu(3)–S(9)–C(25)	111.9 (4)
Cu(1)–P(10)–C(13)	109.7 (4)	Cu(2)–P(11)–C(20)	105.9 (5)
Cu(3)–P(12)–C(27)	109.6 (5)		
C(17)–C(13)–P(10)–Cu(1)	−35		
C(31)–C(27)–P(12)–Cu(3)	−30		
C(24)–C(25)–S(9)–Cu(2)	−40		
C(13)–C(17)–C(18)–S(8)	+52		
C(27)–C(31)–C(32)–S(7)	+55		
C(23)–C(24)–C(25)–C(26)	+95		
Cu(1)–S(7)–Cu(3)–S(9)	−62		
Cu(3)–S(9)–Cu(2)–S(8)	−70		
Cu(2)–S(8)–Cu(1)–S(7)	−73		
C(24)–C(20)–P(11)–Cu(2)	−35		
C(17)–C(18)–S(8)–Cu(1)	−40		
C(31)–C(32)–S(7)–Cu(3)	−49		
C(20)–C(24)–C(25)–S(9)	+58		
C(16)–C(17)–C(18)–C(19)	+95		
C(30)–C(31)–C(32)–C(33)	+107		
S(7)–Cu(3)–S(9)–Cu(2)	+61		
S(9)–Cu(2)–S(8)–Cu(1)	+72		
S(8)–Cu(1)–S(7)–Cu(3)	+69		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] For a definition see, e.g.: Bucourt, R. *Top. Stereochem.* **1974**, *8*, 159–224.

Table II. Crystal Data and Details of Refinement of 11

chem formula	$C_{72}H_{66}Cu_3Fe_3P_3S_3$
fw	1478.594
cryst size, mm	0.60 × 0.15 × 0.02
cryst syst	monoclinic
space group	$P2_1$
a, Å	13.206 (1)
b, Å	18.221 (2)
c, Å	16.028 (1)
β, deg	113.13 (1)
V, Å^3	3546 (2)
Z	2
D(calc), g/cm^3	1.384
data collection instrument	Enraf-Nonius CAD-4
radiation, Å (monochromated)	1.5418 (Cu Kα)
F(000)	1512
μ, cm^{-1}	75.46
temp, °C	21
θ range from data collection, deg	3–75
transmissn factors: max; min	1.00; 0.71
scan time, s	≤45
scan width, deg	1.2
structure soln	Patterson method
no. of variables	397
no. of rflns with $I > 3\sigma(I)$	3615
refinement	full-matrix least squares
R	0.076
R_w	0.081
weighting scheme	$w = 1/\sigma^2(\lvert F_o \rvert)$
max residual electron density, e/Å^3	1.88

In view of our interest in asymmetric catalysis we decided to test the enantiomerically pure complex **11** as catalyst in two of the typical reactions usually mediated by Cu(I) compounds. Despite its low reactivity and high stability, **11** indeed was found to be a catalyst for the 1,4-addition of Grignard reagents to α,β-unsaturated ketones (e.g. cyclohexanone as substrate)[19] but disappointingly gave no asymmetric induction. The same type of outcome was found for the cyclopropanation reaction of diazoacetate esters with olefins:[20] moderate catalytic activity but no induction. After these discouraging preliminary results we decided not to pursue the catalytic chemistry of **11** any further.

Solid-State Structure of 11. In order to confirm the trimeric nature of compound **11**, an X-ray single-crystal structure determination was carried out. Relevant bond lengths, bond angles, and torsion angles are collected in Table I. Data collection parameters are given in Table

---

[19] See e.g.: Posner, G. H. *Org. React.* **1972**, *19*, 1–113.

[20] See e.g.: Maas, G. *Top. Curr. Chem.* **1987**, *137*, 75–253.

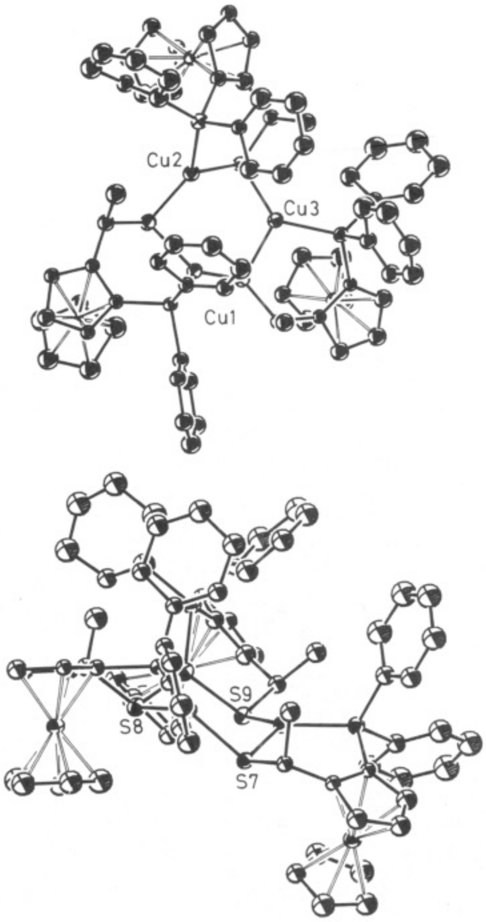


Figure 2. ORTEP drawings of 11 (ellipsoids at the 20% probability level). (a, top) top view showing the approximate C_3 symmetry of the complex; (b, bottom) side view parallel to one ferrocenyl unit.

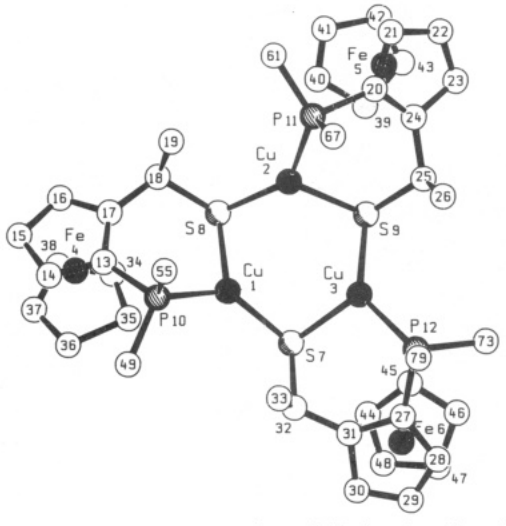


Figure 3. SCHAKAL representation of 11 showing the adopted atom-numbering scheme. All phenyl carbons, except for the Ph ipso C atoms, have been omitted for clarity.

II, whereas the final atom coordinates and isotropic thermal parameters are shown in Table III. The overall geometry of the complex is shown in Figure 2, and the adopted atom-numbering scheme is depicted in the Schakal[21] representation of Figure 3. The complex results from the assemblage of three monomeric CpFe(η^5-C_5H_3-(1-PPh_2)(2-CH(CH_3)S)Cu units and shows only approximate C_3 overall symmetry. Consequently, the monomeric units are only approximately equivalent. Given the absolute configuration *S* for the disubstituted ferrocenyl moiety of the ligand, the crystal structure demonstrates the *R* configuration for the α-carbon atom of the side chain. This unequivocally proves that the S_N1 substitution reaction of **1a** with KSAc indeed occurs with retention of configuration.

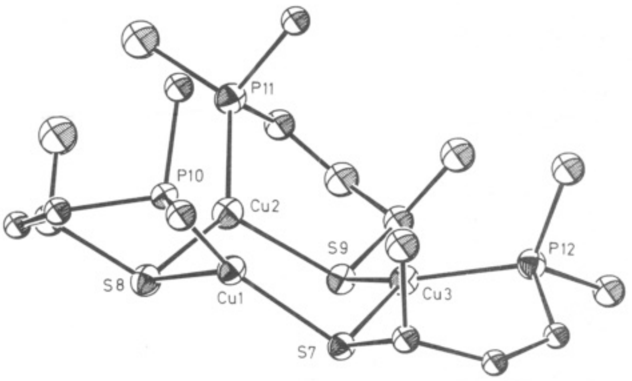


Figure 4. ORTEP drawing of the inner core of 11 (ellipsoids at the 20% probability level), emphasizing the conformational characteristics of the four annulated rings.

The Cu_3S_3 core of the complex, with each sulfur atom bridging two copper atoms (see Figure 4), adopts a distorted *chair* conformation, as is also illustrated by the torsion angles of 61–73° (absolute values) within the ring. All the substituents on this six-membered ring are pseudoequatorially arranged. The three chelate rings assume a distorted *boat* conformation with the two Cp carbon atoms, Cu, and S lying approximately in a plane, whereas the respective phosphorus atoms and the methine carbon atoms are situated above this plane (distances 0.38–0.66 Å). The average bite angle of the chelate rings is 105.1°, which is normal. The geometry around the copper atoms is slightly distorted trigonal planar, as indicated by the sums of the bond angles (359, 359, and 357° for Cu(1), Cu(2), and Cu(3), respectively). The relatively small distances of the copper atoms from the planes defined by their three next-neighboring atoms (0.12, 0.09, and 0.21 Å, respectively) also show the approximate planarity of their first coordination sphere. The same corresponding distances for the three sulfur atoms S(7), S(8), and S(9) are 0.99, 0.98, and 0.77 Å, respectively, evidencing their expected much higher degree of pyramidalization (sums of bond angles 320, 314, and 322°, respectively). In fact, the geometry at the sulfur atoms is best described as tetrahedral.

In Figure 5 the most relevant bonding parameters for **11** and for **3**[12a,b] (the only known compound displaying a closely related structure) are compared. Within the central ring in **11** alternating short (2.178 (6)–2.207 (5) Å) and long (2.251 (6) Å) Cu–S bond distances are observed. Interestingly, the shorter separations are those between each copper atom and the sulfur of the next monomeric unit. Intuitively, one would expect the reverse to be true. These bond lengths are comparable to those found in **3**, where a similar alternating pattern of distances is encountered, but appear to be slightly shorter than previously observed ones.[10i,22] The most important differences between **11** and

---

(21) Keller, E. Schakal88, a Program for the Graphic Representation of Molecular and Crystallographic Models; Kristallographisches Institut der Universität Freiburg: D-7200 Freiburg, Germany.

(22) For a compilation of bond distances of organometallic and coordination compounds see: Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, S. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, Supplement S1–S83.

Table III. Positional Parameters, Equivalent Isotropic Thermal Parameters (Å²), and Their Estimated Standard Deviations for 11

atom	*x*	*y*	*z*	*B*[a]	atom	*x*	*y*	*z*	*B*[a]
Cu(1)	0.7829 (2)	0.696	0.1190 (2)	4.20 (6)	C(43)	0.195 (1)	0.524 (1)	0.049 (1)	5.0 (4)*
Cu(2)	0.6180 (2)	0.5747 (2)	0.1371 (2)	4.91 (7)	C(44)	0.555 (1)	0.954 (1)	0.155 (1)	5.5 (5)*
Cu(3)	0.6606 (2)	0.7291 (2)	0.2623 (2)	4.37 (6)	C(45)	0.509 (2)	0.916 (1)	0.206 (1)	7.2 (6)*
Fe(4)	0.8241 (2)	0.6654 (2)	−0.1206 (2)	4.64 (7)	C(46)	0.491 (2)	0.964 (1)	0.267 (1)	8.5 (6)*
Fe(5)	0.3404 (2)	0.4786 (2)	0.1300 (2)	4.21 (7)	C(47)	0.535 (2)	1.035 (1)	0.250 (1)	7.5 (6)*
Fe(6)	0.6549 (2)	0.9578 (2)	0.2862 (2)	5.03 (8)	C(48)	0.566 (2)	1.025 (1)	0.176 (1)	7.9 (6)*
S(7)	0.7232 (3)	0.7914 (3)	0.1710 (3)	3.8 (1)	C(49)	1.050 (1)	0.728 (1)	0.123 (1)	4.7 (4)*
S(8)	0.6542 (3)	0.6195 (3)	0.0258 (3)	4.8 (1)	C(50)	1.016 (1)	0.799 (1)	0.102 (1)	5.9 (5)*
S(9)	0.5272 (3)	0.6494 (3)	0.1960 (3)	4.3 (1)	C(51)	1.098 (2)	0.856 (1)	0.107 (1)	7.5 (6)*
P(10)	0.9392 (3)	0.6584 (3)	0.1115 (3)	3.6 (1)	C(52)	1.212 (2)	0.827 (1)	0.131 (1)	7.3 (6)*
P(11)	0.6235 (4)	0.4669 (3)	0.2071 (3)	5.0 (1)	C(53)	1.240 (1)	0.759 (1)	0.152 (1)	6.3 (5)*
P(12)	0.7171 (4)	0.7884 (3)	0.3923 (3)	4.4 (1)	C(54)	1.162 (1)	0.702 (1)	0.149 (1)	4.6 (4)*
C(13)	0.911 (1)	0.6180 (9)	0.003 (1)	3.7 (3)*	C(55)	1.016 (1)	0.5894 (9)	0.194 (1)	4.3 (4)*
C(14)	0.976 (1)	0.6215 (9)	−0.050 (1)	3.6 (3)*	C(56)	1.015 (1)	0.514 (1)	0.166 (1)	4.9 (4)*
C(15)	0.921 (1)	0.582 (1)	−0.135 (1)	5.7 (5)*	C(57)	1.069 (1)	0.462 (1)	0.236 (1)	6.9 (5)*
C(16)	0.817 (1)	0.555 (1)	−0.130 (1)	4.3 (4)*	C(58)	1.114 (2)	0.476 (1)	0.324 (1)	7.8 (6)*
C(17)	0.810 (1)	0.5750 (9)	−0.049 (1)	3.7 (3)*	C(59)	1.115 (2)	0.551 (1)	0.353 (1)	7.5 (6)*
C(18)	0.717 (1)	0.547 (1)	−0.023 (1)	5.0 (4)*	C(60)	1.062 (1)	0.605 (1)	0.283 (1)	5.4 (4)*
C(19)	0.745 (2)	0.480 (1)	0.036 (1)	7.6 (6)*	C(61)	0.629 (2)	0.375 (1)	0.160 (1)	7.3 (6)*
C(20)	0.495 (1)	0.462 (1)	0.228 (1)	4.8 (4)*	C(62)	0.556 (1)	0.354 (1)	0.080 (1)	5.5 (5)*
C(21)	0.427 (1)	0.395 (1)	0.222 (1)	5.4 (4)*	C(63)	0.560 (2)	0.286 (1)	0.036 (1)	8.6 (6)*
C(22)	0.339 (1)	0.419 (1)	0.243 (1)	4.7 (4)*	C(64)	0.619 (4)	0.234 (3)	0.098 (3)	13 (2)*
C(23)	0.343 (1)	0.494 (1)	0.257 (1)	5.3 (4)*	C(65)	0.685 (4)	0.242 (4)	0.181 (3)	14 (2)*
C(24)	0.443 (1)	0.521 (1)	0.249 (1)	6.0 (5)*	C(66)	0.685 (3)	0.316 (2)	0.221 (2)	12 (1)*
C(25)	0.485 (1)	0.601 (1)	0.279 (1)	4.6 (4)*	C(67)	0.727 (1)	0.4596 (9)	0.319 (1)	4.1 (4)*
C(26)	0.573 (1)	0.596 (1)	0.378 (1)	6.0 (5)*	C(68)	0.718 (2)	0.423 (1)	0.385 (2)	9.0 (7)*
C(27)	0.755 (1)	0.8824 (9)	0.376 (1)	3.3 (3)*	C(69)	0.797 (2)	0.420 (2)	0.478 (2)	11.3 (8)*
C(28)	0.745 (1)	0.949 (1)	0.417 (1)	6.3 (5)*	C(70)	0.894 (2)	0.465 (1)	0.494 (1)	7.6 (6)*
C(29)	0.784 (1)	1.003 (1)	0.386 (1)	6.4 (5)*	C(71)	0.907 (2)	0.500 (1)	0.431 (1)	7.3 (6)*
C(30)	0.819 (1)	0.981 (1)	0.319 (1)	6.4 (5)*	C(72)	0.825 (2)	0.506 (1)	0.340 (1)	7.1 (5)*
C(31)	0.797 (1)	0.9001 (9)	0.307 (1)	3.4 (3)*	C(73)	0.612 (1)	0.805 (1)	0.440 (1)	5.2 (4)*
C(32)	0.832 (1)	0.8541 (9)	0.241 (1)	3.9 (4)*	C(74)	0.501 (2)	0.792 (1)	0.370 (1)	7.0 (5)*
C(33)	0.937 (1)	0.804 (1)	0.300 (1)	5.9 (5)*	C(75)	0.414 (2)	0.802 (2)	0.408 (2)	11.0 (8)*
C(34)	0.675 (1)	0.719 (1)	−0.171 (1)	5.8 (5)*	C(76)	0.436 (2)	0.813 (2)	0.498 (2)	12 (1)*
C(35)	0.755 (2)	0.759 (1)	−0.094 (1)	8.7 (6)*	C(77)	0.551 (2)	0.823 (2)	0.565 (2)	14 (1)*
C(36)	0.845 (2)	0.776 (1)	−0.141 (1)	8.1 (6)*	C(78)	0.633 (2)	0.814 (1)	0.528 (1)	7.9 (6)*
C(37)	0.803 (2)	0.739 (1)	−0.226 (1)	8.1 (6)*	C(79)	0.838 (1)	0.759 (1)	0.490 (1)	5.5 (5)*
C(38)	0.712 (2)	0.699 (1)	−0.239 (1)	9.0 (7)*	C(80)	0.840 (2)	0.685 (1)	0.517 (1)	9.3 (7)*
C(39)	0.289 (1)	0.563 (1)	0.041 (1)	5.3 (4)*	C(81)	0.935 (2)	0.663 (1)	0.596 (1)	9.6 (7)*
C(40)	0.352 (2)	0.504 (1)	0.012 (1)	6.6 (5)*	C(82)	1.019 (2)	0.708 (1)	0.641 (1)	8.9 (7)*
C(41)	0.294 (2)	0.444 (1)	−0.004 (1)	6.8 (5)*	C(83)	1.006 (2)	0.778 (1)	0.613 (1)	8.5 (6)*
C(42)	0.201 (1)	0.453 (1)	0.026 (1)	6.0 (5)*	C(84)	0.923 (1)	0.804 (1)	0.536 (1)	6.4 (5)*

[a] Starred values denote atoms refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

3 concern (1) the Cu–Cu and S–S distances as well as (2) the angles within the Cu_3S_3 core. Whereas in 3 an acute Cu–S–Cu angle (79.63 (7)°) is detected, paralleled by a rather short Cu–Cu contact (2.828 (1) Å), the corresponding angle in 11 is obtuse, amounting to an average value of 95.9°. Accordingly, the Cu–Cu distance of 3.302 Å is ca. 0.5 Å longer than in 3. For the different types of copper(I) thiolates this distance varies over a wide range (from 2.57 to 4.21 Å; see a compilation of available data in ref 12b). The shorter separations (up to 3.40 Å), combined with an acute Cu–S–Cu angle, have recently been rationalized in terms of an electron-deficient two-electron–three center (2e–3c) Cu–S–Cu interaction, with sp² hybridization for the sulfur atom.[12b] Typical representatives of this class are compound 3 and the recently reported tetramers $[CuSC_6H_2(^iPr)_3]_4$[10b] and $[Cu\{SC_6H_3\text{-}2,6\text{-}(SiMe_3)_2\}]_4$.[10c] Obtuse bridge angles smaller than 120° and Cu–Cu distances from 3.55 to 3.70 Å are interpreted as indicative of a 4e–3c bond, where the sulfur atom is best viewed as sp³ hybridized. For the largest values of both the angle and the Cu–Cu separation, the same interpretation applies, with the difference that now the sulfur is trigonal (sp²). How does 11 fit in this clear-cut type of classification? The relatively long Cu–Cu distance still falls in the range for an electron-deficient Cu–S–Cu bond type. The rather short Cu–P bond lengths (they average 2.225 Å, which is at the lower limit of compiled data for, e.g., Cu–PPh_3 distances[22]), would support this interpretation, as they are indicative of a strong Cu–P interaction. On the other hand, the bridge angle is obtuse, although it is smaller than those typically observed for complexes described by the 4e–3c model. On the basis of these bonding parameters and in view of the models outlined above, we suggest that the Cu–S–Cu unit in 11 has some electron-deficient character but that it clearly has to be treated as a borderline case. In this context it is particularly instructive to note that in the related trimer $[Cu_3(\mu\text{-}SPh)_3(PPh_3)_4]$ reported by Dance and co-workers,[10j] *all* of the three combinations of the Cu–S–Cu angle and the Cu–Cu distance, corresponding to the three different models describe above, are present in the *very same* molecule.

Further important structural features of the trimeric complex 11 are the positions of the sulfur and copper atoms with respect to the ferrocenyl moieties. As illustrated by the corresponding torsion angles (e.g., C(13)–C(17)–C(18)–S(8) = +52° and C(17)–C(13)–P(10)–Cu(1) = −35°, for the positions of S(8) and Cu(1), respectively), each of the three CuS units lies *between* the two planes defined by the two cyclopentadienyl rings. The calculated distances of Cu(1), Cu(2), and Cu(3) from the planes defined by the upper ring of their corresponding ferrocenyl

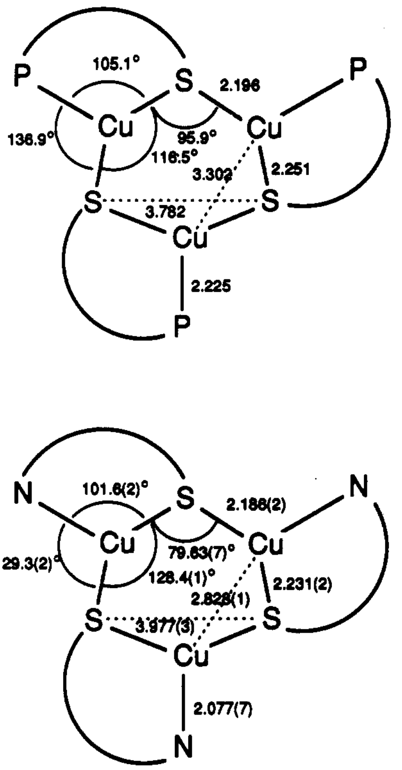


Figure 5. Schematic comparison of (a, top) 11 (average values are given) and (b, bottom) 3 (parameters taken from ref 12a,b), showing the most relevant structural differences of the Cu_3S_3 units.

moieties are 1.20, 1.24, and 1.04 Å, respectively. For S(7), S(8), and S(9) these distances amount to 1.38, 1.36, and 1.44 Å, respectively. This is quite remarkable and is in contrast with the local geometry found, for example, in $[(PPFA)Rh(NBD)]PF_6$[23] (PPFA = (*R**)-dimethyl[1-((*S**)-2-(diphenylphosphino)ferrocenyl)ethyl]amine; NMe_2 instead of S, compared to **5a**), where the six atoms constituting the chelate ring are, within 0.2 Å, coplanar with the disubstituted cyclopentadienyl moiety. Furthermore, each of the three unsubstituted Cp rings in 11 is slightly oriented toward the next copper atom. These two aspects can possibly help us to understand the low reactivity of the complex from a structural point of view. The inner Cu_3S_3 core is sterically protected on its "lower" side by the inward oriented ferrocenyl units, whereas the "upper" side is crowded by the presence of the six phenyl and the three methyl groups.

NMR Studies of 5a and 11 in Solution. The ^1H NMR spectrum of 11 is relatively simple and is characterized by a single set of resonances. This shows that the three monomeric units of the complex are equivalent in solution. Similarly, the ^{31}P NMR spectrum shows only one signal at −19.3 ppm. The ^{31}P coordination shift of ca. +5.3 ppm is rather modest. The observed ^1H pattern is similar to that of the free ligand **5a**. The most notable differences are the high-field shift of the methyl resonance and the low-field shift of the signal due to the unsubstituted Cp ring (from 1.67 to 0.95 and from 3.88 to 4.31 ppm, respectively, in $CDCl_3$). The insufficient solubility of 11 precluded a thorough low-temperature study aimed at ascertaining possible dynamic processes (e.g., conformational changes within the Cu_3S_3 ring, epimerization at sulfur). An interesting structural aspect of 11 is the conformation of the side chain attached to the upper Cp ring.

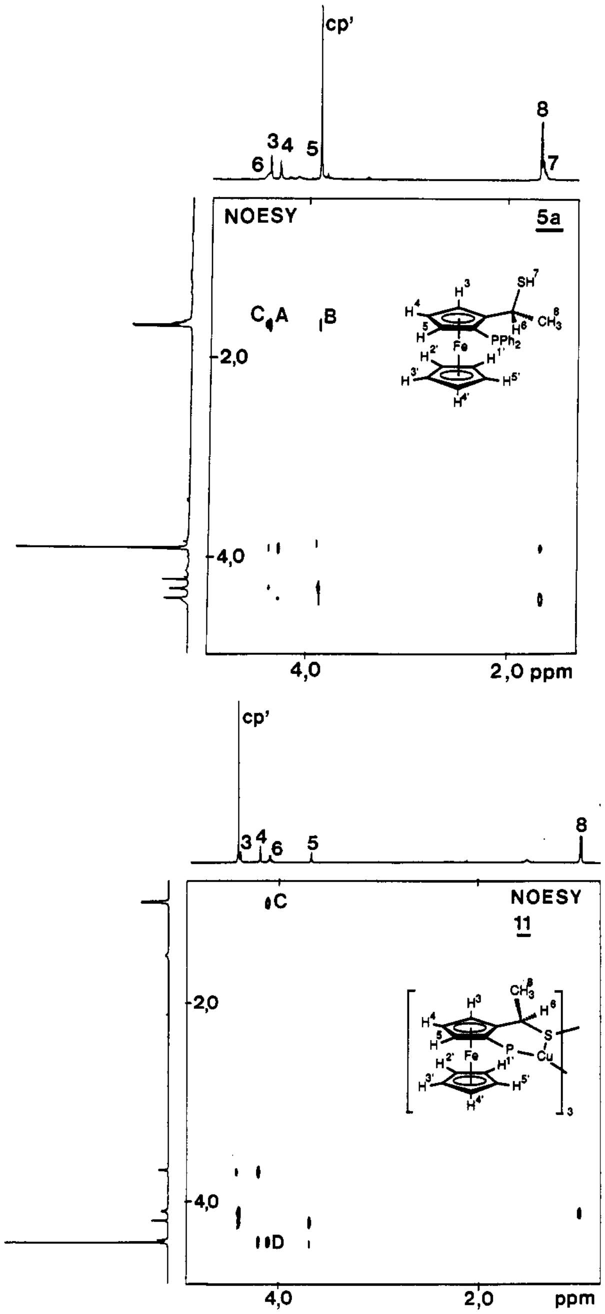


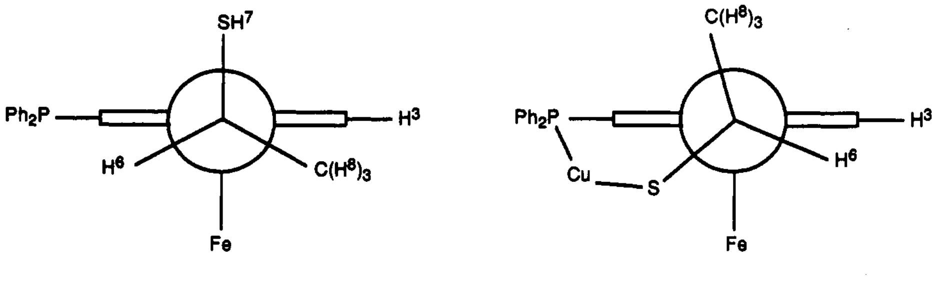
Figure 6. Sections of the 500 MHz 2D NOESY spectra of (a, top) **5a** (in $CDCl_3$) and (b, bottom) 11 (in CD_2Cl_2). Key cross-peaks are indicated: (A) H^8 with H^3; (B) H^8 with Cp; (C) H^8 with H^6; (D) H^3 with H^6.

We previously reported on the utility of 2D NOESY spectroscopy in the elucidation of the conformation of the aliphatic side chain in related ferrocenylphosphines.[24] The phase-sensitive NOESY spectrum of **5a** shows the typical cross-peaks, which allow the assignment of its *preferred time-averaged conformation*. As depicted in Figure 6, strong cross-peaks are observed, arising from the interactions of the $C(H^8)_3$ group with H^3 and the unsubstituted Cp ring, as well as of H^6 with H^8. This information is sufficient to define the relative position of the atoms of the side chain with respect to the Cp ring. H^6 and H^3 are in a *pseudo-trans* orientation relative to each other, and the methyl group $C(H^8)_3$ lies *below* the plane of the upper Cp ring. This conformation is also supported by the

---

[23] Cullen, W. R.; Einstein, F. W. B.; Huang, C.-H.; Willis, A. C.; Yeh, E.-S. *J. Am. Chem. Soc.* **1980**, *102*, 988–993.

[24] Togni, A.; Pregosin, P. S.; Blumer, R. E. *Helv. Chim. Acta* **1991**, *74*, 1533–1543.



5a **11**

Figure 7. Schematic representation of the time-averaged conformations of **5a** and **11** in solution, as elucidated by 2D NOESY (Newman projections along the methine–Cp bonds).

chemical shift of H^6 and by the four-bond coupling constant $^4J(H^6,P)$ of ca. 3 Hz, characteristic of a phosphorus lone-pair effect.[25] The crucial NOE's of H^8 with H^3 and the unsubstituted Cp ring are no longer observed in compound **11**. In the Cu complex a strong NOE arises from H^3 interacting with H^6. These observations are best understood if one assumes a conformation such that H^3 and H^6 are now *pseudo-cis* oriented and the methyl group is located *above* and the sulfur atom *below* the Cp ring. Such a conformation, as illustrated in Figure 7, is qualitatively very similar to that observed in the solid state (vide supra).

Conclusion. We have shown that the stereospecific substitution of the acetate group by thioacetate in ferrocenylphosphines of type **1**, in acetic acid, is a viable method for the synthesis of novel optically active, chelating ligands containing the thiol functionality. The trimeric copper(I) complex **11**, formed upon reaction of $[CuOBu^t]_4$ with the mercaptan **5a**, displays interesting structural features and constitutes a still-rare example of a thiolato complex stabilized by an intramolecularly coordinating ligand. Although its reactivity was not studied in detail, **11** can be considered as exceptionally stable and relatively unreactive, compared with typical Cu thiolato complexes. It is expected that ligands of type **5** should display a rich coordination chemistry with other transition metals as well and possibly constitute an avenue of research toward novel asymmetric catalysts.

Experimental Part

General Considerations. $[CuOBu^t]_4$ (**10**) was prepared by following the protocol reported by Caulton and co-workers[17] but starting from CuI and the more readily available $KOBu^t$ (freshly sublimed). **10** was stored and manipulated in an inert-atmosphere glovebox. The acetates **1** were prepared as described by Hayashi et al.[2] KSAc was purchased from Fluka AG and either used as received or used after recrystallization from H_2O/EtOH. All reactions with air- or moisture-sensitive materials were carried out under Ar using standard Schlenk techniques. Freshly distilled, dry, and oxygen-free solvents were used throughout. Optical rotations were measured with a Perkin-Elmer 241 polarimeter using 10-cm cells. Melting points were measured in open capillaries with a Büchi-510 apparatus and are uncorrected. Low-resolution EI/MS spectra were recorded at 70 eV on a Finnigan MAT 212/SS300 spectrometer. The fast atom bombardment (FAB-MS) spectrum of compound **11** was recorded by using Xe fast atoms (8 keV) in an *o*-nitrobenzyl alcohol matrix on a Finnigan MAT 90 instrument. Merck silica gel 60 (70–230 mesh) was used for flash column chromatography.[26] Thin-layer chromatography (TLC) was performed with Merck silica gel 60 F254 precoated glass plates. Elemental analyses were performed by Analytical Research Services, CIBA-GEIGY AG. Experimental details for the preparation of **4b** and **5b** have been reported elsewhere.[13]

NMR Spectroscopy. Routine ^1H (250.133 MHz) and ^{31}P (101.256 MHz) NMR spectra were recorded with a Bruker AC 250 spectrometer. Chemical shifts are given in ppm relative to internal TMS and external 85% H_3PO_4, respectively, and coupling constants (J) are given in Hz. The assignment of the signals of compounds **5a** and **11** resulted from 2D ^1H COSY, NOESY, and $^1H,^{31}P$ HMQC correlation spectra. All 2D NMR experiments were performed on a Bruker AMX-500 instrument (500.13 MHz), using standard pulse sequences[27] with nonspinning samples, which were degassed by the freeze–thaw method. The 2D phase-sensitive NOESY spectra resulted from a 256 × 2048 data matrix size with 56 transients per t_1 value. The recycle delay time was 2.0 s, and the mixing time was 1.0 or 1.2 s. Employing the TPPI method gave pure absorption-mode spectra. The spectra were obtained by multiplying the data with a cosine squared bell function in both dimensions and zero filling in the F_1 dimension before Fourier transformation. The digital resolution in F_2 was 2.24 Hz per point. T_1 measurements were performed to assist in the determination of the optimal mixing time. The T_1's were measured using the standard inversion recovery technique. Different mixing times have been tested, for example, 0.8, 1.0, and 1.2 s, for optimizing certain aspects of the spectra.

(*R*)-1-[(*S*)-(Diphenylphosphino)ferrocenyl]ethyl Thioacetate (4a). A 4.56-g (10-mmol) sample of **1a** and 2.28 g (20 mmol) of recrystallized KSAc were suspended in 75 mL of acetic acid. The mixture was stirred at 50 °C for 3 h under Ar. Et_2O (300 mL) was added, and the organic phase was washed free of acid with several 100-mL portions of H_2O. The Et_2O phase was then dried over $MgSO_4$, filtered, and evaporated to dryness in vacuo. The orange solid residue was recrystallized from hot EtOH, giving 2.82 g (60%) of **4a**: $[\alpha]^{22}_D = -307.3°$ (c = 0.6, $CHCl_3$); mp 156–159 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.66; ^1H NMR ($CDCl_3$) δ 1.75 (d, J = 7, 3 H), 1.81 (s, 3 H), 3.87–3.92 (m, 1 Cp H), 4.03 (s, C_5H_5), 4.84 (br t, J = 3, 1 Cp H), 4.41–4.45 (m, 1 Cp H), 4.94 (qd, J = 7, 3, 1 H), 7.14–7.25 (m, 5 Ph H), 7.33–7.41 (m, 3 Ph H), 7.54–7.63 (m, 2 Ph H); ^{31}P NMR ($CDCl_3$) δ -24.3; MS[28] m/z 472 (M^+), 429, 396, 363, 276, 212, 183, 165. Anal. Calcd for $C_{26}H_{25}OPSFe$: C, 66.11; H, 5.33; P, 6.56; S, 6.79. Found: C, 66.34; H, 5.49; P, 6.56; S, 6.64. Evaporation of the mother liquor from the above recrystallization afforded a solid residue, which was shown by ^1H NMR spectroscopy to be a ca. 1:1 mixture of **4a** and **6**, along with traces of starting material **1a**.

(*R*)-1-[(*S*)-(Diphenylthiophosphinyl)ferrocenyl]ethyl Acetate (6). A 9.13-g (20-mmol) amount of **1a** was treated with 22.8 g (0.2 mol) of KSAc (not recrystallized) in 300 mL of refluxing acetonitrile for 6 h. The mixture was cooled to room temperature, and 300 mL of H_2O was added. Extraction with Et_2O (2 × 500 mL) afforded a brown-orange residue, which was recrystallized from 800 mL of EtOH, giving 7.8 g (82%) of brown-orange crystals: $[\alpha]^{22}_D = -70.3°$ (c = 0.9, $CHCl_3$); mp 201–202 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.27; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3 H), 1.62 (d, J = 7.5, 3 H), 3.76–3.82 (m, 1 Cp H), 4.34 (s, 5 Cp H), 4.36–4.43 (m, 1 Cp H), 4.67–4.73 (m, 1 Cp H), 6.64 (q, J = 7.5, 1 H), 7.34–7.57 (m, 6 Ph H), 7.60–7.72 (m, 2 Ph H), 7.75–7.86

---

[25] Verkade, J. G., Quin, L. D., Eds. *^{31}P NMR Spectroscopy and Stereochemical Analysis*; VCH: Deerfield Beach, FL, 1987, Vol. 8.

[26] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

[27] Kessler, H.; Gehrke, M.; Griesinger, C. *Angew. Chem.* **1988**, *100*, 507–554; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 490–536 and references cited therein.

[28] The mass-to-charge ratios given correspond to ^{56}Fe fragments; the observed distributions of isotopomers are in agreement with the calculated ones.

(m, 2 Ph H); ^{31}P NMR ($CDCl_3$) δ +42.0; MS[28] m/z 488 (M^+), 428, 363, 329, 275, 253, 183. Anal. Calcd for $C_{26}H_{25}O_2PSFe$: C, 63.94; H, 5.08; P, 6.34; S, 6.56. Found: C, 63.89; H, 5.19, P, 6.42; S, 7.17.

(*R*)-1-[(*S*)-(Diphenylphosphino)ferrocenyl]ethyl Mercaptan (5a). A 3.54-g (7.5-mmol) amount of **4a** was treated with 340 mg (9.0 mmol) of $LiAlH_4$ in 140 mL of Et_2O. The solution was stirred at room temperature for 5 h and then poured onto an ice/water mixture. The pH of the H_2O phase was adjusted to ca. 1 by the addition of 2 N aqueous HCl. The mixture was extracted with Et_2O (2 × 150 mL), the organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated in vacuo. The orange crystalline residue was recrystallized from hot EtOH, giving 2.10 g (65%) of orange needles: $[\alpha]^{22}_D = -368.8°$ ($c = 0.985$, $CHCl_3$); mp 140–141 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.72; ^1H NMR (500.13 MHz, $CDCl_3$) δ 1.65 (m, SH^7), 1.67 (d, partially overlapping with previous m, $J = 7.0$, $C(H^8)_3$), 3.88 (m, $C_5H_5 + H^5$), 4.28 (br t, $J = 3$, H^4), 4.38 (br s, H^3), 4.40 (m, partially overlapping with previous br s, H^6), 7.22–7.32 (m, 5 Ph H), 7.36–7.44 (m, 3 Ph H), 7.55–7.64 (m, 2 Ph H); ^{31}P NMR ($CDCl_3$) δ −24.6; MS[28] m/z 431, 430 (M^+), 428, 396, 364, 363, 277, 276, 261, 213, 212, 166, 165. Anal. Calcd for $C_{24}H_{23}FePS$: C, 66.99; H, 5.39; P, 7.20; S, 7.45. Found: C, 66.86; H, 5.46; P, 7.21; S, 7.59. An alternative preparation is as follows: The unpurified mixture of **4a** and **6** obtained as above was directly treated with excess $LiAlH_4$ in diethyl ether and worked up as described. **5a** was easily separated from (*R*)-1-[(*S*)-(diphenylthiophosphinyl)ferrocenyl]ethanol (7, vide infra) by flash column chromatography on silica gel using hexane/diethyl ether (4:1 v/v) as eluent.

(*R*)-1-[(*S*)-(Diphenylthiophosphinyl)ferrocenyl]ethanol (7). This compound was prepared analogously to **5a** by starting from 472 mg (1.0 mmol) of **6** and 45.5 mg (1.2 mmol) of $LiAlH_4$ in 15 mL of Et_2O: yield 320 mg (74%) of brown-orange crystals; $[\alpha]^{22}_D = -96.3°$ ($c = 0.6$, $CHCl_3$); mp 189–190 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.22; ^1H NMR ($CDCl_3$) δ 1.46 (d, $J = 7$, 3 H), 3.25 (br d, $J = 5$, OH), 3.78–3.84 (m, 1 Cp H), 4.24 (s, C_5H_5), 4.32–4.37 (m, 1 Cp H), 4.62–4.67 (m, 1 Cp H), 5.45–5.57 (m, 1 H), 7.35–7.68 (m, 8 Ph H), 7.82–7.94 (m, 2 Ph H); ^{31}P NMR ($CDCl_3$) δ +43.4; MS[28] m/z 446 (M^+), 428, 412, 381, 363, 253, 183. Anal. Calcd for $C_{24}H_{23}FePOS$: C, 64.59; H, 5.19; P, 6.94; S, 7.18. Found: C, 64.60; H, 5.28; P, 6.74; S, 7.17.

(*R*)-1-[(*S*)-(Diphenylthiophosphinyl)ferrocenyl]ethyl Thioacetate (8). A 2.28-g (4.67-mmol) amount of **6** was treated overnight with 0.81 g (7.11 mmol) of KSAc in 19 mL of CH_3COOH at 50 °C, as described for the preparation of **4a**. After evaporation of the solvent in vacuo, the residue was triturated with CH_2Cl_2 and the organic phase was washed consecutively with 50-mL portions of H_2O, brine, saturated aqueous $NaHCO_3$, and H_2O. Finally, the organic phase was dried over $MgSO_4$ and evaporated to dryness, leaving an oily residue, which was dissolved in hot EtOH. When this solution was cooled and let stand overnight at 4 °C, the product separated as orange crystals, which were collected by filtration, washed with cold EtOH, and dried in vacuo: yield 1.63 g (69%); $[\alpha]^{22}_D = -102.3°$ ($c = 0.555$, $CHCl_3$); mp 228–233 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.41; ^1H NMR ($CDCl_3$) δ 1.69 (d, $J = 7$, 3 H), 1.74 (s, 3 H), 3.77 (m, 1 Cp H), 4.28 (s overlapping with m, 1 Cp H + C_5H_5), 4.51 (m, 1 Cp H), 5.35 (q, $J = 7$, 1 H), 7.26–7.46 (m, 6 Ph H), 7.58–7.69 (m, 2 Ph H), 7.74–7.85 (m, 2 Ph H); ^{31}P NMR ($CDCl_3$) δ +40.4; MS[28] m/z 504 (M^+), 461, 439, 429, 428, 363, 275, 253, 212, 183. Anal. Calcd for $C_{26}H_{25}FePOS_2$: C, 61.91; H, 5.00, P, 6.14. Found: C, 62.25; H, 5.07; P, 6.19.

(*R*)-1-[(*S*)-(Diphenylthiophosphinyl)ferrocenyl]ethyl Mercaptan (9). A 1.6-g (3.17-mmol) amount of **8** was treated overnight with 154 mg (4.07 mmol) of $LiAlH_4$ in 70 mL of refluxing diethyl ether. After workup as described above, orange microcrystals were obtained. These were recrystallized from hot EtOH, giving 1.13 g (77%) of the desired product: $[\alpha]^{22}_D = -77.5°$ ($c = 1.055$, $CHCl_3$); mp 158–159 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.54; ^1H NMR ($CDCl_3$) δ 1.50 (br s, 1 H), 1.65 (d, $J = 7$, 3 H), 3.80 (m, 1 Cp H), 4.23 (s, C_5H_5), 4.30 (m, 1 Cp H), 4.53 (m, 1 Cp H), 5.11 (dq, $J = 7, 7$, 1 H), 7.30–7.53 (m, 6 Ph H), 7.64–7.87 (m, 4 Ph H); ^{31}P NMR ($CDCl_3$) δ +40.7; MS[28] m/z 462 (M^+), 446, 428, 363, 309, 253, 212. Anal. Calcd for $C_{24}H_{23}FePS_2$: C, 62.34; H, 5.01; P, 6.70. Found: C, 62.67; H, 5.13; P, 6.67.

$[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-}C_5H_3(1\text{-PPh}_2)(2\text{-CH}(CH_3)S))\}Cu]_3$ (11). A 400-mg amount of $[CuOBu^t]_4$ (**10**, 2.92 mmol of Cu) was dissolved in 10 mL of toluene, and the clear solution was cooled to 0 °C. A 20-mL solution of 1.258 g (2.92 mmol) of **5a** in the same solvent was added dropwise, and the initially clear orange mixture was stirred at 0 °C for 30 min, whereupon a finely divided precipitate formed. The amount of solid material increased upon adding 20 mL of pentane and stirring the mixture for another 30 min. The product was filtered off, washed with pentane, and dried in vacuo; yield 1.3 g (90%). This material, which was shown by NMR spectroscopy to be >95% pure, was recrystallized from CH_2Cl_2/toluene, giving 858 mg of thin, yellow-orange needles, which were collected by filtration, washed with pentane, and dried under a stream of Ar. One of these needles was found to be suitable for X-ray diffraction (vide infra): $[\alpha]^{22}_D = -454.7°$ ($c = 0.5$, CH_2Cl_2); mp 199–202 °C dec; TLC (hexane/EtOAc, 4:1 v/v) R_f 0.37; ^1H NMR (500 MHz, CD_2Cl_2) δ 0.98 (br d, $J = 7$, $C(H^8)_3$), 3.67 (m, H^5), 4.07 (qd, $J = 7, 6$, H^6), 4.17 (br t, $J = 2.4$, H^4), 4.37 (d, $J = 1.5$, H^3), 4.39 (s, C_5H_5), 7.05–7.30 (m, 5 Ph H), 7.33–7.43 (m, 3 Ph H), 7.57–7.70 (m, 2 Ph H); ^1H NMR (500 MHz, $CDCl_3$) δ 0.95 (br d, $J = 7$, $C(H^8)_3$), 3.60 (m, H^5), 4.09 (br q, $J = 7$, H^6), 4.29 (br t, $J = 2.5$, H^4), 4.31 (s, C_5H_5), 4.40 (m, H^3), 7.10–7.20 (m, 2 Ph H), 7.21–7.32 (m, 3 Ph H), 7.39–7.48 (m, 3 Ph H), 7.67–7.78 (m, 2 Ph H); ^{31}P NMR (CD_2Cl_2) δ −16.8; FAB MS m/z (based on ^{56}Fe and ^{63}Cu) 1539 ($(A_3 + Cu)^+$, where A represents the monomeric unit) 1476 (A_3^+), 1135, 1079, 1047 ($(A_2 + Cu)^+$). Anal. Calcd for $C_{24}H_{22}CuFePS$: C, 58.49; H, 4.50; Cu, 12.89; P, 6.28; S, 6.50. Found: C, 58.42, H, 4.64; Cu, 12.3; P, 5.94; S, 6.24.

Reaction of $[^tBuOCuPPh_3]_2$ with 5a. A 326-mg (1.24-mmol) amount of PPh_3 was added to a solution of 170 mg (1.24 mmol of Cu) of **10** in 20 mL of toluene, and the mixture was stirred at 0 °C for 2 h, giving a pale yellow, clear solution. A 534-mg (1.24-mmol) portion of **5a** was then added. After 30 min at the same temperature a finely divided yellow-orange precipitate formed. ^{31}P NMR spectroscopy showed the presence of **11** and free PPh_3 as the only detectable species. The mixture was treated as described above, and the product was filtered off, washed with pentane, and dried; yield 495 mg (81%). This material was found to be in all respects identical to an authentic sample of **11**.

X-ray Crystallographic Study of 11. A yellow crystal, obtained after recyrstallization from CH_2Cl_2/toluene as described above, was glued at the tip of a MARK glass fiber using ARALDIT RAPID and covered with a thin film of the same glue. Intensity data ($\mp h, +k, +l$), gathered by the $\omega/2\theta$ scan method, were reduced by routine procedures.[29] There was no significant intensity variation for three standard reflections measured every 1 h. Absorption corrections were applied, on the basis of azimuthal scans of six reflections with the diffractometer angle κ near 90°.[30] Because of the limited number of reflections having $I > 3\sigma(I)$, only the heavier atoms were refined anisotropically. Hydrogen atoms could not be localized.

Acknowledgment. We are indebted to Mr. Robert Häusel for skillful preparative work and to Dr. H.-P. Kriemler for mass spectroscopic analyses. Thanks are due to Prof. Gerard van Koten for most valuable discussions and for sending us a preprint of a manuscript[12b] prior to publication. A critical review of the manuscript, as well as NMR technical advice, by Prof. Paul S. Pregosin is also acknowledged.

Supplementary Material Available: Tables of bond distances (S1) and angles (S2) and anisotropic thermal parameters (S3) for 11 (5 pages); a listing of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

---

[29] Calculations were performed on a Micro-Vax II computer using the commercial package SDP DIRDIF.

[30] North, A. C. T.; Phillips, D. C.; Mathew, F. S. *Acta Crystallogr.* 1968, *A24*, 351.