Inorg. Chem. **1985**, *24*, 1367–1375

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Group 11[†] Metal Ions in Poly(donor atom) Environments: X-ray Crystal and Molecular Structure of $[M((R,S)\text{-}1,2\text{-}(5\text{-}R\text{-thio-}2\text{-}CH{=}N)_2\text{-c-Hx})_2](O_3SCF_3)$ (M = Ag(I), R = Me, thio = Thiophene, c-Hx = Cyclohexane) and Silver(I) and Copper(I) Coordination Properties in Solution (^{1}H, ^{109}Ag, and ^{15}N NMR)

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Received May 15, 1984

The 2/1 reactions of the N_2S_2 ligand system (R,S)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx (R = H (**1a**), Me (**1b**); thio = thiophene, c-Hx = cyclohexane) with M = Ag(I), Cu(I) yielded stable mononuclear $[M(N_2S_2)_2](O_3SCF_3)$ complexes. An X-ray crystallographic study of $[Ag(\mathbf{1b})_2](O_3SCF_3)$ defined its molecular structure: triclinic, space group $P\bar{1}$, $a = 9.900$ (4) Å, $b = 11.465$ (4) Å, $c = 19.423$ (6) Å, $\alpha = 106.10$ (3)°, $\beta = 99.95$ (3)°, $\gamma = 90.38$ (3)°, and $Z = 2$ for 5124 independent reflections. The structure was refined to $R = 3.9\%$. The N_2S_2 ligands are coordinated to the group 11 metal center with one thiophene–imine moiety of each ligand via the imine-*N* atoms N(1) (Ag–N(1) = 2.275 (3) Å) and N(3) (Ag–N(3) = 2.281 (3) Å) while the lone pairs of N(2), S(2), N(4), and S(4) are not pointing toward the silver(I) center. The ^{1}H NMR results revealed that in solution at 190 K the same enantiomeric pair is present as has been found in the solid. From the ^{15}N NMR data, the chemical shifts of the resonances representing the two different imine-*N* sites, N(1), N(3) and N(2), N(4), as well as the presence of $^1J(^{15}N\text{–}^{107,109}Ag)$ on both resonances, unambiguously proved the existence of orbital overlap between Ag(I) and N(1), N(3) as well as with the unfavorably positioned (with respect to the group 11 metal center) N(2) and N(4) donor sites; i.e., all four N donor atoms interact with the Ag center. On the basis of the small difference in ^{109}Ag chemical shifts for the $[Ag(\mathbf{1})_2]^+$ cations (R = H, Me; $\Delta\delta(^{109}Ag) = 1$), it is concluded that the thiophene-*S*–Ag interactions are very weak or are not present. This weak affinity of thiophene-*S* atoms for group 11 metal centers can be regarded as the main reason for the formation of these mononuclear $[M(N_2S_2)_2](O_3SCF_3)$ complexes. When stronger donor atoms are present in the "outer" ring system, for instance pyridine-*N* atoms, resulting in the N_4 ligand system, only the dinuclear $[M_2(N_4)_2](O_3SCF_3)_2$ complexes were formed. The copper(I) complex $[Cu(\mathbf{1b})_2](O_3SCF_3)$ has in the solid-state a structure similar to that of the corresponding silver(I) complex. The difference in M–N(1) and M–N(3) distances found in the two structures (M = Cu(I), Ag(I)) is caused by the stronger Cu–N(imine) bonds and the smaller ionic radius of copper(I) compared with that of silver(I). In solution (at 190 K) the $[Cu(\mathbf{1b})_2]^+$ cation exists in at least two different stereoisomeric forms. Above 210 K an intermolecular N_2S_2 ligand-exchange process occurs in solutions of the $[M(N_2S_2)_2](O_3SCF_3)$ complexes, as demonstrated for $[Ag(\mathbf{1})_2]^+$ by the loss of $^3J(^1H\text{–}^{107,109}Ag)$ on the imine-*H*(A) resonances.

Introduction

Coordination chemistry of copper(I) salts with polydentate ligands has become an important research area with respect to the search for model compounds that can mimic one or more of the important specific physical and chemical properties of Cu(I)-containing proteins.[1] In a previous paper[2] we have pointed out that when a rationale is given for the reactivities of the Cu(I) sites in solution, based on conformational and configurational features of model complexes, it is insufficient to know their structures in the solid state (X-ray) and it is far more important to know their structures (and dynamics) in solution. For this reason we are currently studying the structures of copper(I) complexes with a selected series of polydentate ligands both in solution by ^{1}H and ^{13}C NMR and in the solid state by X-ray methods.

It has been shown[2] that detailed information concerning the coordination properties of the polydentate ligand under investigation to copper(I) in solution can be obtained by studying the corresponding silver(I) complexes. Both silver(I) isotopes, ^{107}Ag (51.82%) and ^{109}Ag (48.18%), have $I = {}^1/_2$ and therefore $^nJ(^1H\text{–}^{107,109}Ag)$ in the ^{1}H NMR spectra or $^1J(^{15}N\text{–}^{107,109}Ag)$ in the ^{15}N NMR spectra of silver(I) complexes with polydentate N donor ligands might be observable and give information about the connectivity of the group 11 metal nucleus and the polydentate ligand system. These heteronuclear couplings can only be detected when intermolecular exchange processes are slow on the NMR time scale.[3] Furthermore, although Cu(I) is not a very suitable nucleus to provide high-resolution NMR information[4] direct ^{109}Ag NMR[5] measurements may also help to solve the structures of the complexes in solution through the influence of the polydentate ligand system on the ^{109}Ag chemical shift(s). However, ^{109}Ag has a low γ value[5] and in most cases large T_1 values,[6] which makes it difficult to obtain ^{109}Ag NMR spectra by normal acquisition. But when resolved $^3J(^1H\text{–}^{107,109}Ag)$ splittings are present in the ^{1}H NMR spectra, ^{109}Ag NMR spectra are easily obtained by using the INEPT pulse sequence.[6]

Recently we have reported a detailed NMR study of the copper(I) and silver(I) complexes with the N_4 ligand 1,2-(6-R-py-2-CH=N)$_2$-R′ (R = H, Me; R′ = ethane, (R,S)-cyclohexane; see Figure 1).[2,7] The complexes could only be obtained in a 1/1 metal salt to ligand ratio and have $[M_2(N_4)_2]^{2+}(O_3SCF_3)_2^-$ structures in solution as evidenced by ^{1}H, ^{13}C, INEPT ^{15}N, and ^{109}Ag NMR data irrespective of the connecting C_2 alkanediyl

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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(4) ^{63}Cu or ^{65}Cu chemical shifts and $^3J(^1H\text{–}^{63}Cu)$, $^3J(^1H\text{–}^{65}Cu)$ data are often hard to obtain or are even unobtainable because of the quadrupole moments of ^{63}Cu and ^{65}Cu, which both have $I = {}^3/_2$: Marker, A.; Gunther, M. J. *J. Magn. Reson.* **1982**, *47*, 118 and references cited therein.

(5) Because of the 15% larger γ value ^{109}Ag is the more suitable nucleus for NMR measurements: ^{107}Ag (51.82%) and ^{109}Ag (48.18%) both have $I = {}^1/_2$ and γ values of -1.0828×10^7 and -1.2449×10^7 rad T^{-1} s^{-1}, respectively: Kidd, R. G.; Goodfellow, R. J. "NMR and the Periodic Table"; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978; p 258.

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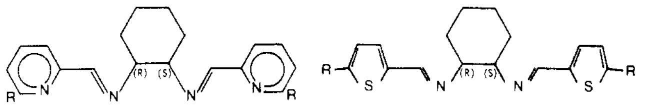

Figure 1. Schematic representation of the N_4 donor ligand (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$-c-Hx (R = H, Me) (left) and the N_2S_2 ligand system (*R*,*S*)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx (R = H (**1a**), Me (**1b**)) (right).

bridging groups, i.e. 1,2-ethanediyl or (*R*,*S*)-1,2-cyclohexanediyl. In these cases we showed that even small stereochemical changes in the ligand skeleton are reflected in relatively large ^{109}Ag chemical shifts; i.e., for R′ = (*R*,*S*)-1,2-cyclohexane and R = H, Me, $\Delta\delta(^{109}Ag) = 32$.

To study the influence of the nature of the donor sites on the coordination properties of these types of polydentate ligands, we have now investigated the bonding features of the N_2S_2 ligand system (*R*,*S*)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx (R = H, Me, thio = thiophene, c-Hx = cyclohexane). (See Figure 1) with copper(I) and silver(I). New information is provided concerning the coordination properties of group 11 metal ions in systems containing N and S donor atoms, and these data may improve the understanding of the structure/function relation of copper(I)-containing biological macromolecules.

In striking contrast to the N_4 donor ligand, the N_2S_2 system produces both dinuclear $[M_2(N_2S_2)_2][O_3SCF_3)_2$ and mononuclear $[M(N_2S_2)_2](O_3SCF_3)$ copper(I) and silver(I) complexes (see Figure 2). The coordination properties and the dynamic behavior of the dinuclear $[M_2(N_2S_2)_2](O_3SCF_3)_2$ as well as the X-ray structure of the silver(I) complex with 5-R = H will be published in a separate paper.[8]

We report in this paper the synthesis and characterization of the $[M(N_2S_2)_2]^+(O_3SCF_3)^-$ complexes with M = Ag(I) (5-R = H, Me), Cu(I) (5-R = Me) and the X-ray and molecular structure of the silver(I) complex with 5-R = Me.[9] A structural study of the complexes in solution by ^{1}H, INEPT ^{15}N, and INEPT ^{109}Ag NMR has also been included.

Experimental Section

Physical Measurements. Fluorine-19 NMR data were obtained in CD_2Cl_2 at 190 K with a Varian XL-100 (CW) apparatus with $CFCl_3$ as external reference (see Results). Hydrogen-1 NMR spectra were recorded in CD_2Cl_2 on Bruker WM 250 and AM 400 spectrometers with tetramethylsilane as reference (see Table IV).

Natural-abundance ^{15}N and ^{109}Ag NMR spectra were recorded on a Bruker AM 300 spectrometer in CD_2Cl_2 at 190 K applying the INEPT sequence, with use of the procedure described in a previous paper.[2] For the ^{15}N and ^{109}Ag chemical shift data respectively $MeNO_2$ in C_6D_6 (80/20 v/v) and $AgNO_3$ (2 M in D_2O) were used as external references (see results).

Preparation of the Compounds. All reactions were carried out under a nitrogen atmosphere in freshly distilled solvents. Thiophene-2-carbaldehyde, 5-methyl-thiophene-2-carbaldehyde, and silver(I) trifluoromethanesulfonate are commercially available. Copper(I) trifluoromethanesulfonate–0.5-benzene was prepared as described in the literature.[10] Pure (*R*,*S*)-1,2-diaminocyclohexane was separated from the commercially available mixture of *cis*-(*R*,*S*) and *trans*-(*R*,*R*;*S*,*S*) isomers via the method described in ref 11. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Utrecht, The Netherlands).

(*R*,*S*)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx, R = H (1a), Me (1b). A solution of 10 mmol of (*R*,*S*)-1,2-diaminocyclohexane in diethyl ether was slowly added to a solution of 20 mmol of 5-R-thiophene-2-carbaldehyde (R = H, Me) in diethyl ether at room temperature. The solution was stirred for 19 h, dried over Na_2SO_4, and filtered. The filtrate was evaporated at low pressure, affording a white powder for **1a**, R = H, and an oily orange-yellow product for **1b**, R = Me. The latter was purified by distillation (240 °C (0.1 mm Hg)) while **1a** could be crystallized from diethyl ether at 233 K. Yields of pure **1a** and **1b** were 70–80%.

Table I. Crystal Data and Details of the Structure Determination

a. Crystal Data	
formula	$C_{37}H_{44}AgF_3N_4O_3S_5$
mol wt	918.0
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	9.900 (4)
b, Å	11.465 (4)
c, Å	19.423 (6)
α, deg	106.10 (3)
β, deg	99.95 (3)
γ, deg	90.38 (3)
V, Å^3	2083 (1)
Z	2
D(calcd), g/cm^3	1.464
D(obsd), g/cm^3	1.459[a]
F(000)	944
μ(Mo Kα), cm^{-1}	7.7
cryst size, mm	0.63 × 0.10 × 0.20
min and max transmission	0.84, 0.93
b. Data Collection	
θ_{min}, θ_{max}, deg	0.1, 25.0
radiation	Mo Kα (Zr filtered), 0.710 69 Å
ω/2θ scan, deg	0.5 + 0.35 tan θ
max time/reflecn, min	1.5
horiz and vert aperture, mm	3, 3
ref reflecns	111, $02\bar{4}$, $\bar{2}04$
total data	8009
total unique data	6148
obsd data ($I > 2.5\sigma(I)$)	5124
T, K	295
c. Refinement	
no. of refined parameters	509
wtg scheme	$w^{-1} = [\sigma^2(F) + 0.00091F^2]/1.3083$
final $R_F = \Sigma(F_o - \lvert F_c\rvert)/\Sigma F_o$	0.039
final $R_{wF} = [\Sigma w(F_o - \lvert F_c\rvert)^2/\Sigma wF_o^2]^{1/2}$	0.041

[a] By flotation in 1,2-dibromoethane and *n*-heptane.

[Ag((*R*,*S*)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx)$_2$](O$_3$SCF$_3$) (R = H, Me). A solution of $[Ag(O_3SCF_3)]$ (1 mmol) in methanol (10 mL) was added to a solution of **1a** or **1b** (2.1 mmol) in methanol (10 mL). The reaction mixture was stirred for 30 min, and during this time a white precipitate was formed. The solid was washed with diethyl ether (3 × 10 mL) and dried in vacuo. The filtrate was set aside at 223 K for 19 h, resulting in the formation of white crystals of [Ag(**1a**)$_2$](O$_3$SCF$_3$) or [Ag(**1b**)$_2$](O$_3$SCF$_3$). The total isolated yields were 90–100%. Anal. Calcd for $[C_{33}H_{36}AgF_3N_4O_3S_5]$ (R = H): C, 45.99; H, 4.21; F, 6.61; N, 6.50. Found: C, 45.93; H, 4.25; F, 6.74; N, 6.53. Calcd for $[C_{37}H_{44}AgF_3N_4O_3S_5]$ (R = Me): C, 48.42; H, 4.83; F, 6.21; N, 6.10. Found: C, 48.21; H, 4.87; F, 6.55; N, 6.03.

[Cu((*R*,*S*)-1,2-(5-Me-thio-2-CH=N)$_2$-c-Hx)$_2$](O$_3$SCF$_3$). A solution of the N_2S_2 ligand (2.1 mmol) in benzene (30 mL) was slowly added to a solution of $[Cu(O_3SCF_3)]\cdot{}^1/_2C_6H_6$ (1 mmol) in benzene (30 mL). After a few minutes a deep yellow precipitate was formed. The reaction mixture is stirred for 30 min, after which the solvent was decanted off. The precipitate was washed with benzene (3 × 10 mL) and diethyl ether (3 × 10 mL) and then dried in vacuo. The complex was obtained in almost quantitative yield. Crystals were obtained by diffusion of a layer of pentane into a saturated CH_2Cl_2 solution of the complex. Anal. Calcd for $[C_{37}H_{44}CuF_3N_4O_3S_5]$: C, 50.87; H, 5.08; F, 6.52; N, 6.41. Found: C, 51.29; H, 5.18; F, 6.28; N, 6.42.

Data Collection and Structure Determination of $C_{37}H_{44}AgF_3N_4O_3S_5$ [Ag(1b)$_2$](O$_3$SCF$_3$). Data of a light yellow, transparent, block-shaped crystal were collected on an Enraf-Nonius CAD-4F diffractometer. Unit cell parameters and standard deviations were determined from the setting angles of 12 carefully centered reflections, as has been described previously.[12] The diffraction intensities of half of the reflection sphere (*h*,±*k*,±*l*) were measured in the ω/2θ scan mode with use of Zr-filtered

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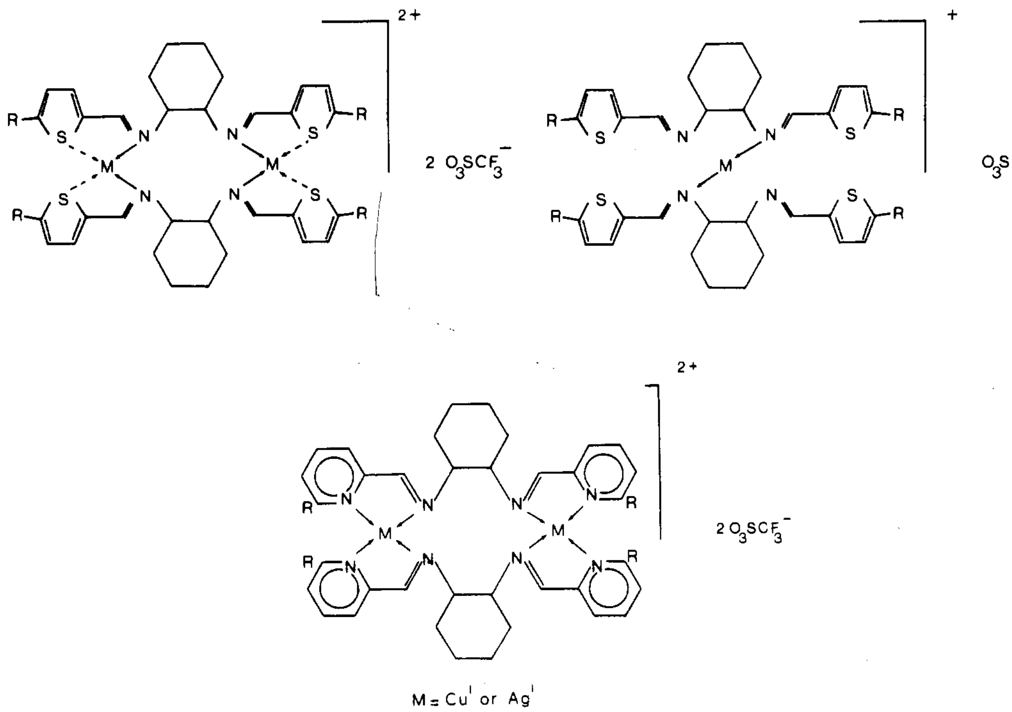

Figure 2. Schematic representation of the complexes $[M_2(N_2S_2)_2](O_3SCF_3)_2$ (top left), $[M(N_2S_2)_2](O_3SCF_3)$ (top right), and $[M_2(N_4)_2](O_3SCF_3)_2$ (bottom) (M = Ag(I), Cu(I)).

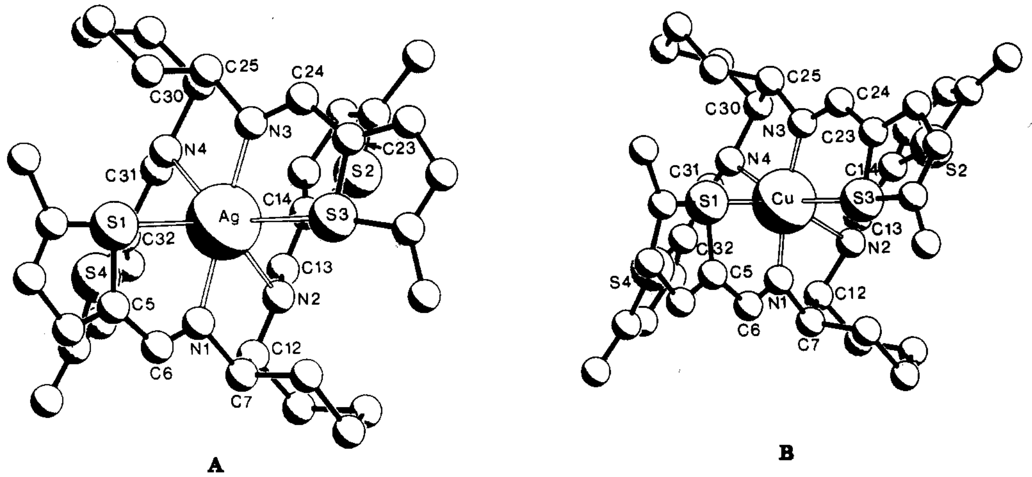

Figure 3. PLUTO drawings of the $[Ag(\mathbf{1b})_2]^+$ (A) and $[Cu(\mathbf{1b})_2]^+$ (B) cations. Hydrogen atoms are omitted for clarity.

Mo Kα radiation. During data collection the intensities of three reference reflections were measured periodically. There was no indication of decay during exposure time; fluctuations in the control reflections were less than 1.5%. Intensity data were corrected for Lorentz and polarization effects and for fluctuations in the reference reflections in the previously described way.[12] A numerical absorption correction was applied. These data are given in Table I.

The structure was solved by standard Patterson and Fourier techniques and refined by anisotropic blocked full-matrix least-squares procedures. Hydrogen atoms were included at calculated positions. The methyl hydrogen atoms were refined as a rigid rotator, allowing the free rotation about the C–CH_3 axis, and with use of a disorder model for the H atoms of C(18) and C(36). The remaining hydrogen atoms were refined in the riding mode on the parameters of their atom of attachment. The final model of 509 parameters converged to $R_F = 0.039$ ($R_{wF} = 0.041$).

A final difference Fourier map was featureless except for a peak having 0.81 e/Å^3 near the anion, indicating some residual disorder and some residual electron density near the Ag atom (highest peak 0.62 e/Å^3). Scattering factors were taken from Cromer and Mann[13] and anomalous dispersion terms for Ag from Cromer and Liberman.[14] The atomic coordinates and thermal parameters are listed in Table II. Calculations were carried out with the programs ILIAS[15] and EUCLID.[16]

Results

The silver(I) and copper(I) complexes, $[M(\mathbf{1})_2](O_3SCF_3)$, we report in this paper, were obtained from the 1/2 molar ratio reactions of either $[Ag(O_3SCF_3)]$ or $[Cu(O_3SCF_3)]\cdot{}^1/_2C_6H_6$ with the N_2S_2 ligand (R,S)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx (R = H, Me), respectively, in methanol or benzene. The elemental analysis data are in agreement with the 1/2 metal salt to ligand ratio. The white silver(I) complexes as well as the yellow copper(I) complex are air and water stable and not light sensitive. They have good solubilities in dichloromethane, are less soluble in methanol, and are insoluble in apolar solvents such as benzene and pentane.

X-ray Crystal and Molecular Structure of $[Ag((R,S)\text{-}1,2\text{-}(5\text{-}Me\text{-}thio\text{-}2\text{-}CH{=}N)_2\text{-}c\text{-}Hx)_2](O_3SCF_3)$. The X-ray crystal structure of the silver(I) complex with the N_2S_2 ligand **1b** (R = Me) shows that the unit cell contains two discrete $[Ag(\mathbf{1b})_2]^+$

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Table II. Final Positional Parameters

atom	*x/a*	*y/b*	*z/c*
Ag(1)	0.17593 (3)	0.27086 (3)	0.23607 (2)
S(1)	0.2394 (1)	0.2711 (1)	0.08734 (6)
S(2)	0.1714 (1)	0.2115 (1)	0.41035 (6)
S(3)	0.4507 (1)	0.3964 (1)	0.33253 (6)
S(4)	0.1419 (1)	0.7710 (1)	0.87929 (6)
S(5)	−0.3132 (1)	−0.1927 (1)	0.25984 (9)
F(1)	0.4176 (4)	0.4083 (3)	−0.2448 (2)
F(2)	0.4889 (5)	0.3363 (4)	−0.1553 (2)
F(3)	0.5593 (4)	0.2715 (4)	−0.2542 (3)
O(1)	0.3698 (4)	0.0931 (4)	0.7629 (3)
O(2)	0.2823 (5)	0.1770 (4)	0.6640 (2)
O(3)	0.2102 (4)	0.2501 (5)	0.7785 (3)
N(1)	0.1145 (3)	0.4481 (3)	0.2117 (2)
N(2)	0.0221 (3)	0.3740 (3)	0.3254 (2)
N(3)	0.3303 (3)	0.1304 (3)	0.2537 (2)
N(4)	0.0494 (3)	0.0651 (3)	0.1912 (2)
C(1)	0.3462 (6)	0.1458 (5)	−0.0349 (3)
C(2)	0.2778 (5)	0.2563 (4)	0.0022 (2)
C(3)	0.2406 (6)	0.3535 (5)	−0.0200 (3)
C(4)	0.1809 (6)	0.4401 (5)	0.0302 (3)
C(5)	0.1758 (4)	0.4103 (4)	0.0929 (2)
C(6)	0.1197 (4)	0.4800 (4)	0.1544 (2)
C(7)	0.0576 (4)	0.5360 (3)	0.2698 (2)
C(8)	0.1744 (4)	0.6024 (4)	0.3304 (2)
C(9)	0.1174 (5)	0.6944 (4)	0.3904 (3)
C(10)	0.0146 (5)	0.6329 (4)	0.4200 (2)
C(11)	−0.0996 (5)	0.5633 (4)	0.3593 (2)
C(12)	−0.0442 (4)	0.4706 (3)	0.2990 (2)
C(13)	−0.0548 (4)	0.2991 (3)	0.3413 (2)
C(14)	−0.0012 (4)	0.2068 (3)	0.3735 (2)
C(15)	−0.0682 (5)	0.1074 (4)	0.3804 (2)
C(16)	0.0187 (5)	0.0356 (4)	0.4151 (2)
C(17)	0.1517 (5)	0.0811 (4)	0.4361 (2)
C(18)	0.2722 (6)	0.0332 (5)	0.4753 (3)
C(19)	0.5695 (5)	0.6172 (4)	0.4269 (3)
C(20)	0.5630 (4)	0.4808 (4)	0.4075 (2)
C(21)	0.6347 (5)	0.4086 (5)	0.4420 (2)
C(22)	0.6022 (4)	0.2821 (4)	0.4080 (2)
C(23)	0.5014 (4)	0.2614 (4)	0.3477 (2)
C(24)	0.4389 (4)	0.1451 (3)	0.3022 (2)
C(25)	0.2863 (4)	0.0049 (3)	0.2113 (2)
C(26)	0.3057 (4)	−0.0143 (4)	0.1324 (2)
C(27)	0.2631 (5)	−0.1423 (4)	0.0867 (3)
C(28)	0.1159 (5)	−0.1756 (4)	0.0899 (3)
C(29)	0.0962 (5)	−0.1555 (4)	0.1685 (3)
C(30)	0.1377 (4)	−0.0252 (3)	0.2152 (2)
C(31)	−0.0780 (4)	0.0537 (3)	0.1927 (2)
C(32)	−0.1770 (4)	0.1325 (3)	0.1703 (2)
C(33)	−0.3074 (4)	0.1469 (4)	0.1848 (2)
C(34)	−0.3766 (4)	0.2348 (4)	0.1571 (2)
C(35)	−0.3009 (4)	0.2879 (4)	0.1209 (2)
C(36)	−0.3402 (6)	0.3860 (5)	0.0846 (3)
C(37)	0.4495 (6)	0.3072 (5)	−0.2285 (3)

cations, each having a twofold noncrystallographic axial symmetry (along the S(1)–Ag–S(3) bisector), together with two $O_3SCF_3^-$ anions. The molecular geometry of the $[Ag(\mathbf{1b})_2]^+$ cation and the adopted numbering scheme are shown in a PLUTO drawing (Figure 3A).

When the conformations of the two ligand skeletons are analyzed, it is clear that both N_2S_2 ligands in the cation coordinate to the metal center via one short imine-*N* bond (Ag–N(1) = 2.275 (3) Å, Ag–N(3) = 2.281 (3) Å). The angle between these two short Ag–N bonds is 153.3 (1)°. The extent of interaction of the remaining three donor sites of each N_2S_2 ligand with the metal center can be deduced from the orientation of the N and S lone pairs in Figure 4. These lone pairs are hardly (N(2), N(4) and S(1), S(3)), or not at all (S(2), S(4)) directed toward the group 11 metal center (see Table III for bond distances). Moreover, the PLUTO drawing in Figure 3A shows that each 5-Me-thio-2-CH=N grouping of the ligands has the *E* configuration around the C=N bond. A conformational analysis revealed that the thiophene rings and the CH=N moieties are almost coplanar (see Table V) as a result of the π conjugation in the thio-2-CH=N system. The PLUTO drawing only shows one of the two possible enantiomers, present in the unit cell, i.e. the one in which the Ag(I) center has the Λ^{17} configuration.

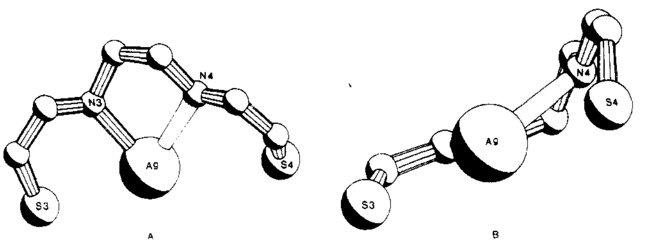

Figure 4. The S(3)–C(23)–C(24)–N(3)–C(25)–C(30)–N(4)–C(31)–C(32)–S(4) chain: (A) view perpendicular to the N(3)–Ag–C(24) plane; (B) projection down the Ag–N(3) bond.

Table III. Bond Distances (Å) and Bond Angles (deg)

Ag(1)–N(1)	2.275 (3)	N(2)–C(13)	1.277 (5)
Ag(1)–N(2)	2.555 (3)	N(3)–C(24)	1.277 (5)
Ag(1)–N(3)	2.281 (3)	N(3)–C(25)	1.466 (5)
Ag(1)–N(4)	2.517 (3)	N(4)–C(30)	1.480 (5)
Ag(1)–S(1)	3.061 (1)	N(4)–C(31)	1.274 (5)
Ag(1)–S(2)	3.641 (1)	C(5)–C(6)	1.441 (6)
Ag(1)–S(3)	3.110 (1)	C(7)–C(12)	1.523 (6)
Ag(1)–S(4)	3.478 (1)	C(13)–C(14)	1.432 (6)
N(1)–C(7)	1.484 (5)	C(23)–C(24)	1.445 (5)
N(1)–C(6)	1.274 (6)	C(25)–C(30)	1.528 (5)
N(2)–C(12)	1.460 (5)	C(31)–C(32)	1.431 (5)
S(1)–C(5)	1.702 (4)	S(3)–C(23)	1.717 (4)
S(2)–C(14)	1.730 (4)	S(4)–C(32)	1.725 (4)

N(1)–Ag(1)–N(2)	72.3 (1)	Ag(1)–N(2)–C(12)	107.7 (2)
N(1)–Ag(1)–N(3)	153.3 (1)	C(12)–N(2)–C(13)	117.4 (3)
N(1)–Ag(1)–N(4)	129.3 (1)	C(24)–N(3)–C(25)	116.6 (3)
N(2)–Ag(1)–N(3)	125.3 (1)	Ag(1)–N(3)–C(24)	128.1 (3)
N(2)–Ag(1)–N(4)	97.5 (1)	Ag(1)–N(3)–C(25)	114.6 (2)
N(3)–Ag(1)–N(4)	72.4 (1)	Ag(1)–N(4)–C(31)	120.9 (2)
S(1)–Ag(1)–S(2)	164.58 (3)	Ag(1)–N(4)–C(30)	109.4 (2)
S(1)–Ag(1)–S(3)	98.45 (4)	C(30)–N(4)–C(31)	116.4 (3)
S(1)–Ag(1)–S(4)	74.83 (4)	S(1)–C(5)–C(4)	109.6 (4)
S(2)–Ag(1)–S(3)	76.31 (4)	N(1)–C(6)–C(5)	125.1 (4)
S(2)–Ag(1)–S(4)	114.65 (4)	N(1)–C(7)–C(12)	110.3 (3)
S(3)–Ag(1)–S(4)	160.44 (4)	N(2)–C(12)–C(7)	110.1 (3)
C(2)–S(1)–C(5)	92.8 (2)	N(2)–C(13)–C(14)	122.7 (4)
C(14)–S(2)–C(17)	92.5 (2)	S(2)–C(14)–C(13)	120.6 (3)
C(20)–S(3)–C(23)	92.7 (2)	S(3)–C(23)–C(24)	122.4 (3)
C(32)–S(4)–C(35)	92.4 (2)	N(3)–C(24)–C(23)	125.0 (4)
Ag(1)–N(1)–C(6)	128.5 (3)	N(3)–C(25)–C(30)	111.2 (3)
Ag(1)–N(1)–C(7)	115.2 (2)	N(4)–C(30)–C(25)	108.8 (3)
C(6)–N(1)–C(7)	116.3 (3)	N(4)–C(31)–C(32)	123.2 (4)
Ag(1)–N(2)–C(13)	113.4 (3)	S(4)–C(32)–C(31)	122.4 (3)

Compounds in Solution. Fluorine-19 NMR spectra of the silver(I) and copper(I) complexes in CD_2Cl_2 at 190 K showed for each complex one singlet resonance with a chemical shift value within the range expected for noncoordinating $O_3SCF_3^-$ anions;[2] δ^{18} −78.7, $[Ag(\mathbf{1a})_2](O_3SCF_3)$; −78.7, $[Ag(\mathbf{1b})_2](O_3SCF_3)$; −78.6, $[Cu(\mathbf{1b})_2](O_3SCF_3)$. These data reveal that the complexes consist in solution of separated $[M(\mathbf{1})_2]^+$ monocations and $(O_3SCF_3)^-$ monoanions.

Hydrogen-1 NMR of $[Ag(\mathbf{1})_2](O_3SCF_3)$. The ^1H NMR spectra in CD_2Cl_2 at 190 K of the silver(I) complexes showed two distinct resonance patterns for the 5-R-thio-2-CH=N ^1H atoms. The assignment of the resonances to two distinct 5-R-thio-2-CH=N moieties, of which the ^1H atoms are denoted A and B in Table IV, was based on ^1H homonuclear decoupling experiments. The presence of a small $^4J(^1H-^1H)$ coupling between the imine-*H* and the ring H-3 resonance in $[Ag(\mathbf{1a})_2]^+$ allowed the assignment of the low-field imine-*H* resonance to the low-field thiophene-^{1}*H* pattern and thus the high-field imine-*H* to the high-field thiophene-^{1}*H* pattern.

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(17) For the abbreviations Δ and Λ denoting the stereochemical configuration of the metal center: Ernst, R. E.; O'Connor, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1967**, *89*, 6104.

(18) A positive δ corresponds to a higher resonance frequency ("deshielding") with respect to the reference frequency.

Table IV. ^{1}H NMR Data (250 MHz)[a] of the N_2S_2 Ligands **1a** and **1b** and the Complexes [Ag(**1**)$_2$](O_3SCF_3)[b] and [Cu(**1b**)$_2$](O_3SCF_3)

			δ					
compds	*T*, K	site	H(im)	H-3	H-4	H-5	5-Me	α-H
1a	190	A	8.35 s	7.40 d	7.05 dd	7.28 d		3.39 m
		B	8.18 s	7.34 d	7.05 dd	7.24 d		
[Ag(**1a**)$_2$]	190	A	8.72 d[c]	7.49 d	7.13 dd	7.63 d		3.55 m
		B	8.01 b	7.35 d	7.10 dd	7.35 d		
1b	190	A	8.22 s	7.03 b	6.70 b		2.45 s	3.35 m
		B	8.07 s				2.39 s	
	293		8.14 s	6.97 d	6.64 d		2.45 s	3.21 m
[Ag(**1b**)$_2$]	190	A	8.60 d[d]	7.45 d	6.87 d		2.47 s	3.49 m
		B	7.90 b	7.12 d	6.77 d		2.38 s	
	293		8.39 s	7.32 d	6.78 d		2.42 s	3.43 m
[Cu(**1b**)$_2$]	293		8.29 s	7.25 d	6.77 d		2.41 s	3.70 m

[a] In CD_2Cl_2 with Me_4Si as reference. Key: s = singlet; d = doublet; dd = doublet of doublets; m = multiplet; b = broad. [b] H(im) resonances appear as doublets due to $^3J(^1H-^{107,109}Ag)$; coupling constants are given in footnotes *c* and *d*. [c] J = 12.3 Hz. [d] J = 12.0 Hz.

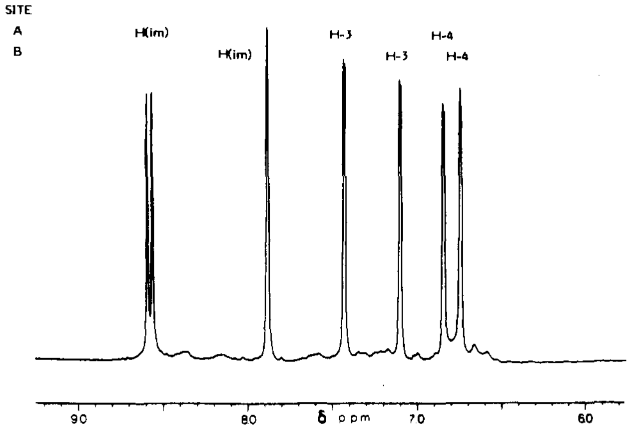

Figure 5. Part of the ^{1}H NMR spectrum (400 MHz) of [Ag(**1b**)$_2$](O_3SCF_3) at 190 K in CD_2Cl_2.

The presence of such a small $^4J(^1H-^1H)$ coupling between the 5-CH_3 substituents and the thiophene-*H*-4 atoms also allowed the assignment of the 5-Me resonances in the spectrum of [Ag(**1b**)$_2$]$^+$. The imine-*H* resonance in the ^{1}H NMR spectra at low field appeared as a doublet due to $^3J(^1H-^{107,109}Ag)$ (δ 8.72, *J* 12.3 Hz for [Ag(**1a**)$_2$]$^+$; δ 8.60, *J* 12.0 Hz for [Ag(**1b**)$_2$]$^+$). The upfield imine-*H* resonance, however, was a broad singlet (see Figure 5) at 190 K. When the temperature is raised above 210 K, broadening of both imine-*H* resonances and loss of $^3J(^1H-^{107,109}Ag)$ was observed. At room temperature the spectra showed one sharp 5-R-thio-2-CH=N ^{1}*H* pattern and the imine-*H* signal appeared as a singlet, indicating that a fast-exchange process is occurring on the NMR time scale at this temperature. In particular the disappearance of $^3J(^1H-^{107,109}Ag)$ above 210 K established that this exchange process takes place intermolecularly.

Hydrogen-1 NMR of [Cu(1b)$_2$](O_3SCF_3). The ^{1}H NMR spectrum in CD_2Cl_2 at 190 K of the copper(I) complex showed a complicated resonance pattern in the thiophene–imine region. From the number of 5-Me-^{1}*H* resonances it could be concluded that the spectrum showed at least six different 5-Me-thio-2-CH=N patterns having different intensities. It was not possible to assign the ^{1}H resonances to distinct 5-Me-thio-2-CH=N ^{1}H patterns with high enough certainty.

Above 210 K the signals broadened and at room temperature only one 5-Me-thio-2-CH=N ^{1}H resonance pattern was observed, in which the imine-*H* resonance appeared as a singlet. Because of the large quadrupole moments of both Cu isotopes, $^3J(^1H-^{63,65}Cu)$ couplings were not observed, and without these data it is not possible to determine whether this process, causing the observed coalescence of the thiophene–imine ^{1}H patterns, is taking place via intra- or intermolecular pathways.

Hydrogen-1 NMR of the Free Ligands 1a and 1b. The ^{1}H NMR spectra of **1a** and **1b** showed at 190 K in CD_2Cl_2 two signals for the imine-H and thiophene 5-R atoms. In the spectrum of **1a** two resonances were also observed for the thiophene-*H*-3 atoms. These data indicate that the ligands have at 190 K a conformation in which the two 5-R-thio-2-CH=N moieties are inequivalent. Above 200 K the 5-R-thiophene-imine H signals broadened, and at 293 K one sharp pattern was observed for the H atoms in **1a** and **1b**.

The ^{13}C NMR spectrum of **1b** at 190 K shows not only two patterns for the 5-methylthiophene–imine ^{13}C atoms but also six separate resonances for the ^{13}C atoms of the (*R*,*S*)-1,2-cyclohexanediyl bridging group. At room temperature, however, one observes only three resonances for the latter bridging group and only one sharp resonance pattern for the 5-methylthiophene–imine ^{13}C atoms. Accordingly, a chair–chair conformational movement of the (*R*,*S*)-1,2-cyclohexanediyl ring becomes fast above 200 K on the ^{1}H NMR time scale. Such a process has also been observed for the N_4 ligand system,[2] which is schematically represented in Figure 1.

INEPT ^{109}Ag and ^{15}N NMR. Because of the presence of resolved $^3J(^1H-^{107,109}Ag)$ in the ^{1}H NMR spectra of the silver(I) complexes, it was possible to measure ^{109}Ag NMR spectra via the INEPT sequence (see ref 2). The spectra (at 190 K) of [Ag(**1**)$_2$]$^+$ in CD_2Cl_2 showed one ^{109}Ag resonance at δ +582 for [Ag(**1a**)$_2$]$^+$ and δ +583[18] for [Ag(**1b**)$_2$]$^+$.

To investigate the coordination of the N_2S_2 ligands to the group 11 metal center in solution, the ^{15}N NMR spectrum of [Ag(**1b**)$_2$]$^+$ and of the free ligand **1b** were measured in CD_2Cl_2. The spectra were obtained, as with the ^{109}Ag NMR spectra, by using the INEPT sequence. The ^{15}N spectrum of the silver(I) complex (at 190 K) showed two resonances, at δ −82.9 and −95.8,[18] to high field of the corresponding free-ligand ^{15}N resonance at δ −52.6 (297 K). The two ^{15}N signals in the spectrum of the complex appeared as a doublet of doublets arising from $^nJ(^{15}N-^1H)^2$ and $^1J(^{15}N-^{107,109}Ag)$. The value for $^1J(^{15}N-^{107,109}Ag)$ amounts to 57 Hz for the signal to high field (i.e. δ −95.8) and is 12 Hz for the lower field signal (i.e. δ −82.9).

These data unambiguously prove that in solutions of the [Ag(N_2S_2)$_2$]$^+$ cations two different imine-*N* sites are present, one with a large and one with a small $^1J(^{15}N-^{107,109}Ag)$ coupling and that both sites have interactions with the silver(I) center (see Discussion).

Discussion

Eichhorn and co-workers[19] were the first to study the coordination properties of the N_2S_2 ligand system 1,2-(thio-2-CH=N)$_2$-etn (etn = ethane), in which a 1,2-ethanediyl group is bridging two thiophene–imine moieties, with copper(II) and nickel(II) salts. It appeared that the C=N bonds of the ligands in these M(N_2S_2)X_2 complexes were highly activated for further reactions probably as a result of the strain in the respective, neighboring five-membered chelate rings. Water et al.[20] reported the structures of two copper(II) complexes resulting from such further reactions,

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Table V. Comparison of the M–N and M–S Distances and a Conformational Analysis of the N_2S_2 Ligands (**1b**) in the Structures of $[Ag(\mathbf{1b})_2]^+$ and $[Cu(\mathbf{1b})_2]^{+}$[a]

Bond Distances (Å)

atoms	Ag(I)	Cu(I)	atoms	Ag(I)	Cu(I)
N(1)	2.275 (3)	1.94 (2)	S(1)	3.061 (1)	2.953 (9)
N(2)	2.555 (3)	2.26 (2)	S(2)	3.641 (1)	4.06 (1)
N(3)	2.281 (3)	1.89 (2)	S(3)	3.110 (1)	3.156 (8)
N(4)	2.571 (3)	2.53 (2)	S(4)	3.478 (1)	3.74 (1)

Torsion Angles (deg)

atoms	Ag(I)	Cu(I)		atoms	Ag(I)	Cu(I)	
S(1)- -N(1)	2.0 (6)	0 (2)	sp[a]	S(3)- -N(3)	−10.1 (6)	−11 (2)	sp
C(5)- -C(7)	177.6 (4)	180 (2)	ap	C(23)- -C(25)	177.7 (4)	171 (2)	ap
C(6)- -C(12)	134.5 (4)	150 (2)	ac	C(24)- -C(30)	125.2 (4)	142 (2)	ac
N(1)- -N(2)	56.7 (4)	61 (2)	sc	N(3)- -N(4)	55.3 (4)	56 (2)	sc
C(7)- -C(13)	−169.6 (4)	−175 (2)	ap	C(25)- -C(31)	−178.7 (3)	180 (2)	ap
C(12)- -C(14)	−174.6 (4)	−177 (2)	ap	C(30)- -C(32)	−179.1 (4)	+172 (2)	ap
N(2)- -S(2)	13.7 (6)	9 (2)	sp	N(4)- -S(4)	14.6 (5)	21 (2)	sp
C(5)- -M	−4.3 (6)	−7 (3)	sp	C(23)- -M	−12.9 (6)	−12 (3)	sp
C(14)- -M	58.8 (5)	76 (2)	sc	C(32)- -M	44.2 (5)	53 (3)	sc

[a] Full data are in ref 27; for explanations of the abbreviations sp = synperiplanar, ap = antiperiplanar, ac = anticlinical, and sc = synclinical, see ref 28.

i.e. $[(Cu(thio\text{-}2\text{-}CH{=}N(CH_2)_2NH_2))_2(\mu\text{-}Cl)_2]Cl_2$ and $[Cu(thio\text{-}2\text{-}CH{=}N(CH_2)_2NH_2)_2](ClO_4)_2$. These are formed by hydrolyses of a C=N bond of the N_2S_2 ligands in the original $[Cu(N_2S_2)Cl]_2Cl_2$ and $[Cu(N_2S_2)_2](ClO_4)_2$ complexes. Various other metal complexes with a 1/1 metal/N_2S_2 molar ratio, i.e. $M(N_2S_2)X_2$ type of structures (M(II) = Co, Cu, Zn, Cd; X = Cl, Br, I, NCS), have been prepared.[21] The preparation of the copper(I) complexes $[Cu(N_2S_2)_2](CuX_2)$ (X = Cl, Br, I) have also been reported,[21] but experiments directed to the synthesis of the corresponding silver(I) complexes failed. The dinuclear ionic structure for the copper(I) complexes was proposed on the basis of molecular conductivity data but could not be established.

In this study we show that in addition to copper(I) species silver(I) complexes with the N_2S_2 ligand (*R*,*S*)-1,2-(5-R-thio-2-CH=N)$_2$-c-Hx (R = H (**1a**), Me (**1b**)) are also accessible. The molecular geometry of these complexes in the solid state consists of discrete $[M(N_2S_2)_2]^+$ cations and $O_3SCF_3^-$ anions. The N_2S_2 ligand system **1** was selected in order to study the influence of different sets of donor atoms, i.e. N_2S_2 (**1**) vs N_4 in (*R*,*S*)-1,2-(6-R-py-2-CH=N)$_2$-c-Hx (see Figure 1), on the bonding features of these potentially quadridentate ligands with silver(I) and copper(I). In order to control the differences in coordination properties, which can be caused by conformational changes,[22] the outer two pyridine-*N* donor sites in the N_4 system applied in this study have been replaced by thiophene-*S* donor units, thus resulting in the N_2S_2 ligand **1**.

In contrast to the results found for the N_4 system, for which only dinuclear complexes $[M_2(N_4)_2](O_3SCF_3)_2$ (M = Ag(I), Cu(I); see Figure 2), could be obtained, reactions of the N_2S_2 ligand **1** with $[M(O_3SCF_3)]$ yielded dinuclear $[M_2(\mathbf{1})_2](O_3SCF_3)_2$ as well as mononuclear $[M(\mathbf{1})_2](O_3SCF_3)$ complexes. The main reason for the formation of the mononuclear complexes can be regarded as the weak affinity of thiophene-*S* atoms for these group 11 metal centers (vide infra). When stronger donor atoms are present in the "outer" ring systems, for instance pyridine-*N* atoms (or imidazole-*N* atoms[23]), only dinuclear $[M_2(N_4)_2](O_3SCF_3)_2$ complexes are formed.

The two different types of complexes, i.e. $[M_2(N_2S_2)_2](O_3SCF_3)_2$ and $[M(N_2S_2)_2](O_3SCF_3)$, could be isolated and studied by NMR spectroscopy separately. When only one of the two complexes is dissolved in CH_2Cl_2, the other type is not formed. However, when mixtures of the two types of silver(I) complexes are prepared, the ^1H NMR spectra show that the silver(I) cations $[Ag_2(\mathbf{1})_2]^{2+}$ and $[Ag(\mathbf{1})_2]^+$ comprise an equilibrium (see eq 1) that is in the slow-exchange limit at 190 K.

$$[Ag_2(\mathbf{1})_2](O_3SCF_3)_2 \underset{-1}{\overset{1}{\rightleftharpoons}} [Ag(\mathbf{1})_2](O_3SCF_3) + [Ag(O_3SCF_3)] \quad (1)$$

Probably because of higher stability of the $Ag^+(O_3SCF_3)^-$ ion pair in solvents such as methanol and diethyl ether the mononuclear $[Ag(\mathbf{1})_2](O_3SCF_3)$ complexes are more stable in these solvents than the dinuclear $[Ag_2(\mathbf{1})_2](O_3SCF_3)_2$ ones. In this paper we restrict ourselves to a discussion of the coordination properties of the N_2S_2 ligands in the $[M(\mathbf{1})_2]^+$ cations.

In the $[M(\mathbf{1})_2]^+$ cations there are eight heteroatoms present, all of which are potential binding sites. It is therefore interesting to see how the N_2S_2 ligands coordinate to the group 11 metal center in the $[Ag(\mathbf{1b})_2]^+$ cation in the solid (see Figure 3A). Before we answer the question as to which of the donor sites in the cation are coordinating to the metal center, it is important to consider the ligand stereochemistry.

The two N_2S_2 ligands in $[Ag(\mathbf{1b})_2]^+$ have almost planar thiophene–imine moieties (see Table V), which leave the conjugation between the thiophene and imine π systems intact. A remarkable feature of the ligand conformation is the s-cis conformation around the (S=)C—C(=N) bonds. Recently[24] we have shown that the free 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (R-DAB, RN=CC=NR, R = cyclohexyl) ligand contains a flat N=CC=N skeleton wherein the (N=)C—C(=N) bond has the s-trans conformation. This observation can be rationalized by the fact that the s-cis formation of the free R-DAB ligand is destabilized with respect to the s-trans conformation because in the former the N lone pairs are directed toward each other. A similar conclusion applies to the free (noncoordinated) thiophene–imine moiety. However, the situation is entirely different when such heterobutadiene ligands are coordinating via the lone pairs of both heteroatoms to a metal center.[24,25] The s-cis conformation of the thiophene–imine moiety now becomes more stabilized because both lone pairs are directed toward the electrophilic metal center. In

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(23) Preliminary results in the study on the coordination properties of the $H_2N_2N_4$ ligand system (*R*,*S*)-1,2-(im-2-CH=N)$_2$-c-Hx (im = imidazole) with Cu(I) and Ag(I) show that the reactions of this system with $[M(O_3SCF_3)]$ (M = Cu(I), Ag(I)) only yielded the dinuclear $[M_2(H_2N_2N_4)_2](O_3SCF_3)_2$ complexes. $^1J(^{15}N\text{–}^{107,109}Ag)$ values indicate that the Ag(I) centers in $[Ag_2(H_2N_2N_4)_2]^{2+}$ have a geometry in solution similar to those in $[Ag_2(N_4)_2]^{2+}$.[2]

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contrast a monodentate coordination via the N atom of the thiophene–imine moiety having the s-trans conformation is destabilized because of steric interactions between the H-3 atom in the noncoordinated thiophene group and the metal center. Accordingly it may be concluded that the observed s-cis conformation of the thiophene–imine moieties in the $[Ag(\mathbf{1b})_2]^+$ cation is a logical one. Considering now the fact that both ligands are primarily bonded to the silver(I) center via one imine-*N* site, i.e. via the short Ag–N(1) and Ag–N(3) bonds, it can be concluded that the S atoms, S(1) and S(3), which are part of the thiophene–imine moieties N(1)=CC=S(1) and N(3)=CC=S(3), are situated close to the silver(I) center as a result of the s-cis conformation.

The values of the (S=)C—C=N—Ag torsion angles (see Table V) show that, probably because of steric interactions between thiophene–imine moieties (i.e. N(2)=CC=S(2) and N(4)=CC=S(4) with N(3)=CC=S(3) and N(1)=CC=S(1), respectively, one thiophene–imine moiety of each ligand (i.e. N(2)=CC=S(2) and N(4)=CC=S(4)) is bent away from the silver(I) center. The possible interactions of these last two thiophene–imine moieties with the Ag^+ center needs further comment. Since the angles around N(2) and N(4), i.e. C(12)–N(2)–C(13) (117.4 (3)°) and C(30)–N(4)–C(31) (116.4 (3)°) point to a planar-trigonal geometry and the C=N bond lengths of 1.277 (5) Å (C(13)–N(2)) and 1.274 (5) Å (C(31)–N(4)] are typically those of double C=N bonds,[2,24] one can conclude that these N atoms are sp^2 hybridized. The silver(I) center clearly does not reside in the C=N—C planes of N(2) and N(4), thus implying that the lone pairs of these N atoms do not interact with the available empty orbitals on Ag^+. From this analysis of the molecular geometry one comes to the conclusion that the silver(I) center is predominantly linearly bonded by the two imine-*N* donor atoms N(1) and N(3). This bonding situation is commonly encountered for monovalent group 11 metal centers.[26] It is, however, the ^{15}N NMR information (the observation of $^1J(^{15}N-^{107,109}Ag)$ on the ^{15}N resonances of $[Ag(\mathbf{1b})_2]^+$ in solution) that provides unambiguously the evidence for the existence of some orbital overlap between the silver(I) center and N(2) and N(4) (vide infra), i.e. for a geometry around the group 11 metal center that is between linear and tetrahedral.

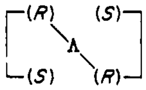
The way in which the two N_2S_2 ligands are folded around the silver(I) center in $[Ag(\mathbf{1b})_2]^+$ gives rise to the existence of two enantiomeric forms for this monocation. The conformation of the silver(I) center is either Λ (see Figure 3A) or Δ.

To test the validity of the assumption that copper(I) can be replaced by silver(I) with retention of the structural features (see Introduction), the X-ray crystal structure determination of the copper(I) complex $[Cu(\mathbf{1b})_2](O_3SCF_3)$ has also been carried out.[9,27] Crystallization of this complex leads to twinned rather than single crystals. Diffractometer data for such a twinned specimen (0.63/0.37 twinning ratio) were collected. Although the current *R* value is still 11.9% for 2983 unique reflections, it can be concluded that, despite the restrictions imposed by the present limited quality of the structure, the overall geometries of the $[M(\mathbf{1b})_2]^+$ cations (M = Ag(I) and Cu(I)) are similar (see Figure 3B for the PLUTO drawing of the $[Cu(\mathbf{1b})_2]^+$ cation). Like the silver(I) center, the copper(I) ion in the $[Cu(\mathbf{1b})_2]^+$ cation seems to be primarily linearly bonded to the respective N donor sites of different N_2S_2 ligands. An analysis of the folding of the ligands around the group 11 metal centers reveals that the conformation of the N_2S_2 ligands in the two complexes does not differ significantly (see Table V). The observations for the silver(I) complex that (i) the 5-Me-thio rings and the CH=N moieties are coplanar and (ii) each (S=)C—C(=N) bond has the s-cis conformation could also be made for the copper(I) complex. One obvious difference lies in the distances between the strongly bonded imine-*N* sites, N(1) and N(3), and the group 11 metal center. The reasons that these distances are longer in the silver(I) cation than in the copper(I) cation arise from the different ionic radii of copper(I) and silver(I) and the fact that Cu(I)–N(imine) interactions are stronger than Ag(I)–N(imine) bonds. This has been observed before when the stabilities of the Cu–N and Ag–N bonds in the $[M(\text{pyridine–imine})_2]^+$ cations were compared.[3] As a consequence there is a contraction of the overall structure on going from the silver(I) to the copper(I) $[M(\mathbf{1b})_2]^+$ cation.

The values for the thiophene–imine torsion angles (S(2)=)C—C=N(2)—M and (S(4)=)C—C=N(4)—M in these cations (see Table V) are larger for M = Cu(I) than for M = Ag(I), indicating that the steric interactions between the thiophene–imine moieties, causing the folding of the S(2)=C-C=N(2) and S(4)=CC=N(4) units, are larger for M = Cu(I) than when M = Ag(I). This increase of the steric interactions is a consequence of the contraction of $[Cu(\mathbf{1b})_2]^+$ and can explain the observation that the two N_2S_2 ligands are not identically coordinated to the copper(I) center.

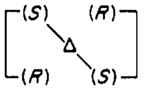
Conformational and Configurational Aspects of the $[M(\mathbf{1})_2]^+$ Cations. As discussed above, the group 11 metal centers in the asymmetric $[M(N_2S_2)_2]^+$ cations have either Δ or Λ configurations. Because of the presence of chiral C atoms, which have a fixed configuration *R* or *S* in the 1,2-cyclohexanediyl bridging groups, these cations in solution can exist in a number of stereoisomeric forms.

The molecular geometry of $[Ag(\mathbf{1b})_2]^+$ (Figure 3A) shows that the (*R*,*S*)-1,2-cyclohexanediyl bridges are positioned in such a way that the structure possesses a twofold axial symmetry. The two imine-*N* sites N(1) and N(3), which are responsible for the almost linear two-coordinate geometry around the group 11 metal center, are directly connected to the bridging C atoms that have the *R* configuration. The structure presented in Figure 3A can then be denoted as



I

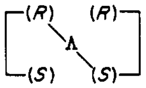
and its enantiomer as



II

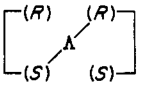
The combined NMR data clearly show that this enantiomeric pair is also present in solution at 190 K.

The presence of the alternative structure of the $[Ag(\mathbf{1})_2]^+$ cations in which the twofold axial symmetry is lost because of a different positioning of one of the (*R*,*S*)-1,2-cyclohexanediyl bridges, being denoted as



III

cannot be exclused a priori. In the case of the latter isomeric form one expects to see in the ^1H NMR spectra in the slow-exchange limit four 5-R-thio-2-CH=N ^1H patterns, while only two such patterns are actually observed at 190 K. However, in solution an exchange process may be considered to be taking place, involving weakening of the interactions of the group 11 metal center with the strongly bonded N sites and concomitant increase of the interactions with the N atoms, which are at longer distances. The isomer then formed is



IV

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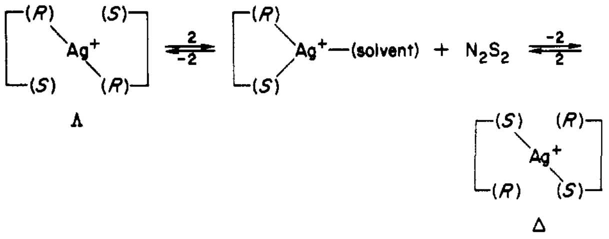
As a result of this, the respective thiophene–imine moieties have interchanged environments; i.e., in the case of an imine-*N* site that is well coordinated in the first place the thiophene ring is directed toward the Ag^+ center (cf. Figure 3A), whereas in the case of a weakening of the imine-*N*–Ag interaction the thiophene–imine moiety is bent away because of steric interactions (vide supra) and vice versa. When this process between the identical structures III and IV becomes fast on the NMR time scale, the four 5-R-thiophene–imine ^1H patterns coalesce into two, which would be in line with the observed multiplicity of these patterns in the ^1H NMR spectra of $[Ag(\mathbf{1})_2]^+$ (at 190 K). However, the two imine-*H* resonances exhibit a large difference in $^3J(^1H-^{107,109}Ag)$ values, which is not in agreement with the occurrence of a fast-exchange process between the identical structures. We therefore conclude that these structures are not present in solutions of the $[Ag(\mathbf{1})_2]^+$ cations.

In general it can be concluded that this large difference in $^3J(^1H-^{107,109}Ag)$ values indicates that no intramolecular exchange processes are taking place at 190 K in solutions of $[Ag(\mathbf{1})_2]^+$ between the imine-*H* atoms of site A and site B (see Table IV). Accordingly, the $[Ag(\mathbf{1})_2]^+$ cations exist in solution at 190 K in the enantiomeric forms denoted as in I and II.

At temperatures above 210 K an exchange process is observed. This is indicated by coalescence of the two 5-R-thiophene–imine ^1H patterns to one such pattern. This process must occur intermolecularly because $^3J(^1H-^{107,109}Ag)$ on the imine-*H*(A) resonances disappear. A study on molecular models of $[M(\mathbf{1})_2]^+$ showed that such a process must involve complete metal–ligand dissociation. The reverse reaction, i.e. association of a N_2S_2 ligand and the $[Ag(N_2S_2)]^+$ intermediate, may occur either with retention or inversion of configuration of the group 11 metal center (see eq 2). This process may be solvent or counterion ($O_3SCF_3^-$) assisted.[3,7]



(2)

In the case of $[Cu(\mathbf{1})_2]^+$ it was not possible to determine the exact structure(s) of the cation in the slow-exchange limit in solution. The presence of at least six 5-Me-thiophene–imine ^1H resonance patterns in the ^1H NMR spectrum at 190 K indicates that at least two different stereoisomers are present. The PLUTO drawing (Figure 3B) of the structure in the solid shows that if this structure is retained in solution four different thiophene–imine ^1H patterns with equal intensities should be observed. This contrasts with the observation of only two such patterns for the silver(I) cations in solution. It has been pointed out that the difference in environment of these four moieties is due to the different manner in which the two N_2S_2 ligands coordinate to the copper(I) center. This difference in coordination behavior is primarily caused by the steric interactions between the thiophene–imine moieties. These steric interactions will determine for a great part the stabilities of the various possible stereoisomers in solution. The observation of six 5-methylthiophene–imine ^1H resonances indicate that (i) according to the Boltzmann population distribution the energy difference between the ground states of at least two different stereoisomers is very small (i.e., both structures are detectable by ^1H NMR) and (ii) the value for $\Delta G^{\ddagger}$ (free energy of activation) is large enough to observe the different stereoisomers separately in the ^1H NMR spectrum at 190 K.

The observation of one sharp 5-methylthiophene–imine ^1H pattern at 294 K reveals also that in the case of $[Cu(\mathbf{1b})_2]^+$ fast-intermolecular-exchange processes are taking place in solution as noted above for the silver(I) complexes.

INEPT ^{109}Ag and ^{15}N NMR. From the X-ray molecular structure and ^1H NMR data (190 K) of $[Ag(\mathbf{1b})_2]^+$ one could come to the conclusion that the silver(I) center in this cation is coordinated only by one N atom, N(1) and N(3) in Figure 3A, of each ligand. However, INEPT ^{109}Ag and especially the INEPT ^{15}N NMR results clearly show that the silver center interacts with all four N centers and only very weakly or not at all with the thiophene-*S* centers, thus demonstrating the potential of these techniques for the study of the coordination properties of the N_2S_2 ligands in the $[Ag(\mathbf{1})_2]^+$ cations.

In a previous paper[2] we have reported that the ^{109}Ag chemical shifts of the silver(I) complexes with the N_4 donor ligands, $[Ag_2((R,S)\text{-}1,2\text{-}(6\text{-R-py-2-CH}{=}N)_2\text{-}c\text{-Hx})_2](O_3SCF_3)_2$ (see Introduction), are very sensitive toward the nature of the 6-R substituent adjacent to the coordinated pyridine-*N* sites ($\delta(^{109}Ag) = +580$ when 6-R = H and +612 when 6-R = Me;[29] $\Delta\delta = 32$). When the 5-R substituent is changed, which is adjacent to the thiophene-*S*- - -Ag interactions in the $[Ag(N_2S_2)_2]^+$ cations, from R = H to Me, a difference in chemical shifts of only $\Delta\delta = 1$ is observed (see Results). This small value of $\Delta\delta(^{109}Ag)$ indicates that the interactions between the silver(I) center and the thiophene-*S* sites in the $[Ag(\mathbf{1})_2]^+$ cations are very weak or are absent.

The extent of interaction of the four N-donor sites with the silver(I) centers in the $[Ag(\mathbf{1})_2]^+$ cations can be investigated directly by measuring the ^{15}N NMR spectra of the complexes. The two resonances found in the ^{15}N NMR spectrum (190 K) of $[Ag(\mathbf{1b})_2]^+$ can be assigned to the two different imine-*N* sites in both enantiomers, i.e. N(1), N(3) and N(2), N(4) (see Figure 3A). The ^{15}N NMR data unambiguously prove that the two different imine-*N* sites interact with the silver(I) center in $[Ag(\mathbf{1b})_2]^+$ in contrast to the conclusions drawn from the ^1H NMR data and X-ray results. With respect to the interpretation of these ^{15}N NMR data in terms of Ag–N interactions, it is important to note that the group 11 metal center is in a formal oxidation state of +1 and has a closed, d^{10}, valence shell. It will therefore mainly use s- and p-type orbitals for binding the N_2S_2 ligands. When this is taken into account, a correlation between $^1J(^{15}N-^{107,109}Ag)$ values and N–Ag(I) bond strengths does not seem to be a prior excluded.[3] Accordingly a larger ^1J value would indicate a more efficient participation of s-orbital density in the N–Ag(I) bonding. The ^{15}N chemical shift behavior of the N_2S_2 ligand, free and coordinated, suggests that for the similarly hybridized (sp^2) imine-*N* sites stronger Ag–N interactions result in a more upfield ^{15}N chemical shift. These correlation features have been observed before for the $[Ag_2(N_4)_2]^{2+}$ dications.[2] Moreover, the large differences in $^1J(^{15}N-^{107,109}Ag)$ and $\delta(^{15}N)$ found for the two imine-*N* resonances then also suggest that the "s" characters of the two different imine-*N*–Ag(I) interactions differ considerably. This is not surprising in view of the fact that the lone pairs of the weakly coordinated imine-*N* sites N(2) and N(4) in the PLUTO drawing of $[Ag(\mathbf{1b})_2]^+$ do not point toward the silver(I) center (see Figure 4) while the lone pairs of N(1) and N(3) do.

These results show that the values of $^1J(^{15}N-^{107,109}Ag)$ depend not only on the Ag–N distances but also on the direction that the lone pairs of the N sites are pointing out and thus on the stereochemistry of the ligand system. It is therefore important to note that not only in coordination chemistry but also in the study of metal-coordinating biological molecules one has to be careful with the interpretation of X-ray molecular structures when stereochemical information (cf. imine-*N* lone-pair orientation and thiophene-*S*- - -Ag(I) interactions) is explained in terms of the presence of metal–donor-site interactions. This study shows that such conclusions can only be drawn when a spectroscopic handle is available to study these interactions directly in solution.

Acknowledgment. The X-ray data were kindly collected by Dr. A. J. M. Duisenberg. Investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization of Pure Research (ZWO) (A.L.S.). J. M. Ernsting is thanked for recording the

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(29) The ^{109}Ag NMR measurements of $[Ag_2(N_4)_2](O_3SCF_3)_2$ were performed in methanol-d_4 at 294 K. The $\Delta\delta/K$ value for the complex with 6-R = Me is −0.25 ppm/K.

250-MHz ^{1}H NMR spectra and Dr. A. Pagelot for recording the 400-MHz ^{1}H NMR spectra.

Registry No. **1a**, 95045-81-1; **1b**, 95045-82-2; [Ag(**1a**)$_2$](O$_3$SCF$_3$), 95045-84-4; [Ag(**1b**)$_2$](O$_3$SCF$_3$), 95045-86-6; [Cu(**1b**)$_2$](O$_3$SCF$_3$), 95045-88-8; ^{15}N, 14390-96-6; ^{109}Ag, 14378-38-2; 5-R-thiophene-2-carbaldehyde (R = H), 98-03-3; 5-R-thiophene-2-carbaldehyde (R = Me), 13679-70-4; (*R*,*S*)-1,2-diaminocyclohexane, 1436-59-5.

Supplementary Material Available: Tables of positional and thermal parameters for all atoms (Table SII) and of observed and calculated structure factors, a complete list of bond lengths and bond angles (Table SIII) of [Ag(**1b**)$_2$](O$_3$SCF$_3$), and an ORTEP drawing containing the complete numbering scheme (41 pages). Ordering information is given on any current masthead page.

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Binuclear Phosphido-Bridged Complexes That Link Titanium and Zirconium to Tungsten and Iron. Crystal and Molecular Structure of ZrW(μ-PPh$_2$)$_2$Cp$_2$(CO)$_4$

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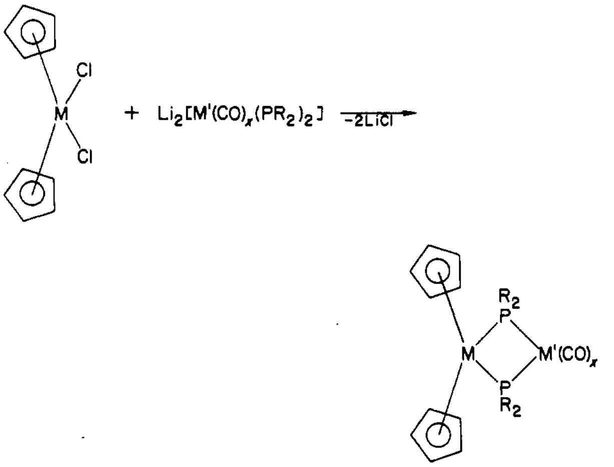
Received August 22, 1984

The new complexes ZrW(μ-PPh$_2$)$_2$Cp$_2$(CO)$_4$, ZrFe(μ-PR$_2$)$_2$Cp$_2$(CO)$_3$ (R = Ph, cyclohexyl), TiW(μ-PPh$_2$)$_2$Cp$'_2$(CO)$_4$ (Cp$'$ = C$_5$H$_4$CH$_3$), and TiFe(μ-PPh$_2$)$_2$Cp$'_2$(CO)$_3$ have been prepared by the reaction of Li$_2$[W(CO)$_4$(PPh$_2$)$_2$] and Li$_2$[Fe(CO)$_3$(PR$_2$)$_2$] with Cp$_2$ZrCl$_2$ and Cp$'_2$TiCl$_2$. They have been spectroscopically characterized, and ZrW(μ-PPh$_2$)$_2$Cp$_2$(CO)$_4$ has been further defined by an X-ray diffraction study. It crystallizes in the space group $P2_1/c$ with a = 14.644 (4) Å, b = 16.932 (4) Å, c = 17.003 (3) Å, β = 100.13 (2)°, V = 4150 (3) Å^3, and Z = 4. The structure refined to R = 0.047 and R_w = 0.067 for the 3340 reflections with $I > 2\sigma(I)$. The W and Zr atoms are bridged by two μ-PPh$_2$ ligands with the Zr further coordinated by two η^5-C$_5$H$_5$ ligands and the W by four CO's. The Zr center has a pseudotetrahedral coordination geometry, and W has a nearly perfect octahedral ligand arrangement. The W–Zr distance is 3.289 (1) Å, implying a weak metal–metal interaction at best.

Heterobimetallic complexes are of current interest because of the possibility of obtaining unique chemistry and of stabilizing ligands in unusual coordination modes as a consequence of combining metals with widely different sets of chemical properties.[1] Particularly interesting are combinations of oxophilic group 4[17] transition metals with metals from groups 6–10[17] as these may alter the stability and/or reactivity of formyl, acyl, carbene, and other ligands involved in carbon monoxide reduction chemistry.[2] Complexes with bridging ligands are desirable since the latter should effectively hold the metals in close proximity and prevent metal separation during reaction.

Using the general synthetic reaction of eq 1, we have been able to prepare a series of bis(phosphido)-bridged TiW, TiFe, ZrW, and ZrFe complexes. The syntheses of these complexes, some of their general reactivity characteristics, and the X-ray structural characterization of the ZrW derivative are described herein. Similar TiMo(μ-PPhH)$_2$Cp$_2$(CO)$_4$ and ZrMo(μ-PPhH)$_2$Cp$_2$(CO)$_4$ complexes were earlier prepared by Johannsen and Stelzer,[3] but structural details were not given. Baker[4] has also mentioned the preparation and structure determination of a similar HfMo(μ-PEt$_2$)$_2$Cp$_2$(CO)$_4$ complex.



(1)

Experimental Section

All manipulations were carried out in standard Schlenk glassware under N$_2$ that had been purified by passage over BASF catalysator and Linde 5-Å molecular sieves. Solvents were reagent grade or better and were dried by stirring over Na/benzophenone followed by distillation under N$_2$. Methyllithium, PhLi, n-BuLi, Li[BHEt$_3$], Cp$_2$ZrCl$_2$ (Cp = η-C$_5$H$_5$) (Aldrich Chemical Co.), W(CO)$_6$, PCy$_2$H (Cy = cyclohexyl), PPh$_2$H, PPh$_2$Me (Strem Chemical Co.), Fe(CO)$_5$ (Alfa Chemical Co.), and Cp$'_2$TiCl$_2$ (Cp$'$ = η^5-C$_5$H$_4$CH$_3$) (Pressure Chemical Co.) were purchased from commercial sources. Spectroscopic instruments used in this work have been previously described.[1b]

Preparation of Fe(CO)$_3$L$_2$ (L = PPh$_2$H, PCy$_2$H). To a hexane solution of Fe(CO)$_5$ (2.5 g, 12.8 mmol) in a 500 mL Schlenk flask was added PPh$_2$H (4.4 mL, 25.1 mmol). This solution was irradiated with a Pyrex-filtered Hanovia 450-W medium-pressure Hg-discharge lamp for 22 h while being stirred. The formation of a yellow precipitate of Fe(CO)$_3$(PPh$_2$H)$_2$ was observed as the reaction progressed. The solution was filtered, and Fe(CO)$_3$(PPh$_2$H)$_2$ was collected as a yellow powder in 40% yield (2.22 g, 4.3 mmol). This known[5] compound was spectroscopically characterized. ^{1}H NMR (benzene-d_6): δ 7.9 (PPh$_2$*H*, d, J_{PH} = 363 Hz). The corresponding Fe(CO)$_3$(PCy$_2$H)$_2$ complex was similarly prepared from Fe(CO)$_5$ and PCy$_2$H. ^{1}H NMR (benzene-d_6): δ 4.82 (PCy$_2$*H*, d, J_{PH} = 334 Hz). MS: m/e 536 (M$^+$).

Preparation of ZrW(μ-PPh$_2$)$_2$Cp$_2$(CO)$_4$ (1). Methyllithium (1.3 M, 2.56 mL, 3.48 mmol) was added via syringe to a THF (20 mL) solution of *cis*-W(CO)$_4$(PPh$_2$H)$_2$[6] (1.62 g, 1.74 mmol) at 22 °C. The resultant orange solution was stirred for 15 min and added via transfer needle to a 20-mL THF solution of Cp$_2$ZrCl$_2$ (0.500 g, 1.71 mmol). This solution was allowed to stir for 3 h at 22 °C, the solvent was removed in vacuo, and the residue was extracted with benzene until the washings were colorless. Removal of the benzene in vacuo left yellow **1** in 92% yield (1.36 g, 1.54 mmol). Recrystallization from toluene at 0 °C gave ana-

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