

Transition metal complexes with sulfur ligands

Part LVI*. First metal complexes of the crown thioether bzo₂-18S6 and its tertiarybutyl derivative ^{bu}bzo₂-18S6 with Ru, Ag, Cr, Mo, W and Fe. X-ray structure analysis of [Ru(bzo₂-18S6)](PF₆)₂·2CH₃NO₂

Dieter Sellmann**, Hans-Peter Neuner, Rainer Eberlein, Matthias Moll and Falk Knoch

Institut für Anorganische Chemie der Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-8520 Erlangen (F.R.G.)

(Received April 10, 1990)

Abstract

In order to investigate the coordination behaviour of the macrocyclic crown thioether bzo₂-18S6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane) and the properties of its metal compounds, the ruthenium and silver complexes [Ru(bzo₂-18S6)]²⁺ and [Ag(bzo₂-18S6)]⁺ were synthesized. [Ru(bzo₂-18S6)](PF₆)₂·2CH₃NO₂ crystallizes in space group *P2₁/c* with *a* = 1151.7(4), *b* = 554.1(2), *c* = 2695.8(13) pm, *β* = 100.00(4)°, *Z* = 2 and *D*_{calc} = 1.90 g/cm³; *R* = 0.072, *R*_w = 0.052. The ruthenium center is surrounded by the six sulfur atoms of the ligand in almost ideal octahedral geometry. Reaction of bzo₂-18S6 with [M(CO)₃L₃] (M = Cr, Mo, W; L = CH₃CN, EtCN) yields the corresponding complexes [M(CO)₃(bzo₂-18S6)], indicating that the crown thioether will not act as a hexadentate ligand, if the metal center carries strongly bound coligands. The tertiarybutyl derivative of bzo₂-18S6, ^{bu}bzo₂-18S6 (2,3,11,12-bis(2',4'-di-tertiarybutyl-benzo)-1,4,7,10,13,16-hexathiacyclooctadecane), is obtained by template alkylation of [Fe(CO)^{bu}S₅'] (^{bu}S₅'²⁻ = 2,2'-bis(2-mercapto-3,5-di-tertiarybutyl-phenylthio)diethylsulfide(2-)) with bis(β-bromoethyl sulfide), followed by acidic hydrolysis of the primary product [Fe(^{bu}bzo₂-18S6)]Br₂. As the structure of [Fe(^{bu}bzo₂-18S6)]Br₂ remained uncertain, free ^{bu}bzo₂-18S6 was reacted with Fe(CF₃SO₃)₂ to give [Fe(^{bu}bzo₂-18S6)](CF₃SO₃)₂ which was characterized by NMR spectroscopy.

Introduction

Crown thioether chemistry has experienced an impressive growth during the last few years. The development of new syntheses [2–4] of preparative amounts of crown thioethers such as 9S3, 12S4 or 18S6 (9S3 = 1,4,7-trithiacyclononane, 12S4 = 1,4,7,10-tetrathiacyclododecane, 18S6 = 1,4,7,10,13,16-hexathiacyclooctadecane) made possible the systematic investigation of the coordination chemistry of these ligands. Crown thioether metal complexes can exhibit unusual coordination numbers [5], redox behaviour [6, 7] and spectroscopic properties [8]. The nine-membered crown thioether trithiacyclononane, 9S3, has proved to possess particularly good ligating properties. This was first shown by the synthesis of [M(9S3)₂]²⁺ (M = Ni, Co, Cu) [9] and subsequently by other studies, especially those of Cooper and Rawle [10], Schröder *et al.* [11] and Wieghardt *et*

al. [12]. In other crown thioethers, e.g. 12S4, 15S5, 18S6 or 24S6, the sulfur donors preferably adopt an exodentate orientation [3], and these macrocycles often display only a low tendency to chelate a single metal ion [10].

Our interest in this class of compounds is based on two facts. In numerous oxidoreductases, e.g. hydrogenases, CO dehydrogenases or nitrogenases, the active centers consist of transition metals in coordination spheres dominated by sulfur donors. These enzymes catalyze reactions which are difficult to achieve *in vitro*, hence the metal sulfur centers must be regarded as highly efficient catalysts and the same may hold for (special) metal crown thioether complexes. Secondly, we recently obtained the new crown thioether bzo₂-18S6 (2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadecane) via template alkylation of the 'S₅'²⁻ thioether thiolate ligand in [Fe(CO)'S₅'] ('S₅'²⁻ = 2,2'-bis(2-mercapto-phenylthio)diethylsulfide(2-)) with bis(β-bromoethyl)sulfide [13] (for ligand abbreviations see Fig. 1).

*Part LV, see ref. 1.

**Author to whom correspondence should be addressed.

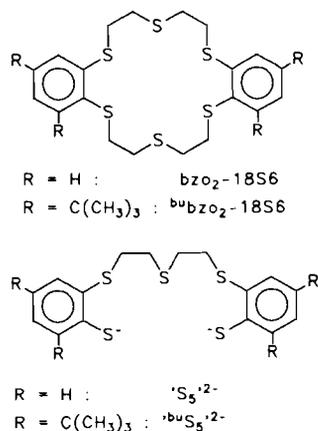
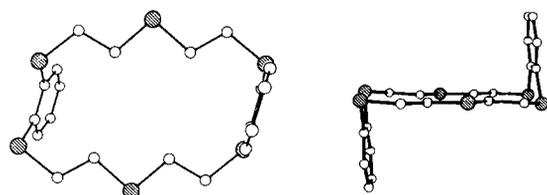


Fig. 1. Used ligands and abbreviations.

Fig. 2. Molecular structure of $\text{bzo}_2\text{-18S6}$.

The primary product of this reaction analyzed for $[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$, but could not be recrystallized in order to yield single crystals for X-ray structure analysis. In polar solvents, e.g. DMF, $[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$ decomposed and $\text{bzo}_2\text{-18S6}$ was set free. Its X-ray structure determination showed that the eighteen-membered ring forms a nearly perfect plane to which the benzene rings stand vertically and all sulfur atoms are exodentate [13] (Fig. 2).

Clearly, such a configuration disfavours octahedral coordination and explains the easy decoordination of $\text{bzo}_2\text{-18S6}$ from the iron center in $[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$.

Anticipating that the formation of metal sulfur bonds which are more stable could overcome this conformational disadvantage and lack of octahedral preorganization, we reacted $\text{bzo}_2\text{-18S6}$ with other metal compounds and now obtained Ru(II), Ag(I) as well as $\text{M}(\text{CO})_3$ complexes ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). When we attempted the template alkylation of $[\text{Ru}(\text{CO})\text{S}_5]$ with bis(β -bromoethyl)sulfide we isolated $[\text{Ru}(\text{CO})\text{bzo-9S3}(\text{Br})_2]$ [14] containing the nine-membered crown thioether bzo-9S3 (2,3-benzo-1,4,7-trithiacyclononane). This result showed the important influence of metal centers on the course of template alkylations and in order to gain deeper insight into these reactions we also investigated the template alkylation of $[\text{Fe}(\text{CO})\text{S}_5]$ ($\text{S}_5^{2-} = 2,2'$ -bis(2-mercapto-3,5-di-tertiarybutyl-phenylthio)diethylsulfide- $(2-)$).

Experimental

General

All operations were carried out under nitrogen, Schlenk techniques being used; reactions were monitored by IR spectroscopy as far as possible. Solvents were dried and distilled before use.

Spectra were recorded on the following instruments. IR: Zeiss IMR 16 IR spectrometer (KBr pellets, solutions in CaF_2 cuvettes with compensation of solvent bands). NMR: Jeol JNM-PMX 60, JNM-GX 270 spectrometer. UV-Vis spectra: Shimadzu UV-260 spectrophotometer. Mass spectra: Varian MAT 212 mass spectrometer (EI and FD mode). Cyclovoltammograms: PAR 264 A with ROTEL A equipped with a glassy carbon working electrode, Ag/AgCl reference electrode and platinum counter electrode. Redox potentials are referred to NHE via ferrocene as an internal standard.

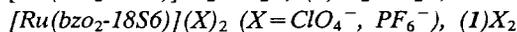
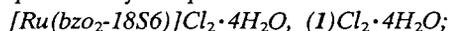
$[\text{Fe}(\text{CO})\text{S}_5]$ [15], bis(β -bromoethyl)sulfide [16], $\text{bzo}_2\text{-18S6}$ [13] and $[\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ($\text{M} = \text{Cr}, \text{Mo}$), $[\text{W}(\text{CO})_3(\text{EtCN})_3]$ [17] were prepared by literature methods. Other reagents were purchased from the following companies: AgCF_3SO_3 : Aldrich; NH_4PF_6 , LiClO_4 : Fluka.

Caution: bis(β -bromoethyl)sulfide is a mustard gas analogue and must be handled with care!

X-ray structure determination of $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{NO}_2$

Single crystals (c. $0.5 \times 0.1 \times 0.03$ mm) separated from a nitromethane solution of $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2$ into which ether was slowly diffused. They were sealed in glass capillaries under N_2 . The structure was solved by direct methods. Non-hydrogen atoms were refined anisotropically and the aromatic hydrogen atoms were placed at calculated positions and refined as rigid groups. The H atoms of the methyl groups were placed in ideal tetrahedral positions and rotated around the central carbon atom during refinement. Table 1 contains crystal data and data collection procedures; Table 2 the final atomic coordinates.

Preparation of compounds



A solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (404 mg, 1.5 mmol) in 15 ml of DMSO is heated to 190°C for 15 min and $\text{bzo}_2\text{-18S6}$ (710 mg, 1.5 mmol) is added. The mixture is kept at 140°C for 45 min and the precipitated white powder is filtered off, washed with 10 ml of DMSO and 2×10 ml of CH_2Cl_2 , and dried *in vacuo*. Recrystallization from MeOH which contains a few milliliter of H_2O yields small, white needles, which are separated and dried *in vacuo*.

TABLE 1. Summary of crystallographic data and data collection procedures of $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{NO}_2$

Formula	$[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{NO}_2$
M_r	$\text{C}_{20}\text{H}_{24}\text{F}_{12}\text{P}_2\text{RuS}_6 \cdot 2\text{CH}_3\text{NO}_2$ 969.88
Space group	$P2_1/c$
Crystal system	monoclinic
Cell dimensions	
a (pm)	1151.7(4)
b (pm)	554.1(2)
c (pm)	2695.8(13)
β ($^\circ$)	100.00(4)
Molecules/unit cell	2
Cell volume (pm ³)	$1694(1) \times 10^6$
D_{calc} (g/cm ³)	1.90
Diffractometer	Nicolet R3m/V
Radiation	Mo-K α
Scan technique	ω -scan
Scan speed ($^\circ/\text{min}$)	3–15
$2\theta_{\text{max}}$ ($^\circ$)	56
Reflections collected	6718
Independent reflections	4093
σ -Criterion	$F > 6\sigma$
Observed reflections	2325
Program	SHELXTL PLUS
Parameters refined	224
R	0.072
R_w	0.052
Temperature of measurement	213 K

Two portions of $(1)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ (210 mg, 0.3 mmol each) are each dissolved in 5 ml of H_2O . Upon addition of 116 mg of NH_4PF_6 or 70 mg of LiClO_4 (0.66 mmol each) dissolved in 1 ml of H_2O the corresponding salts of $[\text{Ru}(\text{bzo}_2\text{-18S6})]^{2+}$ precipitate as white powders. They are filtered off, washed with H_2O and MeOH and dried *in vacuo*.

$[\text{Ru}(\text{bzo}_2\text{-18S6})]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, $(1)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$: yield 526 mg (50%). *Anal.* Calc. for $\text{C}_{20}\text{Cl}_2\text{H}_{32}\text{O}_4\text{RuS}_6$: C, 34.28; H, 4.60. Found: C, 34.22; H, 4.55%.

$[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2$, $(1)(\text{PF}_6)_2$: yield 135 mg (48%). *Anal.* Calc. for $\text{C}_{20}\text{F}_{12}\text{H}_{24}\text{P}_2\text{RuS}_6$: C, 28.33; H, 2.85. Found: C, 28.13; H, 3.18%.

$[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, $(1)(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$: yield 95 mg (36%). *Anal.* Calc. for $\text{C}_{20}\text{Cl}_2\text{H}_{28}\text{O}_{10}\text{RuS}_6$: C, 30.30; H, 3.56. Found: C, 30.06; H, 3.32%.

$[\text{Ag}(\text{bzo}_2\text{-18S6})]\text{CF}_3\text{SO}_3$, $(2)\text{CF}_3\text{SO}_3$

AgCF_3SO_3 (150 mg, 0.58 mmol) is dissolved in 50 ml of THF and added dropwise to $\text{bzo}_2\text{-18S6}$ (270 mg, 0.58 mmol) in 100 ml of THF. The solvent is removed *in vacuo* and the residue is extracted with 30 ml of CH_2Cl_2 . Cooling to -20°C yields colourless crystals of $(2)\text{CF}_3\text{SO}_3$. They are separated, washed with cold CH_2Cl_2 , and dried *in vacuo*. Workup of the mother liquor gives further $(2)\text{CF}_3\text{SO}_3$.

$[\text{Ag}(\text{bzo}_2\text{-18S6})]\text{CF}_3\text{SO}_3 \cdot \text{CH}_2\text{Cl}_2$, $(2)\text{CF}_3\text{SO}_3 \cdot \text{CH}_2\text{Cl}_2$: yield 195 mg (47%). *Anal.* Calc. for $\text{AgC}_{22}\text{Cl}_2\text{H}_{26}\text{F}_3\text{O}_3\text{S}_7$: C, 33.09; H, 3.28; S, 28.10. Found: C, 32.78; H, 3.02; S, 28.09%.

$[\text{Ag}(\text{bzo}_2\text{-18S6})]\text{PF}_6$, $(2)\text{PF}_6$

To a solution of $\text{bzo}_2\text{-18S6}$ (456.8 mg, 1.0 mmol) in 60 ml of $\text{CH}_2\text{Cl}_2/\text{THF}$ (1:5) solid AgPF_6 (252.8 mg, 1.0 mmol) is added and the resulting mixture is refluxed for 1 h. The colourless solution is filtered, the filtrate evaporated to dryness *in vacuo* and the white residue is redissolved in 30 ml of CH_2Cl_2 . At -30°C colourless crystals precipitate which are separated and dried *in vacuo*. Further product can be obtained from the mother liquor.

$[\text{Ag}(\text{bzo}_2\text{-18S6})]\text{PF}_6$, $(2)\text{PF}_6$: yield 559 mg (79%). *Anal.* Calc. for $\text{AgC}_{20}\text{F}_6\text{H}_{24}\text{PS}_6$: C, 33.85; H, 3.41. Found: C, 33.83; H, 3.27%.

$[\text{M}(\text{CO})_3(\text{bzo}_2\text{-18S6})]$ ($M = \text{Cr}$ (3), Mo (4), W (5))

A total of 0.5 mmol of $[\text{M}(\text{CO})_3(\text{CH}_3\text{CN})_3]$ ($M = \text{Cr}$, Mo) or $[\text{W}(\text{CO})_3(\text{EtCN})_3]$ and $\text{bzo}_2\text{-18S6}$ (230 mg, 0.5 mmol) are heated in boiling CH_3CN for about 5 min in order to dissolve the educts. The reaction mixture is cooled to room temperature, filtered, and the filtrate is evaporated to dryness. Recrystallization

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{pm}^2 \times 10^{-1}$) of $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2 \cdot 2\text{CH}_3\text{NO}_2$

	x	y	z	$U(\text{eq})^a$
Ru(1)	5000	5000	0	14(1)
S(1)	6655(2)	2637(4)	319(1)	19(1)
S(2)	5408(2)	7244(4)	750(1)	18(1)
S(3)	3743(2)	2632(4)	400(1)	19(1)
C(1)	7214(8)	3822(18)	938(3)	22(3)
C(2)	6936(8)	6452(20)	1012(3)	25(3)
C(3)	2256(8)	3808(18)	177(3)	20(3)
C(4)	2225(9)	6460(21)	47(3)	27(3)
C(15)	3984(7)	3699(17)	1039(3)	18(3)
C(14)	3455(7)	2384(19)	1389(3)	26(3)
C(13)	3624(8)	3186(20)	1886(3)	34(3)
C(12)	4317(8)	5225(25)	2030(3)	36(3)
C(11)	4850(8)	6443(19)	1690(3)	29(3)
C(10)	4678(7)	5631(16)	1192(3)	21(3)
P(1)	10325(2)	-1472(6)	1120(1)	33(1)
F(1)	9122(5)	-176(16)	879(3)	66(3)
F(2)	10999(5)	17(17)	757(2)	60(2)
F(3)	10611(7)	537(17)	1530(3)	94(4)
F(4)	9629(6)	-2984(15)	1472(2)	69(3)
F(5)	10012(6)	-3528(13)	700(3)	64(3)
F(6)	11511(6)	-2829(17)	1336(3)	86(3)
C(5)	8857(9)	109(31)	2461(4)	63(5)
N(1)	7898(9)	1608(20)	2202(3)	47(4)
O(1)	8037(11)	3755(18)	2218(4)	94(5)
O(2)	7010(6)	648(16)	1982(3)	52(3)

^aEquivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

of the residue from CH_2Cl_2 (+20 \rightarrow -20 $^\circ\text{C}$) gives $[\text{Cr}(\text{CO})_3(\text{bzo}_2\text{-18S6})]$ as yellow crystals, $[\text{Mo}(\text{CO})_3(\text{bzo}_2\text{-18S6})]$ and $[\text{W}(\text{CO})_3(\text{bzo}_2\text{-18S6})]$ as beige microcrystals.

$[\text{Cr}(\text{CO})_3(\text{bzo}_2\text{-18S6})]$ (3): yield 235 mg (79%). *Anal.* Calc. for $\text{C}_{23}\text{CrH}_{24}\text{O}_3\text{S}_6$: C, 46.60; H, 4.08; S, 32.45. Found: C, 46.74; H, 3.50; S, 32.97%.

$[\text{Mo}(\text{CO})_3(\text{bzo}_2\text{-18S6})] \cdot \text{CH}_2\text{Cl}_2$ (4 \cdot CH_2Cl_2): yield 275 mg (76%). *Anal.* Calc. for $\text{C}_{24}\text{Cl}_2\text{H}_{26}\text{MoO}_3\text{S}_6$: C, 39.94; H, 3.63. Found: C, 40.19%; H, 3.52%.

$[\text{W}(\text{CO})_3(\text{bzo}_2\text{-18S6})] \cdot \text{CH}_2\text{Cl}_2$ (5 \cdot CH_2Cl_2): yield 165 mg (45%). *Anal.* Calc. for $\text{C}_{24}\text{Cl}_2\text{H}_{26}\text{O}_3\text{S}_6\text{W}$: C, 35.61; H, 3.24. Found: C, 35.58; H, 2.77%.

$[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$ (6)

$[\text{Fe}(\text{CO})_5\text{S}_5]$ (541.5 mg, 0.8 mmol) and bis(β -bromoethyl)sulfide (361.4 mg, 1.46 mmol) are refluxed in 120 ml of THF until the decarbonylation of the educt is completed (21 h). The resulting brown solution is evaporated to dryness and the brown residue is digested with 50 ml of Et_2O /hexane (1:1) to remove excess bis(β -bromoethyl)sulfide. The brown powder is separated by filtration and dried *in vacuo*.

$[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$ (6): yield 465 mg (65%). *Anal.* Calc. for $\text{Br}_2\text{C}_{36}\text{FeH}_{56}\text{S}_6$: C, 48.21; H, 6.29. Found: C, 46.91; H, 6.11%.

$\text{bzo}_2\text{-18S6}$ (7)

$[\text{Fe}(\text{bzo}_2\text{-18S6})]\text{Br}_2$ (6) (413 mg, 0.46 mmol) is dissolved in 45 ml of THF and 1 ml of concentrated HCl is added. The colour of the solution immediately turns to yellow. The solvent is removed *in vacuo* and the residue is dissolved in 20 ml of CH_2Cl_2 . The CH_2Cl_2 extract is washed with 40 ml of H_2O and dried over Na_2SO_4 . Filtration over SiO_2 and removal of the solvent *in vacuo* yields $\text{bzo}_2\text{-18S6}$.

$\text{bzo}_2\text{-18S6}$ (7): yield 299.4 mg (96%). *Anal.* Calc. for $\text{C}_{36}\text{H}_{56}\text{S}_6$: C, 63.47; H, 8.29. Found: C, 62.64; H, 8.93%.

$[\text{Fe}(\text{bzo}_2\text{-18S6})](\text{CF}_3\text{SO}_3)_2$ (8)

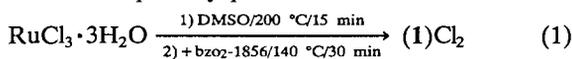
A solution of AgCF_3SO_3 (205.5 mg, 0.80 mmol) in 10 ml of MeOH is added to a solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (80.0 mg, 0.40 mmol) in 20 ml of MeOH. The precipitated AgCl is filtered off and the filtrate evaporated to dryness *in vacuo*. The residue is redissolved in 10 ml of dioxane and $\text{bzo}_2\text{-18S6}$ (272.5 mg, 0.40 mmol) is added. The mixture is heated to reflux for 1 h, at which a violet powder precipitates. The product is filtered off, washed with dioxane and diethyl ether and dried *in vacuo*.

$[\text{Fe}(\text{bzo}_2\text{-18S6})](\text{CF}_3\text{SO}_3)_2$ (8): yield 385.3 mg (93%). *Anal.* Calc. for $\text{C}_{38}\text{F}_6\text{FeH}_{56}\text{O}_6\text{S}_8$: C, 44.09; H, 5.45. Found: C, 44.66; H, 5.53%.

Results and discussion

Synthesis and properties of $[\text{Ru}(\text{bzo}_2\text{-18S6})]^{2+}$ (1)²⁺ and $[\text{Ag}(\text{bzo}_2\text{-18S6})]^+$ (2)⁺

The $[\text{Ru}(\text{bzo}_2\text{-18S6})]^{2+}$ cation, (1)²⁺, formed in the reaction according to eqn. (1) and (1)Cl₂ was isolated as primary product.

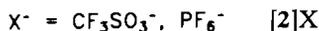
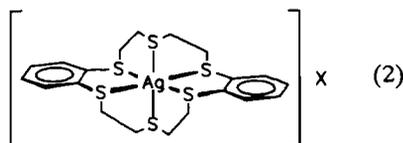
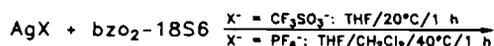


When the deep brown solution of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in DMSO is heated, the colour changes and finally becomes yellowish-green. Major product in the solution is then $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ which is reacted *in situ* with $\text{bzo}_2\text{-18S6}$. Other Ru complexes, too, may take part in the reaction, because attempts to synthesize (1)Cl₂ from isolated $[\text{Ru}(\text{DMSO})_4\text{Cl}_2]$ and $\text{bzo}_2\text{-18S6}$ led to remarkably lower yields of only 30%.

Metathesis of (1)Cl₂ with NH_4PF_6 or LiClO_4 in water yielded $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{PF}_6)_2$, (1)(PF₆)₂, and $[\text{Ru}(\text{bzo}_2\text{-18S6})](\text{ClO}_4)_2$, (1)(ClO₄)₂, respectively, which form colourless crystals. The chloride crys-

tallizes as tetrahydrate, $(1)Cl_2 \cdot 4H_2O$, and is well soluble only in MeOH and H_2O ; the hexafluorophosphate easily dissolves in organic solvents such as THF or CH_3CN . $[Ru(bzo_2-18S6)]^{2+}$ is stable towards CO. Even at 80 °C under 100 bar of CO no reaction of $(1)Cl_2$ with CO could be observed although ruthenium carbonyl complexes with thioether ligands, e.g. $[Ru(CO)_2\{H_3CC(CH_2SCH_3)_3\}Cl_2]$ [18] or $[Ru(CO)_2S_5]$ [14] are usually very stable. The cation of $(1)Cl_2$ is stable towards concentrated sulfuric acid, only exchange of the anion takes place yielding $(1)SO_4$.

Salts of the silver complex $[Ag(bzo_2-18S6)]^+$, $(2)^+$, could be obtained only with non-coordinating anions, such as triflate or hexafluorophosphate and, according to eqn. (2), $(2)CF_3SO_3$ or $(2)PF_6$ were isolated, respectively.



$(2)CF_3SO_3$ is soluble in nitromethane and THF; $(2)PF_6$ in CH_2Cl_2 , CH_3CN and nitromethane. Although single crystals of both salts suitable for X-ray structure analysis could be obtained, a structure determination was not possible because the salts decomposed in the X-rays.

X-ray structure determination of $(1)(PF_6)_2 \cdot 2CH_3NO_2$

The crystal structure of $(1)(PF_6)_2$ consists of discrete cations and anions, the cations lying on crystallographic centers of symmetry. Figure 3 shows the molecular structure of the $[Ru(bzo_2-18S6)]^{2+}$ cation; Table 3 lists selected distances and angles.

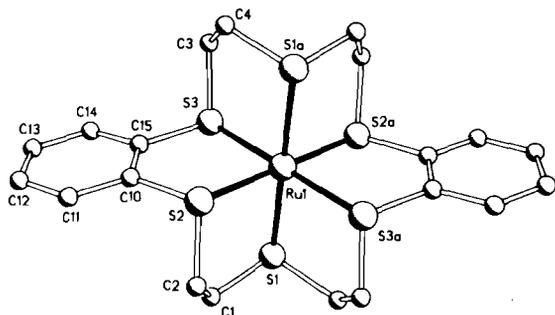


Fig. 3. Molecular structure of $[Ru(bzo_2-18S6)]^{2+}$ in $(1)(PF_6)_2$ (H atoms omitted).

TABLE 3. Selected distances (pm) and angles ($^\circ$) of $(1)^{2+}$ in $(1)(PF_6)_2 \cdot 2CH_3NO_2$

Ru(1)–S(1)	234.9(2)	S(2)–Ru(1)–S(1)	87.5(1)
Ru(1)–S(2)	235.0(2)	S(3)–Ru(1)–S(1)	92.4(1)
Ru(1)–S(3)	235.1(2)	S(3)–Ru(1)–S(2)	87.2(1)
S(1)–C(1)	180.0(9)	C(1)–S(1)–Ru(1)	105.6(3)
S(2)–C(2)	182.8(9)	C(2)–S(2)–Ru(1)	103.7(3)
S(2)–C(10)	180.8(8)	C(10)–S(2)–Ru(1)	104.7(3)
S(3)–C(3)	183.2(9)	C(10)–S(2)–C(2)	98.8(4)
S(3)–C(15)	179.2(8)	C(3)–S(3)–Ru(1)	105.2(3)
C(1)–C(2)	151.9(11)	C(15)–S(3)–Ru(1)	104.4(3)
C(3)–C(4)	151.6(11)	C(15)–S(3)–C(3)	100.1(4)
C(15)–C(14)	141.1(11)	C(2)–C(1)–S(1)	115.2(7)
C(15)–C(10)	136.0(11)	C(1)–C(2)–S(2)	113.1(7)
C(14)–C(13)	139.0(11)	C(4)–C(3)–S(3)	114.0(8)
C(13)–C(12)	140.2(15)	C(14)–C(15)–S(3)	117.1(7)
C(12)–C(11)	136.7(13)	C(10)–C(15)–S(3)	122.5(6)
C(11)–C(10)	139.5(10)		

In the centrosymmetric $(1)^{2+}$ the ruthenium is surrounded by the six sulfur atoms of bzo_2-18S6 in almost ideal octahedral geometry. The Ru–S bond lengths (average 235.0 pm) are identical within experimental accuracy and the maximum deviation of the S–Ru–S angles from rectangularity is only 2.8°. In this respect $(1)^{2+}$ compares well with the cation of $[Ru(9S3)_2](CF_3SO_3)_2$ or $[Ru(9S3)_2][B(C_6H_5)_4]_2 \cdot 2DMSO$, respectively, where average Ru–S distances of 233.9 pm and angles of $90 \pm 2.35^\circ$ were found [7]. Thus, in $(1)^{2+}$ no ligand compression effects as in $[Ni(18S6)]^{2+}$ [19] are detectable.

Spectra and electrochemistry of $(1)(PF_6)_2$ and $(2)CF_3SO_3$

IR spectra of $(1)(PF_6)_2$ and $(2)CF_3SO_3$ in the range of 4000–400 cm^{-1} yield no information with regard to structure and show only the typical ligand and anion bands. In the mass spectra the $(1)^{2+}$ and $(2)^+$ cations at $m/2e = 279$ and $m/e = 564$, respectively, are detected.

The centrosymmetric structure of $(1)^{2+}$ is reflected in the NMR spectra of $(1)(PF_6)_2$. The 1H NMR spectrum displays a set of three symmetric multiplets, one for the C_6H_4 and two for the C_2H_4 protons; the ^{13}C NMR spectrum shows only three and two signals for the aromatic and C_2H_4 carbon atoms, respectively. The number of ^{13}C signals is indicative of a C_2 axis, a mirror plane or a center of inversion, the center of symmetry being proved by the X-ray structure determination. Although the structure of the $(2)^+$ cation could not be determined by X-ray structure analysis, it can be reliably deduced from the NMR spectra. They are almost identical with the spectra of $(1)^{2+}$, particularly the ^{13}C NMR spectrum showing the same number of signals which indicates analogous structures of $(1)^{2+}$ and $(2)^+$ and the structure drawn in eqn. (2). (For NMR data see Table 4).

Samples of $(2)PF_6$ which were prepared at temperatures above 40 °C show splittings of the ^{13}C signals, which may arise from two possible isomers of $(2)^+$, because the crown thioether can wrap around the Ag^+ ion in two different ways [20]. The first yields a *meso*, the second a *racemic* product as shown in Fig. 4. At room temperature only the *meso* isomer forms.

The electronic spectrum of $(1)Cl_2$ shows one d-d band at 348 nm ($\epsilon = 152 \text{ l mol}^{-1} \text{ cm}^{-1}$) attributable to the $^1A_{1g} \rightarrow ^1T_{1g}$ transition of octahedral Ru(II). As further transition bands are obscured by ligand bands, determination of the Racah parameter and ligand field strength was not possible. According to the d^{10} system of Ag^+ , $(2)PF_6$ exhibits no d-d bands.

The cyclic voltammogram of $(1)(PF_6)_2$ in acetonitrile shows no oxidation wave up to 2.0 V indicating high stability of $(1)^{2+}$ towards oxidation. In this respect, $(1)^{2+}$ very much resembles $[Ru(9S3)_2]^{2+}$, which is also very stable towards oxidation [7], and contrasts with the $[Ru(9N3)_2]^{2+}$ complex ($9N3 = 1,4,7\text{-triazacyclononane}$) showing a low redox potential at +0.37 V versus NHE [20]. The unusual stabilization of the Ru(II) oxidation state in thioether complexes is discussed to be due to the π -acceptor abilities of ligands, which presumably not only involve sulfur d-orbitals but also $\sigma^* \text{-S-C}$ orbitals [10]. $(1)^{2+}$ shows no reduction wave either within the range of 0 to -1.3 V versus NHE.

The redox behaviour of $(2)PF_6$ extremely contrasts with that of $(1)(PF_6)_2$. $(2)PF_6$ shows two significant signals: one quasireversible redox potential at +0.01 V and one irreversible oxidation wave at +0.29 V (Fig. 5). The former we assign to a $(2)^+/(2)^0$ couple as the redox potential of an uncoordinated metal ion is normally lowered by complexation (cf. $E^0(Ag/Ag^+) = +0.799 \text{ V}$). The latter may involve a $(2)^+/(2)^{2+}$ couple. The dication is expected to undergo rapid chemical reactions which lead to cleavage of S-C bonds in the ligand. This contrasts with the redox behaviour of $[Ag(9S3)_2]^+$, which can be reversibly oxidized at +1.30 V versus NHE [5].

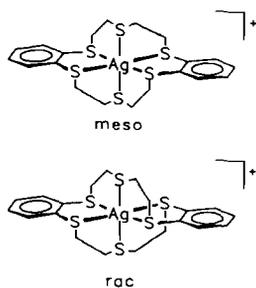


Fig. 4. *meso* and *racemic* $(2)^+$.

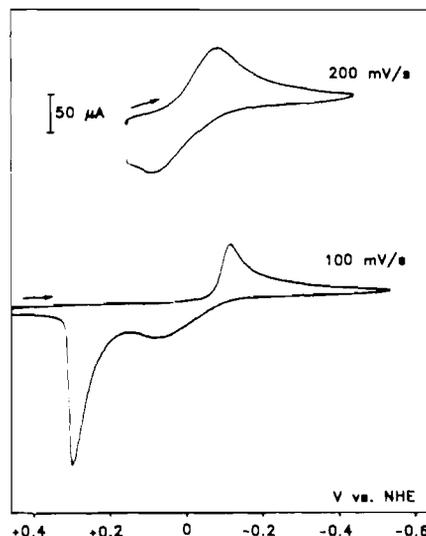
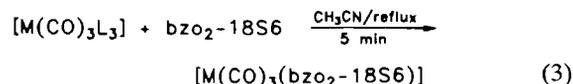


Fig. 5. Cyclic voltammogram of $(2)PF_6$ (10^{-3} M in CH_3CN , 0.1 M $TBAClO_4$).

Synthesis and properties of $[M(CO)_3(bzo_2-18S6)]$

($M = Cr, Mo, W$)

$(1)^{2+}$ and $(2)^+$ show that the formation of six (strong) metal S bonds can overcome the conformational disadvantage for octahedral ligation of free bzo_2-18S6 . This, however, is possible only if six coordination sites at the metal center are easily accessible. Coordination of only three of the six thioether atoms of bzo_2-18S6 is expected, if the metal center carries firmly bound coligands. This is obviously the case in $[M(CO)_3(bzo_2-18S6)]$ ($M = Cr, Mo, W$), which are obtained according to eqn. (3).



$M = Cr, Mo; L = CH_3CN$

$M = W; L = EtCN$

$[Cr(CO)_3(bzo_2-18S6)]$ (3), $[Mo(CO)_3(bzo_2-18S6)]$ (4) and $[W(CO)_3(bzo_2-18S6)]$ (5) form yellowish microcrystals which are soluble in CH_2Cl_2 , CH_3CN and DMF. The KBr IR spectra of 3-5 exhibit two intense ν_{CO} bands with the typical pattern of $M(CO)_3$ fragments with local C_{3v} symmetry [21]. Accordingly, only three of the six donor atoms of bzo_2-18S6 can ligate the metal center, as indicated in Fig. 6.

Such an asymmetric bonding of bzo_2-18S6 should give rise to 12 different signals in the aromatic region of the ^{13}C NMR spectrum. Ten signals are observed, two of them with higher intensity indicating that they result from unresolved peaks. The FD mass spectra of 3-5 prove the mononuclear structure of the complexes. In all cases, peaks of the molecular ions were observed. No ions indicating binuclear

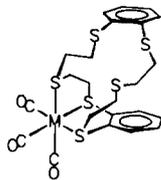
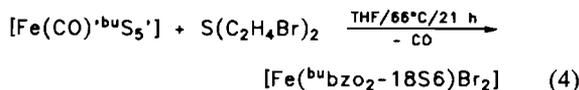


Fig. 6. Proposed structure of $[M(CO)_3(bzo_2-18S6)]$; $M = Cr, Mo, W$.

complexes, e.g. $[\mu-(bzo_2-18S6)\{Cr(CO)_3\}_2]$ were detected. In this point bzo_2-18S6 contrasts with the behaviour of $18S6$ which forms $[\mu-(18S6)\{Mo(CO)_3\}_2]$ [22].

Synthesis and properties of $[Fe(b^u bzo_2-18S6)Br_2]$ (6), $b^u bzo_2-18S6$ (7) and $[Fe(b^u bzo_2-18S6)](CF_3SO_3)_2$ (8)

Template alkylation of $[Fe(CO)'b^u S_5']$ with bis(β -bromoethyl)sulfide yielded a brown product which analyzed for $[Fe(b^u bzo_2-18S6)Br_2]$ (6) (eqn. (4)).

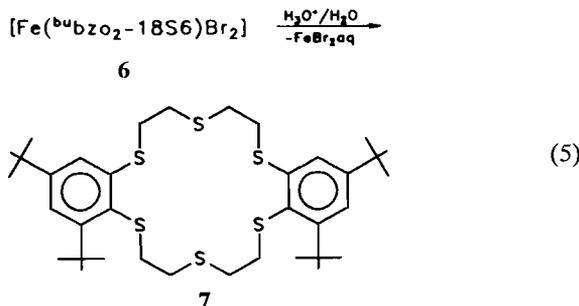


6

Thus, with respect to the formation of crown thioethers, the template reactions of $[Fe(CO)'S_5']$ [13] and $[Fe(CO)'b^u S_5']$ practically take the identical course and contrast with the template alkylation of $[Ru(CO)'S_5']$ which yields $[Ru(bzo-9S3)(CO)Br_2]$ as major product [14]. It also makes no difference whether in the reaction according to eqn. (4) *meso*- or *'trans'*- $[Fe(CO)'b^u S_5']$ [23] or a mixture of the two of them is used. 6 is well soluble in organic solvents, but decomposes in donor solvents such as MeOH, CH₃CN and acetone decoordinating the crown thioether.

Hydrolysis of 6 with concentrated HCl yields the crown thioether 7 (eqn. (5)) as a white powder. It recrystallizes from boiling n-butanol as long, colourless needles, having a melting point of 199 °C.

7 is well soluble in THF and chlorinated hydrocarbons, sparingly soluble in MeOH, diethyl ether, hexane and pentane and insoluble in H₂O.



The FD mass spectrum of 6 shows signals at $m/e = 815$ and 680 which are assigned to $[Fe(b^u bzo_2-18S6)Br]^+$ and $b^u bzo_2-18S6$, respectively.

The EI mass spectrum of 7 exhibits the signal of the molecular ion at $m/e = 680$ and the signals appearing at lower m/e values correspond with fragment ions of 7.

The structure of 6 remains uncertain. It is difficult to obtain 6 with reproducible elemental analysis and it could not be decided whether 6 represented an ionic complex with $\eta^6-b^u bzo_2-18S6$ and bromide counter anions, or a neutral complex containing $\eta^4-b^u bzo_2-18S6$ and two covalently bound bromide ligands. The 1H NMR spectrum of this substance was indistinguishable from the 1H NMR spectrum of pure $b^u bzo_2-18S6$. In order to obtain a fully characterizable Fe species, $[Fe(b^u bzo_2-18S6)](CF_3SO_3)_2$ (8) was synthesized according to eqn. (6).

$FeCl_2 \cdot 4H_2O$ was converted into $Fe(CF_3SO_3)_2$, which was subsequently reacted with $b^u bzo_2-18S6$. 8 forms a light violet powder which is soluble in EtNO₂ and MeOH. The 1H NMR spectrum indeed differs remarkably from that of 6, as shown in Fig. 7.

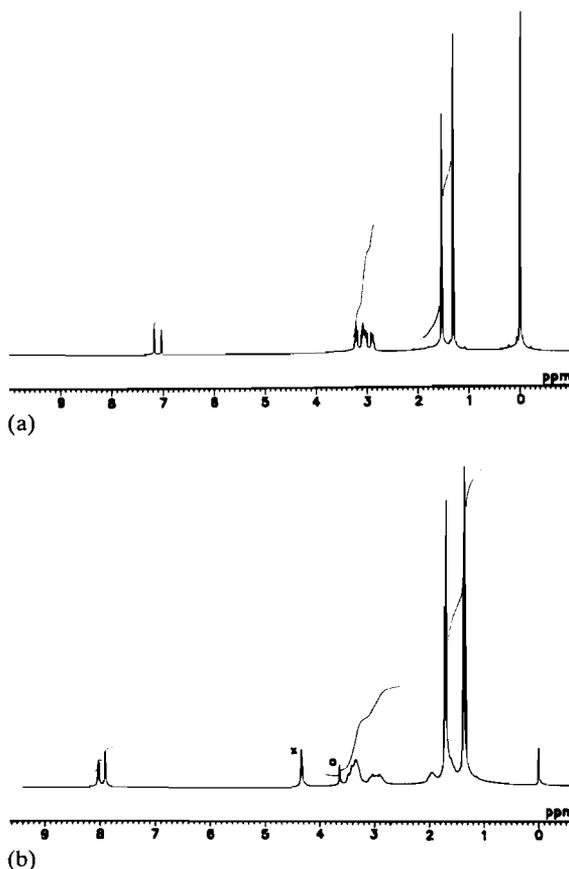
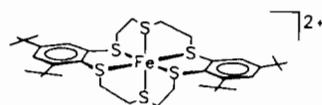


Fig. 7. 1H NMR spectra of (a) $b^u bzo_2-18S6$ in CCl_4 and (b) $[Fe(b^u bzo_2-18S6)](CF_3SO_3)_2$ in CD_3NO_2 ; x = CHD₂NO₂, o = traces of dioxane.

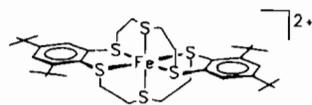
TABLE 4. Spectroscopic data of the crown thioether compounds

Compound	^1H NMR ^a (ppm)	^{13}C NMR ^a (ppm)	FD-MS	$\nu(\text{CO})^b$ (cm^{-1})
(1)(PF ₆) ₂	8.05, 7.70 (m, Ar-H, 8) 3.50, 3.30, 2.90, 1.78 (m, CH ₂ -S, 16) ^c	134.0, 133.75, 133.7 (Ar-C) 46.6, 36.3 (CH ₂ -S)	279	
(2)CF ₃ SO ₃	7.57, 7.40 (m, Ar-H, 8) 3.45, 3.03 (m, CH ₂ -S, 16) ^d	134.1, 132.2, 129.7 (Ar-C) 35.9, 31.7 (CH ₂ -S)	564	
3	8.0–7.0 (m, Ar-H, 8) ^e 4.0–2.4 (m, CH ₂ -S, 16)	235.5, 230.2, 224.2 (CO) 139–127 (Ar-C) 27–43 (CH ₂ -S)	593	1910, 1800
4	7.6–6.6 (m, Ar-H, 8) ^d 3.5–2.0 (m, CH ₂ -S, 16)		637	1925, 1815
5			724	1915, 1800
7	7.2, 7.1 (s, Ar-H, 4) ^e 3.0 (m, CH ₂ -S, 16) 1.6, 1.3 (s, ^t bu-H, 36)		680	
8	8.02, 7.91 (s, Ar-H, 4) ^f 3.35, 2.94, 1.97 (m, CH ₂ -S, 16) 1.70, 1.35 (s, ^t bu-H, 36)	159.9, 153.5, 139.4, 131.3, 128.8 (Ar-C) 51.2, 49.6, 39.4, 38.5, 37.9, 36.6, 32.4, 31.3 (Al-C)		

^aRelative to TMS, s=singlet, m=multiplet. ^bIn KBr. ^cIn CD₃CN. ^dIn CD₂Cl₂. ^eIn CCl₄. ^fIn CD₃NO₂.

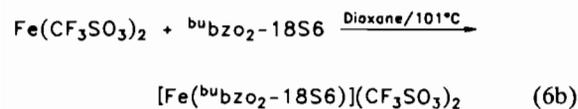
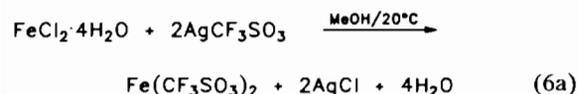


(a)



(b)

Fig. 8. *meso* (a) and *trans* (b) configuration of the [Fe(^{bu}bzo₂-18S6)]²⁺ cation.



8

Both ^1H and ^{13}C NMR spectra of isolated **8** indicate a highly symmetric structure of the [Fe(^{bu}bzo₂-18S6)]²⁺ cation. The ^1H NMR spectrum shows only two signals for the aromatic as well as the tertiarybutyl protons. The C₂H₄ protons show splittings similar

to that of bzo₂-18S6 in (1)²⁺. The ^{13}C NMR spectrum exhibits five signals for the aromatic C atoms, one more intensive than the others, four signals for the C₂H₄, and two pairs of signals for the tertiarybutyl C atoms. The number of signals in the NMR spectra demands that the cation contains either a mirror plane, C₂ axis or a center of inversion. Accordingly, the cation of **8** must adopt the *meso* structure shown in Fig. 8(a) because the racemic *trans* complex (Fig. 8(b)) possesses no element of symmetry. The latter should show four tertiarybutyl signals in the ^1H NMR spectrum and twice as many ^{13}C signals as the *meso* form.

Spectroscopic data of the crown thioether compounds are summarized in Table 4.

Conclusions

Coordination of bzo₂-18S6 to Ru(II) and Ag(I) leads to the homoleptic thioether complexes [Ru(bzo₂-18S6)]²⁺ and [Ag(bzo₂-18S6)]⁺, respectively. [Ru(bzo₂-18S6)]²⁺ represents the first example of a ruthenium complex, [Ag(bzo₂-18S6)]⁺ the first mononuclear silver complex with an 18S6 crown thioether ligand. With the parent ligand 18S6 the polymeric [Ag(18S6)Br]_∞ was described recently. It crystallizes as a one-dimensional polymer in which AgBr is linked by 18S6 ligands [5a].

The results show that, despite its unfavourable preorganization with only exodentate thioether

atoms, bzo₂-18S6 can form very stable complexes. [Ru(bzo₂-18S6)]²⁺ withstands even concentrated H₂SO₄ or carbon monoxide under high pressure. It is also redox inert within a wide range of potential. Reaction of bzo₂-18S6 with M(CO)₃ entities yields [M(CO)₃(bzo₂-18S6)] in which the crown thioether acts only as tridentate ligand.

The influence of the metal center on the coordination behaviour of bzo₂-18S6 is further revealed by its reactions with Fe(II) and Ru(II). Fe(II) yields the homoleptic thioether complexes only in the absence of coordinating anions; the homoleptic coordination of Ru(II) is not prevented by chloride ions.

Supplementary material

Further details of X-ray crystal structure analysis have been deposited and can be obtained from the Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen 2 by citing the deposition no. CSD 320060, the authors and reference.

Acknowledgements

These investigations were supported by the Deutsche Forschungsgemeinschaft, by the Fonds der Chemischen Industrie and by a donation of RuCl₃·xH₂O by Degussa AG, Hanau, F.R.G. We gratefully acknowledge this support.

References

- 1 D. Sellmann, S. Fünfgelder, G. Pöhlmann, F. Knoch and M. Moll, *Inorg. Chem.*, in press.
- 2 J. Buter and R. M. Kellog, *J. Org. Chem.*, **46** (1981) 4481.
- 3 R. E. Wolf, Jr., J. R. Hartman, J. M. E. Storey, B. M. Foxman and S. R. Cooper, *J. Am. Chem. Soc.*, **109** (1987) 4328.
- 4 D. Sellmann and L. Zapf, *J. Organomet. Chem.*, **289** (1985) 57.
- 5 (a) J. Clarkson, R. Yagbasan, P. J. Blower, S. C. Rawle and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, (1987) 950; (b) P. J. Blower, J. A. Clarkson, S. C. Rawle, J. R. Hartman, R. E. Wolf Jr., R. Yagbasan, S. G. Bott and S. R. Cooper, *Inorg. Chem.*, **28** (1989) 4040.
- 6 A. J. Blake, A. J. Holder, T. I. Hyde and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1987) 987.
- 7 (a) S. C. Rawle, T. J. Sewell and S. R. Cooper, *Inorg. Chem.*, **26** (1987) 3769; (b) M. N. Bell, A. J. Blake, M. Schröder, H.-J. Küppers and K. Wiegardt, *Angew. Chem.*, **99** (1987) 253.
- 8 J. R. Hartman, E. J. Hintsä and S. R. Cooper, *J. Am. Chem. Soc.*, **108** (1986) 1208.
- 9 W. N. Setzer, C. A. Ogle, G. S. Wilson and R. S. Glass, *Inorg. Chem.*, **22** (1983) 266.
- 10 S. R. Cooper and S. C. Rawle, *Acc. Chem. Res.*, **4** (1988) 21.
- 11 A. J. Blake, A. J. Holder, T. I. Hyde, Y. V. Roberts, A. J. Lavery and M. Schröder, *J. Organomet. Chem.*, **323** (1987) 261.
- 12 H. J. Küppers, A. Neves, C. Pomp, D. Ventur, K. Wiegardt, B. Nuber and J. Weis, *Inorg. Chem.*, **25** (1986) 2400.
- 13 D. Sellmann, P. Frank and F. Knoch, *J. Organomet. Chem.*, **339** (1988) 345.
- 14 D. Sellmann, F. Knoch and C. Wronna, *Angew. Chem., Int. Ed. Engl.*, **27** (1988) 691.
- 15 D. Sellmann, G. Binker, M. Moll and Ch. E. Campana, *Inorg. Chim. Acta*, **130** (1987) 221.
- 16 W. Steinkopf, J. Herold and J. Stöhr, *Ber. Dtsch. Chem. Ges.*, **53** (1920) 1007.
- 17 B. L. Ross, J. G. Grasselli, W. M. Ritchey and H. D. Kaesz, *Inorg. Chem.*, **2** (1963) 1023.
- 18 E. Böhlen, *Thesis*, Friedrich-Alexander Universität, Erlangen-Nürnberg, F.R.G., 1982.
- 19 E. J. Hintsä, J. R. Hartman and S. R. Cooper, *J. Am. Chem. Soc.*, **105** (1983) 3738.
- 20 D. St. C. Black and I. A. McLean, *Aust. J. Chem.*, **24** (1971) 1401.
- 21 D. M. Adams, *Metal-Ligand and Related Vibrations*, Arnold, London, 1967.
- 22 G. J. Grant, J. P. Carpenter, W. N. Setzer and D. G. Van Derveer, *Inorg. Chem.*, **28** (1989) 4128.
- 23 D. Sellmann, G. Binker, M. Moll and E. Herdtweck, *J. Organomet. Chem.*, **327** (1987) 403.