stoppers and wheels. This could be important for measuring the hydrogen-bonding strength between wheel and axle, and for the application of mechanical bonds in polymers,[11] in which a temperature-dependent change of the relationship between structure and property is desired.

Experimental Section

The typical procedure for the synthesis of rotaxanes by melting down wheel and axle is exemplified by the preparation of rotaxane **2cy**: Wheel **1c** (200 mg, 0.2 mmol) was carefully mixed with axle **3y** (123 mg, 0.2 mmol). Portions of 20–30 mg of this mixture were poured into glass tubes, melted by heating to 350 °C for a short time with a hot-air blower, and subsequently quenched in cold water [12]. The solidified melt was dissolved with a mixture of chloroform and methanol (5/1). The combined crude products were purified by column chromatography. M.p.: 240 °C; $R_f = 0.6$ (dichloromethane/ethyl acetate, 20/1, silica gel 40–63 µm); yield 25 mg (8%).

Received: December 12, 1996
Revised version: February 14, 1997 [Z9879IE]
German version: *Angew. Chem.* 1997, *109*, 1248–1250

Keywords: macrocycles · mechanical binding · rotaxanes · supramolecular chemistry · synthetic methods

---

[1] F. Vögtle, M. Händel, S. Meier, S. Ottens-Hildebrandt, F. Ott, T. Schmidt, *Liebigs Ann.* **1995**, 739; L. F. Lindoy, *Nature* **1995**, *376*, 293; A. G. Johnston, D. A. Leigh, A. Murphy, J. P. Smart, M. D. Deegan, *J. Am. Chem. Soc.* **1996**, *118*, 10662; F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, W. Schmidt, *Synthesis* **1996**, 353; F. Vögtle, T. Dünnwald, M. Händel, R. Jäger, S. Meier, G. Harder, *Chem. Eur. J.* **1996**, *2*, 640; F. Vögtle, F. Ahuis, S. Baumann, J. L. Sessler, *Liebigs Ann.* **1996**, 921; R. Jäger, M. Händel, J. Harren, K. Rissanen, F. Vögtle, *ibid.* **1996**, 1201; review on the synthesis of molecules with mechanical bonds: R. Jäger, F. Vögtle, *Angew. Chem.* **1997**, *109*, 967; *Angew. Chem. Int. Ed.* **1997**, *36*, 930.

[2] C. A. Hunter, *J. Chem. Soc. Chem. Commun.* **1991**, 749; F. J. Carver, C. A. Hunter, R. J. Shannon, *ibid.* **1994**, 1277; F. Vögtle, S. Meier, R. Hoss, *Angew. Chem.* **1992**, *104*, 1628; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1619; F. Vögtle, R. Jäger, M. Händel, S. Ottens-Hildebrandt, *Pure Appl. Chem.* **1996**, *68*, 225.

[3] a) I. T. Harrison, *J. Chem. Soc. Chem. Commun.* **1972**, 231; *J. Chem. Soc. Perkin Trans. 1* **1974**, 301; b) G. Schill, W. Beckmann, N. Schweickert, H. Fritz, *Chem. Ber.* **1986**, *119*, 2647; c) M. Asakawa, P. R. Ashton, R. Ballardini, V. Balzani, M. Belohradsky, M. T. Gandolfi, O. Kocian, L. Prodi, F. M. Raymo, J. F. Stoddart, M. Venturi, *J. Am. Chem. Soc.* **1997**, *119*, 302.

[4] We thank Dipl.-Chem. R. Jäger for providing substances and for fruitful discussions.

[5] We know from experience that Stuart/Briegleb models of large molecules are often too flexible, whereas CPK models are usually too rigid.

[6] It is conceivable that at high temperatures the rotaxane construction takes place by a bond cleavage (e.g. CO–NH) and subsequent threading and recombination. The fact that we could not find any catenanes refutes a mechanism of bond cleavages in the wheel, particularly since the number of the amide bonds (although sterically more hindered) is twice the number of those in the axle. Furthermore we could not find any thermal/pyrolytic cleavage/recombination of amide bonds in the literature apart from transamidations, which proceed by addition and elimination at 200 °C: H. R. Kricheldorf, E. Leppert, G. Schilling, *Makromol. Chem.* **1975**, *176*, 1629.

[7] S. Ottens-Hildebrandt, T. Schmidt, J. Harren, F. Vögtle, *Liebigs Ann.* **1995**, 1855.

[8] Pseudorotaxanes are compounds with a mechanical bond between wheel and axle in which the stopper groups are not sterically demanding enough to hold the wheel on the axle.

[9] G. Schill, H. Zollenkopf, *Nachr. Chem. Tech.* **1967**, *15*, 149; I. T. Harrison, S. Harrison, *J. Am. Chem. Soc.* **1967**, *89*, 5723; C. Wu, P. R. Lecavalier, Y. X. Shen, H. W. Gibson, *Chem. Mater.* **1991**, *3*, 569; J.-C. Chambron, V. Heitz, J.-P. Sauvage, *J. Chem. Soc. Chem. Commun.* **1992**, 1131; D. J. Cardenas, P. Gavina, J.-P. Sauvage, *Chem. Commun.* **1996**, 1915; H. Sleiman, P. Baxter, J.-M. Lehn, K. Rissanen, *J. Chem. Soc. Chem. Commun.* **1995**, 715; B. L. Allwood, N. Spencer, H. Shahriari-Zavareh, J. F. Stoddart, D. J. Williams, *ibid.* **1987**, 1064; P. R. Ashton, P. T. Glink, J. F. Stoddart, P. A. Tasker, A. J. P. White, D. J. Williams, *Chem. Eur. J.* **1996**, *2*, 729; A. C. Benniston, A. Harriman, V. Lynch, *Tetrahedron Lett.* **1994**, *35*, 1473; H. Ogino, *J. Am. Chem. Soc.* **1981**, *103*, 1303; T. V. S. Rao, D. D. Lawrence, *ibid.* **1990**, *112*, 3614; R. Isnin, A. E. Kaifer, *ibid.* **1991**, *113*, 8188; G. Wenz, E. van der Bey, L. Schmidt, *Angew. Chem.* **1992**, *104*, 758; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 783; S. Anderson, H. L. Anderson, *ibid.* **1996**, *108*, 2075 bzw. **1996**, *35*, 1956; A. Harada, J. Li, M. Kamachi, *Nature* **1993**, *364*, 516; G. Wenz, B. Keller, *GIT Fachz. Lab.* **1994**, 608; M. Born, H. Ritter, *Angew. Chem.* **1995**, *107*, 342; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 309; H. W. Gibson, S. Liu, P. Lecavalier, C. Wu, Y. X. Shen, *J. Am. Chem. Soc.* **1995**, *117*, 852; P. E. Mason, I. W. Parsons, M. S. Tolley; *Angew. Chem.* **1996**, *108*, 2405; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2238; Y.-M. Jeon, D. Whang, J. Kim, K. Kim, *Chem. Lett.* **1996**, 503; Z.-T. Li, P. C. Stein, J. Becher, D. Jensen, P. Moerk, N. Svenstrup, *Chem. Eur. J.* **1996**, *2*, 624; recent reviews: H. W. Gibson, M. C. Bheda, P. T. Engen, *Prog. Polym. Sci.* **1994**, *19*, 843; D. B. Amabilino, J. F. Stoddart, *Chem. Rev.* **1995**, *95*, 2725.

[10] We thank Prof. Dr. P. von R. Schleyer (Universität Erlangen-Nürnberg, Prof. Dr. J. Gasteiger (Computer-Chemie-Centrum Erlangen-Nürnberg), and Dr. B. Schürmann (Humboldt-Universität Berlin) for the cooperation with calculations.

[11] Y. Geerts, D. Muscat, K. Müllen, *Makromol. Chem.* **1995**, *196*, 3425; D. Muscat, A. Witte, W. Köhler, K. Müllen, Y. Geerts, *Macromol. Rapid Commun.* **1997**, *18*, 233.

[12] We have also tried to synthesize these rotaxanes by slowly heating corresponding mixtures of wheel and axle in an oil bath (to 320 °C). This led to decreased yields of the corresponding rotaxanes and increased portions of by-products.

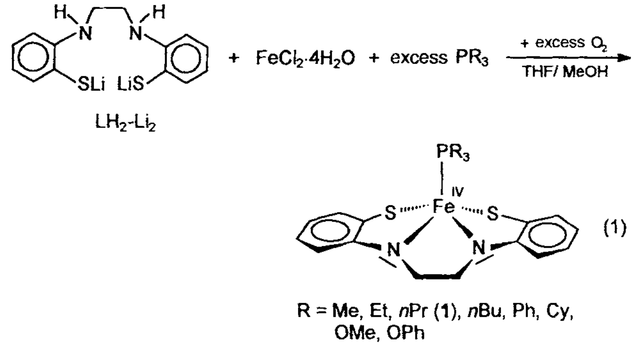
A Convenient Way to Novel Fe^{IV} Complexes with Mixed N/S/P Coordination Spheres and "Innocent" Ligands**

Dieter Sellmann,* Susanne Emig,
Frank W. Heinemann, and Falk Knoch

Dedicated to Professor Walter Siebert on the occasion of his 60th birthday

Iron complexes with high-valent Fe^{IV} centers are discussed as reactive intermediates in numerous enzymatic processes that are catalyzed, for instance, by heme peroxidase, cytochrome P450, methane monooxygenase, ribonucleotide reductase, isopenicillin N synthase, and other enzymes.[1] The diversity of these reactions suggests that also a rich nonbiological Fe^{IV} chemistry should be accessible.[2] However, only a few ligands proved to be sufficiently oxidation resistant and able to stabilize Fe^{IV} centers. These ligands are mainly tetrapyrrolic ligands[3] and other N_4 donor ligands[2, 4] or ligands with sulfur donors.[5] We have now obtained Fe^{IV} complexes with a mixed N/S/P coordination sphere from readily accessible starting materials in a remarkably easy way. The one-pot reaction according to Equation (1) yields the Fe^{IV} complexes $[Fe^{IV}(PR_3)(L)]$ in yields of more than 85%.

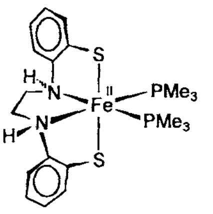
Equation (1) shows that the oxidation $Fe^{II} \rightarrow Fe^{IV}$ is accompanied by a deprotonation of the amine functions in the LH_2^{2-} ligand and formation of the tetraanionic L^{4-} ligand [LH_4 = 1,2-ethanediamide-*N*,*N'*-bis(2-benzenethiol). The reaction initially



---

[*] Prof. Dr. D. Sellmann, Dipl.-Chem. S. Emig, Dr. F. W. Heinemann, Dr. F. Knoch
Institut für Anorganische Chemie der Universität Erlangen-Nürnberg
Egerlandstrasse 1, D-91058 Erlangen (Germany)
Fax: Int. code +(9131) 85-7367
e-mail: sellmann@anorganik.chemie.uni-erlangen.de

[**] Transition-Metal Complexes with Sulfur Ligands, Part 122. We thank the late Prof. G. Ritter and E. Giese for the Moessbauer measurements. Part 121: D. Sellmann, A. Hennige, *Angew. Chem.* **1997**, *109*, 270–271; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 276-278.



2

yields suspensions of [Fe^{II}(LH$_2$)] complexes. Upon contact with air, the color of these suspensions turns from brown into deep blue-green, and the respective Fe^{IV} complexes precipitate as red-violet microcrystals. The primary formation of Fe^{II} complexes was proved by isolation and characterization of [Fe^{II}(PMe$_3$)$_2$(LH$_2$)] (**2**).[6]

The complexes resulting according to Equation (1) exhibit largely analogous properties. [Fe^{IV}(P*n*Pr$_3$)(L)] (**1**) has been characterized comprehensively, and is readily soluble in common solvents (THF, CH_2Cl_2) yielding deep blue-green solutions. The color is attributed to a strong band at 684 nm in the UV/Vis spectrum (CH_2Cl_2), which is assigned to a ligand-to-metal charge transfer (LMCT) transition. Complex **1** is paramagnetic ($\mu_{eff} = 2.76\ \mu_B$, 295 K, solid state). The magnetism is appropriate for two unpaired electrons and an "intermediate-spin" d^4 Fe^{IV} center with a $S = 1$ ground state[4b, c, 5a] and gives rise to paramagnetically shifted signals in the ^{1}H NMR spectrum of **1**. The ^{1}H NMR spectrum and likewise the ^{13}C{^{1}H} NMR spectrum of **1** indicate that **1** possesses C_s symmetry; thus, the molecular structure determined by X-ray structure analysis for the solid state (Figure 1) is retained in solution.[7]

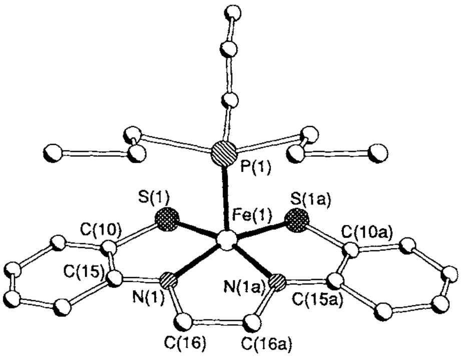
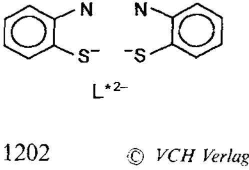


Figure 1. Molecular structure of **1** (H atoms omitted). Selected distances [pm]: Fe(1)–P(1) 220.2(3), Fe(1)–S(1) 218.5(2), Fe(1)–N(1) 184.0(6), N(1)–C(15) 134.8(8), N(1)–C(16) 147.2(7), C(16)–C(16a) 154.2(13), S(1)–C(10) 171.1(7).

Complex **1** possesses crystallographically imposed C_S symmetry and a distorted tetragonal pyramidal Fe center. The Fe–N distances (184.0(6) pm) are similar to those in reported Fe^{IV} amido complexes (d(Fe–N) = 186–192 pm)[4b, c, g] and are distinctly shorter than in the related [Fe^{II}(L^1)(L^2)(LH$_2$)] complexes (L^1 = PR$_3$; L^2 = CO, PR$_3$; d(Fe–N) = 206–209 pm).[6b] Because Fe–N distances longer than 200 pm correspond to Fe–N single bonds,[8] the distances in **1** indicate Fe–N multiple-bond character. Similar arguments hold for the Fe–S distances (218.5(2) pm). Comparably short Fe–S distances are found in square-pyramidal [Fe^{IV}(PMe$_3$)(*o*-$C_6H_4S_2$)$_2$] (218.5 pm), which exhibits an average Fe–S bond order of 1.5.[5a] The angle sums of 360° around the N atoms corroborate the amide character of the N donors. In addition, the averaged N–C and C–C distances in the N–C_2H_4–N bridge of the L^{4-} ligand exclude the formation of the Schiff base ligand glyoxal-bis(2-mercaptoanil)(2–) (L^{*2-}), which can potentially form from LH$_2^{2-}$ by dehydrogenation.[9]



L^{*2-}

The zero-field Moessbauer spectra of **1** consist of one doublet at 298 K and 4.2 K (Table 1, Figure 2). The low isomer shifts δ and the large and the large quadrupole splitting ΔE_Q, which is nearly temperature independent, are consistent with a five-coordinate Fe^{IV} ($S = 1$) center in a tetragonal-pyramidal coordination.[2, 4a, b, g, 5a] The Moessbauer data rule out resonance structures such as **B** and **C** for the [Fe(L)] core of **1**, which suggest an intramolecular redox reaction between the Fe center and the ligand.

The resonance structures **B** and **C** would implicate that the L ligand is a dithiolene-type "noninnocent" ligand that, due to the $S = 1$ magnetism of **1**, coordinates either as a monoradical a Fe^{III} ($S = 1/2$) center or as a diradical a Fe^{II} ($S = 0$) center. However, Fe^{III} ($S = 1/2$) complexes and Fe^{II} ($S = 0$) complexes exhibit isomer shifts δ in the ranges of 0.16 to 0.38 mm s^{-1} and 0.18 to 0.51 mm s^{-1},[10] which is quite different from the isomer shift of $\delta = 0.0396(2)$ mm s^{-1} for **1**.

Table 1. Moessbauer parameters of **1**.

T [K]	δ [mm s^{-1}] [a]	ΔE_Q [mm s^{-1}] [b]	Γ [mm s^{-1}] [c]
298.0	–0.0442(20)	3.0226(40)	0.2285(63)
4.2	0.0396(2)	3.1596(3)	0.2361(5)

[a] δ Isomer shift relative to α-iron at 298 K. [b] ΔE_Q Quadrupole splitting. [c] Γ Linewidth.

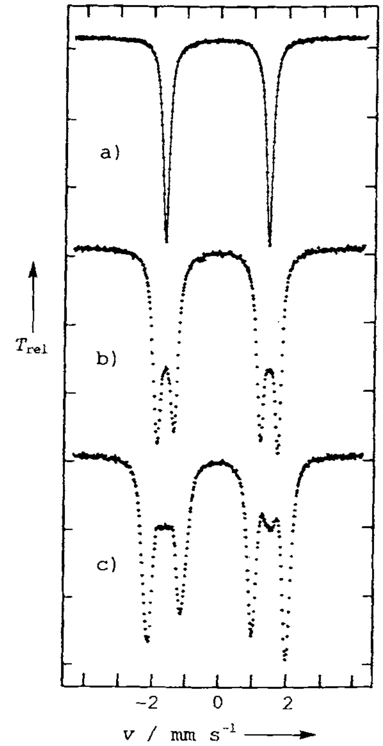
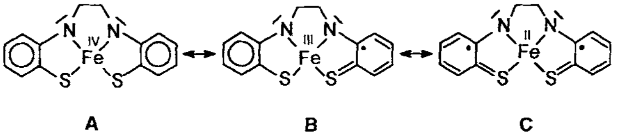


Figure 2. Moessbauer spectra of polycrystalline **1** at 4.2 K; a) in the zero-field, b) in an applied field of 2.5 T, and c) in an applied field of 5.0 T.



Finally, the high-valent character of the Fe center is also revealed by the cyclic voltammogram of **1** (Figure 3). It displays two quasireversible redox waves at +0.04 V and –0.86 V (CH_2Cl_2, vs. NHE). They are assigned to Fe^{IV}/Fe^{III} and Fe^{III}/Fe^{II} redox couples and appear at relatively positive potentials when compared with the corresponding redox waves of the related complex [Fe^{IV}(PMe$_3$)(*o*-$C_6H_4S_2$)$_2$] (– 0.31 V, – 1.07 V, vs. NHE; acetone).[5a]

The results show that novel Fe^{IV} complexes are readily accessible from simple starting materials. To the best of our knowledge, **1** and its analogues are the first Fe^{IV} complexes with a mixed N/S/P coordination sphere. Spectroscopic and structural data corroborate the results accumulated over the past years that 1,2-benzenedithiolate or the related *o*-aminothiophenolate behave as quite usual dithiolate or aminethiolate ligands.[5a, 9b] These ligands show no tendency to break up their aromatic

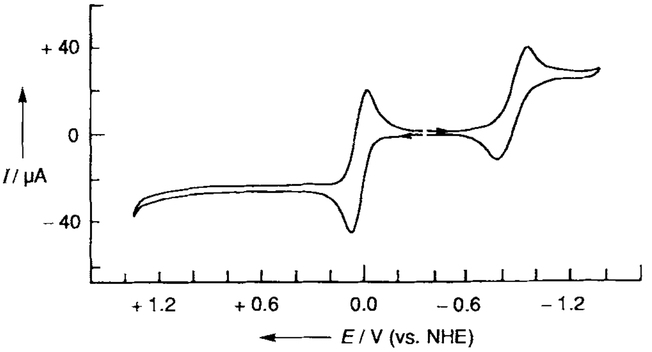


Figure 3. Cyclic voltammogram of **1** in CH_2Cl_2 (1×10^{-3} M; 1×10^{-1} M $NnBu_4PF_6$, $v = 0.02\ Vs^{-1}$).

systems by release of electrons from the benzene rings in order to become "dithiolene-type" ligands. The data rather indicate that the stabilization of Fe^{IV} centers by "hard" N and "soft" S donors is essentially due to π donation from the amide and thiolate functions and rule out "noninnocence" of the L^{4-} ligand, if something like "innocence" of ligands exists at all!

Experimental Section

All operations were carried out under N_2 at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. LH_4 was prepared according to literature methods [11]. **1**: To a yellow solution of LH_4 (280 mg, 1 mmol) in THF (5 mL) and MeOH (25 mL) a 1 N solution of LiOMe (2 mL, 2 mmol) in MeOH, $FeCl_2 \cdot 4H_2O$ (200 mg, 1 mmol), and $PnPr_3$ (1 mL, 5 mmol) were added. The resulting brown suspension was stirred for 1.5 h in contact with air and for 2 h under N_2. The precipitated red-violet microcrystals of **1** were separated, washed with MeOH (50 mL), H_2O (30 mL), and Et_2O (20 mL), and dried in vacuo for 1 d. Yield: 440 mg (90%). Elemental analysis of $C_{23}H_{33}FeN_2PS_2$ (488.48): Calcd C 56.55, H 6.81, N 5.73, S 13.13; found C 56.32, H 6.78, N 5.72, S 12.97; ^1H NMR (269.6 MHz, $CDCl_3$): $\delta = 19.30$, 12.13 (2 s, 4 H; C_2H_4), 8.09, 5.87 (2 d, 4 H; C_6H_4), 7.01, 4.95 (2 t, 4 H; C_6H_4), 0.85–0.6 (m, 6 H; CH_2), 0.47 (t, 9 H; CH_3), (− 0.4)–(− 0.6) (m, 6 H; PCH_2); $^{13}C\{^1H\}$ NMR (67.70 MHz, CD_2Cl_2): $\delta = 157.6$, 140.1, 123.4, 122.9, 120.6, 115.6 (C_6H_4), 51.7 (C_2H_4), 25.4, 15.9, 15.1 ($P(C_3H_7)_3$); MS (FD, CH_2Cl_2): $m/z = 488$ [M^+]; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 339 (10500), 373 (11000), 441 (9900), 684 (25800); $\mu_{eff} = 2.76\ \mu_B$ (295 K); CV (CH_2Cl_2, 295 K, 0.1 M $NnBu_4PF_6$; E vs. NHE [V]): $E^{\circ\prime}$ +0.04 ($[\mathbf{1}]^0/[\mathbf{1}]^-$), $E^{\circ\prime}$ −0.86 ($[\mathbf{1}]^-/[\mathbf{1}]^{2-}$).

Received: November 22, 1996 [Z 9805 IE]
German version: *Angew. Chem.* **1997**, *109*, 1250–1252

Keywords: iron · Moessbauer spectroscopy · N ligands · S ligands

---

[1] a) P. R. Ortiz de Montellano, *Cytochrome P-450: Structure, Mechanism and Biochemistry*, Plenum, New York, **1986**; b) B. G. Fox, J. G. Borneman, L. P. Wackett, J. D. Lipscomb, *Biochemistry* **1990**, *29*, 6419–6427; c) B. G. Fox, W. A. Froland, J. E. Dege, J. D. Lipscomb, *J. Biol. Chem.* **1989**, *264*, 10023–10033; d) T. E. Elgren, J. B. Lynch, C. Juarez-Garcia, E. Münck, B.-M. Sjöberg, L. Que, Jr., *ibid.* **1991**, *266*, 19265–19268; e) J. E. Baldwin, E. P. Abraham, *Nat. Prod. Rep.* **1988**, *5*, 129–145; f) T. A. Dix, S. Benkovic, *J. Acc. Chem. Res.* **1988**, *21*, 101–107; g) P. H. Buist, D. M. Marecak, *J. Am. Chem. Soc.* **1992**, *114*, 5073–5080.

[2] K. L. Kostka, B. G. Fox, M. P. Hendrich, T. J. Collins, C. E. F. Rickard, L. J. Wright, E. Münck, *J. Am. Chem. Soc.* **1993**, *115*, 6746–6757.

[3] a) J. T. Groves, Z. Gross, M. K. Stern, *Inorg. Chem.* **1994**, *33*, 5065–5072; b) E. Vogel, S. Will, A. Schulze Tilling, L. Neumann, J. Lex, E. Bill, A. X. Trautwein, K. Wieghardt, *Angew. Chem.* **1994**, *106*, 771–775; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 731–735; c) J. T. Groves, R. Quinn, T. J. McMurry, M. Nakamura, G. Lang, B. Boso, *J. Am. Chem. Soc.* **1985**, *107*, 354–360; d) D. R. Englisch, D. N. Hendrickson, K. S. Suslick, *Inorg. Chem.* **1985**, *24*, 121–122; e) W. Hiller, J. Strähle, A. Datz, M. Hanack, W. E. Hatfield, L. W. Haar, P. Gütlich, *J. Am. Chem. Soc.* **1984**, *106*, 329–335; f) C. Ercolani, M. Gardini, V. L. Goedken, G. Pennesi, G. Rossi, U. Russo, P. Zanonato, *Inorg. Chem.* **1989**, *28*, 3097–3099.

[4] a) C. C. Cummins, R. R. Schrock, *Inorg. Chem.* **1994**, *33*, 395–396; b) U. Knof, T. Weyhermüller, T. Wolter, K. Wieghardt, E. Bill, C. Butzlaff, A. W. Trautwein, *Angew. Chem.* **1993**, *105*, 1701–1704; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1635–1638; c) T. J. Collins, B. G. Fox, Z. G. Hu, K. L. Kostka, E. Münck, C. E. F. Rickard, L. J. Wright, *J. Am. Chem. Soc.* **1992**, *114*, 8724–8725; d) V. M. Leovac, L. S. Jovanovic, V. I. Cesljevic, L. J. Bjelica, N. J. Evic, *Polyhedron* **1992**, *11*, 1029–1035; e) N. V. Gerbeleu, Y. A. Simonov, V. B. Arion, V. M. Leovac, K. I. Turta, K. M. Indrichan, D. I. Gradinaru, V. E. Zavodnik, T. I. Malinovskii, *Inorg. Chem.* **1992**, *31*, 3264–3268; f) V. M. Leovac, R. Herak, B. Prelesnik, S. R. Niketic, *J. Chem. Soc. Dalton Trans.* **1991**, 2296–2299; g) T. J. Collins, K. L. Kostka, E. Münck, E. S. Uffelman, *J. Am. Chem. Soc.* **1990**, *112*, 5637–5639.

[5] a) D. Sellmann, M. Geck, F. Knoch, G. Ritter, J. Dengler, *J. Am. Chem. Soc.* **1991**, *113*, 3819–3828; b) D. Petridis, D. Niarchos, B. Kanellakopulos, *Inorg. Chem.* **1979**, *18*, 505–509; c) H. Miyamae, S. Sato, Y. Saito, K. Sakai, M. Fukuyama, *Acta Crystallogr. Sect. B* **1977**, *33*, 3942–3944; d) E. F. Epstein, I. Bernal, *Inorg. Chim. Acta* **1977**, *25*, 145–155; e) F. J. Hollander, R. Pedelty, D. Coucouvanis, *J. Am. Chem. Soc.* **1974**, *96*, 4032–4034; f) R. L. Martin, N. M. Rohde, G. B. Robertson, D. Taylor, *ibid.* **1974**, *96*, 3647–3649; g) A. Pasek, D. K. Straub, *Inorg. Chem.* **1972**, *11*, 259–263; h) D. L. Johnston, W. L. Rohrbaugh, W. D. Horrocks, *ibid.* **1971**, *10*, 1474–1479.

[6] a) D. Sellmann, U. Reineke, G. Huttner, L. Zsolnai, *J. Organomet. Chem.* **1986**, *310*, 83–93; b) D. Sellmann, S. Emig, unpublished results.

[7] X-ray crystal structure analysis of **1** was made on a Siemens P4 four-circle diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 71.073$ pm, graphite monochromator, $T = 200$ K, ω scan, $3^\circ \leq 2\theta \leq 54^\circ$). The structure was solved by SHELXTL-PLUS and refined by using the program package SHELXL93. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in the difference Fourier map and refined with fixed isotropic displacement parameters. **1**: $C_{23}H_{33}FeN_2PS_2$, crystals from THF/MeOH, $0.50 \times 0.30 \times 0.20$ mm³, orthorhombic, space group *Pnma*, $a = 826.6(3)$, $b = 1510.6(4)$, $c = 1926.3(5)$ pm, $V = 2.405(12)$ nm³, $\rho_{calcd} = 1.35$ g cm^{-3}, $Z = 4$, $R_1 = 0.0613$, $wR_2 = 0.1336$, 3305 measured reflections, 2741 independent reflections, 771 observed reflections [$F > 4.0\sigma(F)$], 139 refined parameters. With greater accuracy the molecular structure of [$Fe(PPh_3)(L)$] was also determined by X-ray crystal structure analysis. The relevant parameters of [$Fe(PPh_3)(L)$] are nearly identical with those of **1**. Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository numbers CSD-406037 (**1**) and CSD-406038 ([$Fe(PPh_3)(L)$]).

[8] a) D. Sellmann, T. Hofmann, F. Knoch, *Inorg. Chim. Acta* **1994**, *224*, 61–71; b) T. Jüstel, T. Weyhermüller, K. Wieghardt, E. Bill, M. Lengen, A. X. Trautwein, P. Hildebrandt, *Angew. Chem.* **1995**, *107*, 744–747; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 669–672.

[9] a) D. Sellmann, M. Hannakam, F. Knoch, M. Moll, *Z. Naturforsch. B* **1992**, *47*, 1545–1549; b) D. Sellmann, R. Ruf, F. Knoch, M. Moll, *Inorg. Chem.* **1994**, *34*, 4745–4755.

[10] "Mössbauer Spectroscopy": P. Gütlich, *Top. Appl. Phys.* **1975**, *5*, 67.

[11] D. Sellmann, O. Käppler, F. Knoch, M. Moll, *Z. Naturforsch. B* **1990**, *45*, 803–816.

New Motifs in Aurophilic Self-Assembly: Synthesis and Structures of $[Au(NH{=}CMe_2)_2]CF_3SO_3$ and $[Au(C{\equiv}CSiMe_3)(CNtBu)]$[**]

José Vicente,* María-Teresa Chicote,* María-Dolores Abrisqueta, Rita Guerrero, and Peter G. Jones*

The triflate salt of the complex $[Au(NH_3)_2]^+$ prepared by Mingos et al.[1, 2] reacts very slowly with acetone to give the first iminogold(I) complex $[Au(NH{=}CMe_2)_2]CF_3SO_3$ (**1**, Scheme 1).

---

[*] Prof. Dr. J. Vicente, Prof. Dr. M.-T. Chicote, Ldas. M.-D. Abrisqueta, R. Guerrero
Grupo de Química Organometálica
Departamento de Química Inorgánica
Facultad de Química
Universidad de Murcia, Aptdo. 4021, E-30071 Murcia (Spain)
Fax: Int. code +(68)364143
e-mail: jvs@fcu.um.es
Prof. Dr. P. G. Jones
Institut für Anorganische und Analytische Chemie der Universität
Postfach 3329, D-38023 Braunschweig (Germany)
Fax: Int. code +(531)391-5387
e-mail: p.jones@tu-bs.de

[**] This work was supported by Dirección General de Investigación Científica y Técnica (PB92-0982-C) and the Fonds der Chemischen Industrie. M.-D. A. and R. G. are grateful to Ministerio de Educación y Ciencia (Spain) for Grants.