On the Nature of Arene η^6 Interactions in the Solid State and the Use of Cylindrophanes as Ligands for Sandwich Complexation of Metals with Longer-Range Interactions with the Benzene Ring

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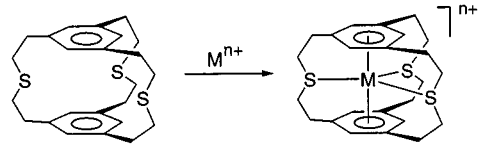
A novel mode of containment for metal ions which participate in longer-range interactions with aryl rings (≥ 2.5 Å) is demonstrated in the preorganized cylindrical host **1**. Three equatorial sulfur atoms in **1** hold metals in a trigonal planar ligand field between two apical benzene centroids at an M–Ar distance of about 3 Å. Evidence of an interaction between the π electrons and the metals is gained by ^{1}H NMR spectroscopy of the complexes, and support for the general description of metal–arene contacts in the 2.5–3.5 Å range as "bonds" is derived from a statistical study of η^6-coordination in the solid state. Crystal structures of [Ag(**1**)]BF$_4$ and [Cu(**1**)]BF$_4$ confirm the first examples of arene Ag^I and Cu^I sandwich complexation and indeed the only structurally characterized Cu^I-aryl centroid interaction. The two isomeric *tris*-sulfoxides derived from **1** show less tendency to interact with metals ions.

Introduction

Since the discovery of ferrocene and transition metal-benzene complexes in the 1950's, there has been a constant fascination with the way metals interact with aromatic rings. The paradigmatic interaction involving neutral arenes is the η^6 mode of complexation, in which most group 3–10 metals participate.[1] We recently noted the bimodal nature of the arene–metal distance histogram generated from solid-state structures in the Cambridge Structural Database (CSD), which neatly divides this interaction into two categories, i.e. classic, short-range η^6 bonding, and longer-range aryl centroid–metal contact.[2] The *sym*-[5.5.5]trithiacyclophane macrobicycle **1**[3] was designed to take advantage of the fact that the mean value for the latter is around 3 Å (corresponding to the distance between the midpoint of the cavity and the center of each ring), which made possible the first structural characterization of the Ag^I and Cu^I arene sandwich complexes **2**. A divalent heteroatom (O, S) is required at the "equatorial" positions in ligands such as **1** because hydrogens occupy the cavity in the NH and hydrocarbon analogs,[4] but since the longer-range metal–arene interaction is weak, the complexes **2** owe their overall stability to the consequent trigonal-planar heteroatom ligand set. The analysis and reasoning which led to the design of "cylindrophane" **1**, and the subsequent preparation of novel cryptates **2**, are now presented in full.



1 **2**

Results and Discussion

Statistical Analysis of η^6-Metal Complexation

To appreciate the design principles behind **1**, it is first instructive to look in some detail at the nature of the interactions of metals with benzene rings. Although an account of η^6-benzene and arene complexes was included in Orpen et al.'s general analysis of coordination complexes in the CSD,[5] the study only tabulated data for 15 η^6-bonded *d*-block metals (vs. 29 in this analysis), with the longer-range noncovalent metal–arene contacts outside its remit.

The sampling of a cylindrical volume 0.5 Å in radius extending from the centroid of any benzene or aryl ring in the CSD was accomplished by constructing a query in QUEST3D[6] as follows: Three points were defined on a six-membered ring; point *x*, one C-atom of the ring; point *o*, the centroid of the ring; and point *y*, the centroid of one of the C–C bonds parallel to *xo* (Figure 1).

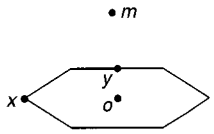


Figure 1. The QUEST3D query dialog used to generate parameters *om*, *xôm*, and *yôm*

Discrepancies in the 2D representation of arenes in the Database necessitates the use of both delocalized aromatic

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1434–1948/00/0303–0485 $ 17.50+.50/0

and "cyclohexatriene" arguments for the bonding in the ring. A metal atom at point m would have x,y coordinates $x_m = om \times \cos(x\hat{o}m)$ and $y_m = om \times \cos(y\hat{o}m)$. The radius of the cylinder (r) was defined by the relationship $x_m^2 + y_m^2 \leq r^2$, and the height of the cylinder was simply limited by constraining om. Choosing an arbitrary value of 5 Å for om produced a total of 2525 observations of metal atoms occupying this space. The om vs $x\hat{o}m$ scattergram (Figure 2a) reveals a massive data island centered around om = 1.7 Å corresponding to the plethora of η^6-complexes of the central transition metals. A discontinuity then precedes a second, more diffuse set of observations between ca. 2.5–3.5 Å. Subtracting the Bondi half-thickness of the benzene ring (1.77 Å) from this range of values gives a difference which is less than the van der Waals radius of the metal in most cases,[7] hence interactions of some description are indicated in this region (vide supra). Finally, the upward trend in the plot towards the 5 Å limit arises from the fixed relationships between metals and proximal rings in the numerous [2.2]paracyclophane η^6-metal complexes and μ-bridged bis(η^6-metal) species in the Database (Figure 3).

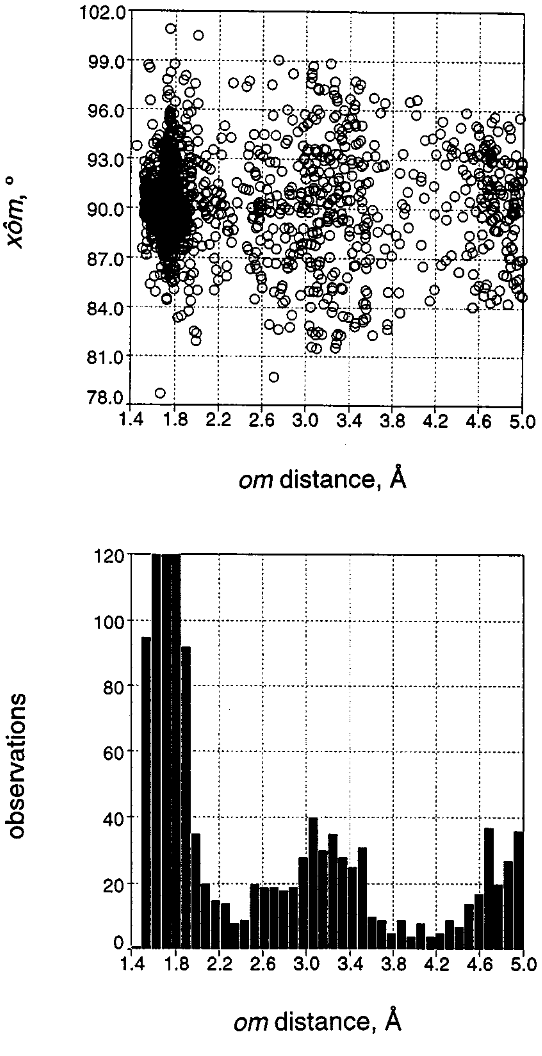


Figure 2. (a: top) *xôm* angle vs *om* distance scatterplot. (b: bottom) *om* distance histogram; the off-scale histogram bins between ca. 1.6–1.8 Å represent a total of 1648 observations

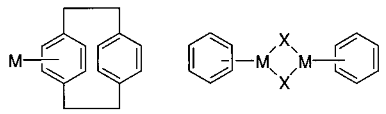


Figure 3. Increasing observations beyond 4.5 Å in the data presented in Figure 2 are due to relationships between metals and the *more distant* benzene rings in the above structures

While statistical arguments are useful for generally characterizing the second maximum as a "bonding" region, individual cases are open to interpretation. Clearly, a sound basis for a cohesive electrostatic interaction can be derived from numerous gas phase studies between metal ions and aromatic systems, where bond energies on the order of 100 kJ mol^{-1} are typical.[8] Inspection of the datapoints individually gives valuable insights into the nature of the species involved. Analysis of both maxima by elemental composition, for example, leads to a reorganization of at least some of the data based on observed trends. Hence it becomes evident that the lanthanides and uranium, although formally in the second maximum in the plots in Figure 2, belong to the "short-range" bonding curve in the graphical representation of the data (Figure 4) taken from Tables 1 and 2. Likewise, some of the observations of Li–Ar contacts are contained within the first peak. After manual removal of redundant data arising from redeterminations, there are 1972 observations of short-range η^6 bonding to transition metals where the π-system can be counted in the valence electron set, and 328 other contacts which will simply be referred to as "longer-range."[9]

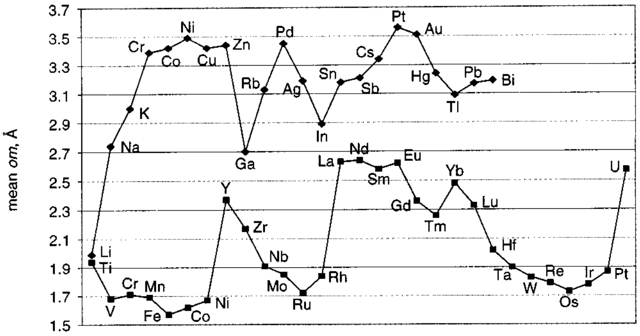


Figure 4. Mean longer-range (upper curve) and short-range (lower curve) Ar centroid–metal contact distances (*om*) by element with increasing atomic number

Certain elements appear to participate in both modes of complexation, i.e. divalent Cr, Co, Ni, and Pt, which in coordinatively unsaturated, square-planar complexes include a long-range arene contact over the vacant orbital. These, however, represent a total of only 18 observations and, in general, the longer-range complexes involve more-or-less exclusively main-group metals and some transition metals with filled *d*-shells. Indeed, apart from Ag^{I} and Hg^{II}, the case for including any transition metal among the longer-range complexes is debatable.

Table 1. Statistics for short-range Ar centroid–metal complexes

Metal	Observations	*om* Range	Mean *om*
Ti	25	1.74–2.11	1.94
V	24	1.59–1.87	1.68
Cr	728	1.52–1.82	1.71
Mn	38	1.55–1.77	1.69
Fe	116	1.46–2.18	1.57
Co	36	1.58–1.85	1.62
Ni	3	1.61–1.71	1.67
Y	5	2.26–2.53	2.37
Zr	33	1.98–2.37	2.17
Nb	24	1.82–2.02	1.91
Mo	55	1.72–1.95	1.85
Ru	672	1.58–2.01	1.72
Rh	41	1.76–1.90	1.84
La	2	2.54–2.72	2.63
Nd	5	2.58–2.71	2.64
Sm	8	2.52–2.67	2.58
Eu	5	2.55–2.68	2.62
Gd	2	2.22–2.51	2.36
Tm	2	2.16–2.36	2.26
Yb	2	2.48	2.48
Lu	1	2.33	*2.33*
Hf	12	1.91–2.33	2.02
Ta	3	1.83–1.94	1.90
W	32	1.74–2.00	1.83
Re	5	1.75–1.86	1.79
Os	56	1.61–1.83	1.73
Ir	24	1.72–1.89	1.78
Pt	1	1.87	*1.87*
U	12	2.54–2.60	2.57

Table 2. Statistics for longer-range Ar centroid-metal complexes

Metal	Observations	*om* Range	Mean *om*
Li	29	1.67–2.45	1.99
Na	29	2.29–3.56	2.74
K	73	2.69–3.27	3.00
Cr^{II}	1	3.39	3.39
Co^{II}	3	3.26–3.56	3.42
Ni^{II}	7	3.42–3.55	3.49
Cu^{II}	4	3.25–3.55	3.42
Zn	1	3.44	3.44
Ga^{I}	15	2.42–3.00	2.70
Rb	4	3.11–3.17	3.13
Pd^{II}	3	3.38–3.50	3.45
Ag^{I}	4	2.89–3.37	3.19
In^{I}	3	2.83–2.95	2.89
Sn^{II}	9	2.45–3.58	3.18
Sb^{III}	24	2.96–3.34	3.21
Cs	49	3.10–3.57	3.34
Pt^{II}	3	3.55–3.59	3.56
Au$^{I,\ III}$	2	3.48–3.55	3.51
Hg^{II}	11	3.05–3.52	3.24
Tl^{I}	24	2.85–3.52	3.09
Pb^{II}	6	2.78–3.43	3.17
Bi^{III}	24	2.67–3.56	3.19

Trends in the lower curve in Figure 4 are periodic and consistent with the electronic nature of the metals involved. The upper curve, on the other hand, shows the anticipated progression within the alkali metal series, although a conspicuous discontinuity occurs at gallium, indium, and thallium. This evidence of a comparatively strong interaction in these cases is consistent with the anomalous solubility of monovalent group 13 salts in aromatic hydrocarbons. This phenomenon was examined in detail by Schmidbaur in the 1980s and rationalized in terms of a particularly effective overlap of the empty LUMO set of *p*-orbitals on the metal with the HOMO of the arene.[10]

Since the issue at hand is sandwich complexation in **1**, the dataset for longer-range contacts was also scrutinized for other occurrences of this mode of assembly. Twenty three examples of metals simultaneously coordinated to two or more aryl rings are found, most involving the alkali and group 13 metals, but in all but a few cases the *o*···*m*···*o* angle was considerably less than 180°. One notable exception was [Cs(*p*-xylene)$_2$]$^+$, with a mean *om* distance of 3.4 Å and $o\hat{m}o$ = 176.7°.[11] Also relevant here are the π-cation complexes between 1,3-alternate calix[4]arenes and metal ions, four examples of which meet the general search criteria set out in the present work, although again, $o\hat{m}o$ ranges from 138.8 to 159.8°.[12]

Finally, two examples of other purpose-designed, mixed π-heteroatom ligands also emerge in this search. In the first, a crown ether incorporates a single aromatic ring whose centroid is involved in longer-range bonding to either Tl^I (*om* = 2.96 Å)[13] or Ag^I (*om* = 2.89 Å).[14] The second involves a tripodal *tris*(pyrazoylmethyl)benzene ligand for ruthenium.[15]

Cylindrophane 1 and Complexes 2

As mentioned above, the utility of a receptor such as **1** derives from its Ar···Ar bisector distance, which coincides approximately with the second maximum of the histogram in Figure 2. This provides an opportunity to study metals residing in a trigonal planar heteroatom ligand field and their interactions with the apical benzene centroids. Although **1** was designed to possess a high degree of conformational stability, molecular dynamics simulations indicate an accordion-like flexibility along the axis which runs through the rings, which gives the ligand the potential to accommodate metals throughout a range of preferred *om* distances.[16]

Preorganization in cylindrophanes such as **1** is achieved through careful regard for the conformational preferences of chains which link aromatic rings together, and the structural arguments in the design of these molecules have been discussed in detail.[4] The synthesis of **1** was carried out as described[2] and the stable complexes [Ag(**1**)]BF$_4$ and [Cu(**1**)]BF$_4$ were prepared by simple mixing of **1** with the tetrafluoroborate salts of the respective metals. The ^{1}H-NMR spectra (CDCl$_3$) of the complexes indicated no loss of symmetry and gave evidence of a substantial interaction between the metals and the ligand by the marked shifts of the S–CH$_2$ signal (+0.6–0.7 ppm). Most interesting, however, was the downfield shift of the aromatic protons (+0.20 ppm in [Ag(**1**)]BF$_4$, 0.12 ppm in [Cu(**1**)]BF$_4$), supporting the view that the phenyl rings in [M(**1**)]$^+$ do not simply block the apical positions but actually coordinate to the metal center.

Final proof of the structure was gained by X-ray crystallography of the complexes. Because [Ag(**1**)]BF$_4$ and [Cu(**1**)]BF$_4$ are isostructural, only the latter is shown in Figure 5. Relevant angles and distances for each complex are presented in Table 3.[17] A mirror plane passes through the metal and the three sulfur atoms which surround it with molecular C_3 symmetry. While trigonal planar coordination is unusual for Ag^I and Cu^I,[18] the bis(η^6)-complexation of the metals presented here is unique. Even simple η^6-coordination is unprecedented in the case of Cu^I, although this species is known to participate in η^1-complexation to arenes,[19] which is also the preferred mode of interaction for Ag^I.[20]

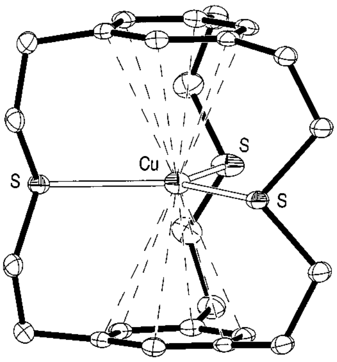


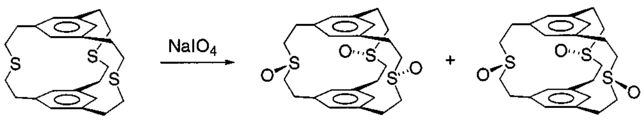
Figure 5. A view of the complex cation in the crystal structure of [Cu(**1**)]BF_4

Table 3. Selected geometric parameters for [Ag(**1**)]BF_4 and [Cu(**1**)]BF_4

	[Ag(**1**)]BF_4	[Cu(**1**)]BF_4
S–M, Å	2.577(2)	2.370(2)
	2.578(2)	2.380(3)
	2.631(2)	2.412(3)
S–M–S, °	117.72(5)	119.00(9)
	119.98(6)	119.91(9)
	122.31(5)	121.08(9)
M–centroid, Å	2.92	2.97
M–centroid–M, °	177.5	178.4

Cyclic voltammetry of [Cu(**1**)]BF_4 in MeCN/CH_2Cl_2 (1:1) gave a CV reminiscent of a metal deposition/stripping wave, with sharp oxidation and reduction peaks at E_{pa} = –0.61 V and E_{pc} = –0.87 V vs. Fc/Fc^+. When the solvent was switched to neat CH_2Cl_2, little if any current was measured up to the working limit of the platinum electrode. This result implied sufficient dissociation of the complex in the presence of acetonitrile to give a measurable concentration of electrochemically active, "free" Cu^I, whereas in the less-polar solvent system the cylindrophane effectively shields the metal and thus prevents redox activity. Analogous experiments with the silver complex had a similar outcome, with E_{pa} = –0.28 V and E_{pc} = –0.72 V and an irreversible anodic wave at 0.60 V vs Fc/Fc^+ in 1:1 MeCN/CH_2Cl_2.

Perhaps the most obvious modification of **1** is oxidation to the *tris*-sulfoxide. Modelling shows that in conformers where the three oxygens point into the cavity, the distance from these sites to the center of the trigonal plane they define is a convenient 2.3 Å, compared, for example, to 3.1 Å in the trioxa analog of **1**.[4] Thus, reaction of **1** with sodium periodate in aqueous THF provided the isomeric sulfoxides **3** (12%) and **4** (62%) (Scheme 1). Even after chromatography, both of these compounds showed substantial [M + Na]$^+$ peaks in the FAB mass spectra, attributed to the presence of Na^+ in the oxidation reaction. However, sulfoxide **3** showed no noteworthy changes in the ^1H NMR spectrum during titration with a range of metal ions (in CD_3OD), while the unsymmetric **4** interacted only weakly and non-specifically with Na^+, Ag^+, and Cu^+.



1 **3** **4**

Scheme 1. Synthesis of *tris*-sulfoxide cylindrophanes **3** and **4**

Attempts to crystallize **3** or **4** in the presence of $NaBF_4$ led in one instance to the observation of very small crystals (of **4**), the structure of which could be determined using synchrotron radiation, but which did not include the metal (Figure 6). As might have been predicted, the sulfur lone pairs occupy the cavity in preference to the oxygens, which renders the complexation of metals in the cavity less favorable, despite the potentially more appropriate heteroatom-metal distance. The Ar···Ar separation in **4** is 5.66 Å in the crystal, i.e. slightly closer than in the metal complexes of **1** (cf. Table 3).

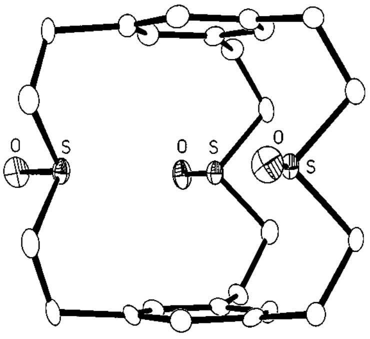


Figure 6. X-ray crystal structure of **4**

Conclusion

The encapsulation of metal ions in cylindrophane **1** provides a general approach to effective metal sandwich complexation in cases where longer (> 2.5 Å) aryl centroid–metal contacts are required. Two complexes, [Ag(**1**)]BF_4 and [Cu(**1**)]BF_4, have been prepared and characterized by NMR spectroscopy and X-ray crystallography. Together they constitute uncommon examples of Cu^I and Ag^I coordination in a trigonal-planar ligand field, a rare example of η^6-coordination to Ag^I, the first example of η^6-coordination to Cu^I, and, of course, the only examples of Cu^I and Ag^I sandwich complexes.[21] A detailed statistical analysis of metal-η^6 species in the solid state establishes a context for the study, and the population of metals in longer-range contact to the benzene ring supports the general characterization of such interactions as bonding. Although this means of association is energetically inferior to short-range η^6-complexation, this work nevertheless draws awareness to its availability as a noncovalent "design principle."

The metal–arene distances of ca. 3 Å in [Ag(**1**)]BF$_4$ and [Cu(**1**)]BF$_4$ invite speculation as to which other metals in Table 2 might give stable cylindrophane complexes, or indeed whether the lanthanides in Table 1, with metal–arene distances as great as 2.7 Å, might, as trivalent ions, complete their valence shell with the 18 electrons present in **1**. Basic modifications to the cylindrophane framework also suggest themselves, among them the use of phosphorus as the equatorial heteroatom, the transformation of which into the corresponding phosphane oxide would force the three O sites into the cavity between the rings (in preference certainly to any alkyl/aryl group on P). Work along these lines continues.

Experimental Section

[Ag(1)]BF$_4$: To a solution of the ligand **1** (51 mg, 0.12 mmol) in CH$_2$Cl$_2$ (5 mL) was added AgBF$_4$ (24 mg, 0.12 mmol) and the solution was stirred in the dark for 24 h. The solvent was evaporated and the residue dissolved in acetonitrile, preabsorbed onto silica and chromatographed (10% MeOH/CHCl$_3$) to give a white solid (48 mg, 64%), m.p. 270 °C (dec). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.95 (t, 12 H), 3.24 (m, 12 H), 6.93 (s, 6 H). – ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 34.0, 37.6, 127.4, 141.0; – MS (FAB): *m/z* 521 (23) [M^+]; elemental analysis calcd for C$_{24}$H$_{30}$S$_3$AgBF$_4$: C, 47.31, H, 4.96; found: C, 47.36, H, 4.90.

[Cu(1)]BF$_4$: To a solution of the ligand **1** (37 mg, 0.089 mmol) in a mixture of CH$_2$Cl$_2$ (1.5 mL) and MeCN (0.5 mL) was added [Cu(MeCN)$_4$]BF$_4$ (28 mg, 0.089 mmol) and the solution was stirred overnight. The solvent was evaporated and the residue chromatographed (5% MeOH/CHCl$_3$) to give a white solid (41 mg, 82%), m.p. 240 °C (dec). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.90 (t, 12 H), 3.16 (br s, 12 H), 6.85 (s, 6 H). – ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 33.4, 36.7, 126.3, 140.8. – HRMS (ES-TOF): *m/z* calcd. for C$_{24}$H$_{30}$S$_3$Cu: 477.0806; found 477.0780 (M^+).

***Tris*-sulfoxides 3 and 4:** To a solution of the sulfide **1** (274 mg, 0.661 mmol) in a mixture of THF (30 mL) and water (2 mL) was added sodium periodate (0.465 g, 2.17 mmol). The reaction was stirred for 12 h, filtered and the solvent evaporated. The residue was dissolved in methanol, preabsorbed onto silica gel, and chromatographed (12% MeOH/CHCl$_3$) to give **3** (37 mg, 12%) and **4** (190 mg, 62%), both as a white solids.

3: m.p. 300 °C (dec.). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.59–2.71 (m, 6 H), 2.92–3.15 (m, 18 H), 6.88 (s, 6 H). – ^{13}C NMR (67.8 MHz, CDCl$_3$): δ = 29.2, 55.7, 128.1, 139.4. – HRMS (FAB): *m/z* calcd. for C$_{24}$H$_{31}$S$_3$O$_3$: 463.1435; found: 463.1437 (M^+ + H).

4: m.p. 280 °C (dec.). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.47–2.63 (m, 7 H), 2.83–3.09 (m, 19 H), 6.73 (s, 2 H), 6.86 (s, 2 H), 7.02 (s, 2 H). – ^{13}C NMR (67.8 MHz, CDCl$_3$) δ = 28.2, 29.1, 54.1, 55.2, 55.4, 126.0, 127.9, 129.3, 139.7, 139.9, 140.5. – HRMS (FAB): *m/z* calcd. for C$_{24}$H$_{31}$S$_3$O$_3$ 463.1435; found: 463.1432 (M^+ + H).

Cyclic Voltammetry of [Ag(1)]BF$_4$ and [Cu(1)]BF$_4$: Cyclic voltammograms (CVs), 100 mV s^{-1}, were recorded at 22±2°C in the solvent indicated using an EG & G Princeton Applied Research (PAR) Model 173 potentiostat. The supporting electrolyte was tetraethylammonium tetrafluoroborate (0.2 M). A three-compartment electrochemical cell was employed using nitrogen-purged solutions, with a platinum wire working electrode, a platinum-mesh counter electrode, and a sodium chloride saturated calomel reference electrode. The platinum wire working electrode was pre-treated before measurements by anodisation, then cathodisation, (1 min each at 100 mA in 1 M sulfuric acid) followed by washing with deionised water, then acetonitrile and finally air dried.

Crystal Data for 4: Colorless needle from methanol, C$_{24}$H$_{30}$O$_3$S$_3$, M = 462.7, monoclinic, a = 8.891(2), b = 14.763(3), c = 17.928(4) Å, β = 100.695(6)°, U = 2312.3(9) Å^3, T = 150(2) K, space group $P2_1/c$ (no. 14), Z = 4, μ(Mo-$K\alpha$) = 0.344 mm^{-1}, 15450 reflections measured of which the 4904 unique to 2$\theta_{\max}$ 52° (R_{int} = 0.088) were used in all calculations. The final $wR(F^2)$ was 0.328, R_1 = 0.116. Data were collected on the Bruker SMART CCD area detector diffractometer on Station 9.8 at CLRC Daresbury Laboratory, using synchrotron radiation with a wavelength of 0.6917 Å. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132651. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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[1] With the apparent exception of Tc and Pd; scandium(0) η^6-complexes have been prepared (see F. G. N. Cloke, *Chem. Soc. Rev.* **1993**, *22*, 17–24), but do not appear in the present study since no X-ray crystal structures have been published.

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[3] The term "macrobicycle" as applied here is used as an analogy to cryptand macrobicycles with aromatic rings counted as bridgeheads, and is not intended to be a formal description of the ring system.

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