5,12-Methano[2.2.2]paracyclophane: A New Ligand for π-Complexation in a Cavity. Improved Synthesis and the Characterization of Its Silver(I) Perchlorate Complex[†,1]

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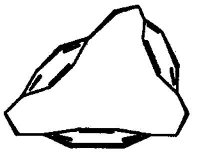
The consequences of a bridging methylene group in 1, i.e. as in 2, on the geometry and ability to complex Ag(I) were studied. Compound 2 was prepared in three steps and 36% overall yield from 1 in a new procedure and characterized through X-ray crystallography. The X-ray crystal structure of its endo complex (3) with $AgClO_4$ shows three independent molecules in the crystal lattice. The geometry of the ligand in 3 is like that in 2. Ag is 2.48–3.00 Å from the nearest Ar-C, is 0.13–0.31 Å outside of the cavity of 2, and binds nearly symmetrically across the C(5)–C(6), C(11)–C(12), and C(23)–C(24) bonds. Compound 2 is shown to be a weaker complexing agent for Ag(I) than [2.2.2]-paracyclophane. Practical and theoretical ramifications of the bonding mode are discussed.

It is known that small metal cations can combine with aromatic hydrocarbons to form π-complexes.[2,3] This complexation is especially effective for [2.2.2]paracyclophane, 1, and related structures[4] that possess π-electron-rich cavities. Cyclophane 1 not only forms endohedral complexes with soft metals, but also can form exohedral complexes of varying metal–ligand stoichiometry with chromium(0),[5] arsenic(III),[6] antimony(III),[6] and bismuth(III).[6] In the endohedral complexes of 1, the exact location of the metal atom in relation to the "π-prismand" cavity depends on its coordination number and the size of the cation: silver(I)[4,7] coordinates $3 \times \eta^2$ and is symmetrically bound 0.23–0.24 Å outside the cavity, while gallium(I),[8] tin(II),[9] and germanium(II)[9] complex in the $3 \times \eta^6$ mode, well within the cavity.



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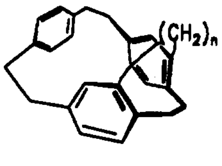

2, n = 1

We are interested in modifying the shape and size of the cavity of 1 and related structures and the stability of the resulting metal complexes. From molecular models, it is apparent that the effects of introducing a second bridge between adjacent aromatic rings, as in 2, may involve constricting or expanding the associated side of the cavity, in either case resulting in a shape like a funnel, having two opposing entrances of unequal size at which endohedral complexation could occur. Here we report the first member of this series, 5,12-methano[2.2.2]paracyclophane (2, $n = 1$) and the characterization of its complex 3 with silver(I) perchlorate. Hydrocarbon 2 has been synthesized previously by Tabushi.[10,11] However, since the reported synthesis was not suitable for the preparation of the amounts required for this study, we developed the route described below.

Ligand Synthesis. Friedel–Crafts reaction of 1 with oxalyl chloride at 0 °C afforded the bridged ketone 4 in 65% yield. Treatment of 4 with excess[12] 1,3-propanedithiol and boron trifluoride etherate gave dithioketal 5, which was smoothly reduced with Raney nickel under Mozingo conditions[13] to provide 2 in 36% overall yield from 1 (Scheme I).

Ligand Crystal Structure. Insight into the geometry of 2 was provided through its X-ray crystallographic structure[14] (Figure 1). Two independent molecules of 2 having virtually identical geometries occur per asymmetric unit; average values are cited below. Introduction of the methylene bridge into 1 changes its geometry. The dihedral angle between the mean planes of the doubly bridged aromatic rings is increased from the ideal 60° found in 1[15] to 96.5°, and their centers are separated by 4.45 Å. The dihedral angles between the first (C(3)–C(8)) and third (C(19)–C(24)) and between the second and third aromatic rings are correspondingly reduced to 43.8° and 45.0°. The geometry of 2 also forces C(4) and C(13) to within 3.74 and 3.77 Å of C(21) and C(20), respectively. The two doubly bridged aromatic rings are planar to within 0.015 Å.

[†] Metallocenophanes, Part VI. Part V: Hopf, H.; Dannheim, J. *Angew Chem. Int. Ed. Engl.* **1988**, *27*, 701.

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[13] Mozingo, R.; Wolf, D. E.; Harris, S. A.; Folkers, K. J. *J. Am. Chem. Soc.* **1946**, *65*, 347.

[14] X-ray measurements: measurements were performed at −95 °C on a Siemens R3 diffractometer using monochromated Mo Kα radiation and ω-scans. The structures were solved by direct methods and refined anisotropically on *F*. H atoms were included using a riding model. Crystal data for 2: $C_{25}H_{24}$, FW = 324.2, space group $P2_12_12_1$, $a = 10.419(5)$, $b = 10.392(4)$, $c = 32.980(15)$ Å, $Z = 8$, $D_{calc} = 1.207$ g cm^{-3}, $6 < 2\theta < 52°$, $R = 0.0434$ for 5391 unique reflections with $F > 4\sigma(F)$.

[15] Cohen-Addad, C.; Baret, P.; Chautemps, P.; Pierre, J.-L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1983**, *C39*, 1346.

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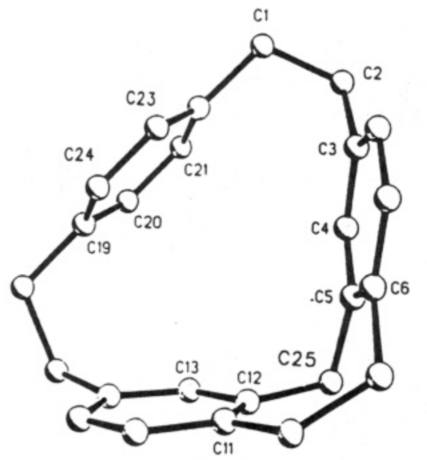
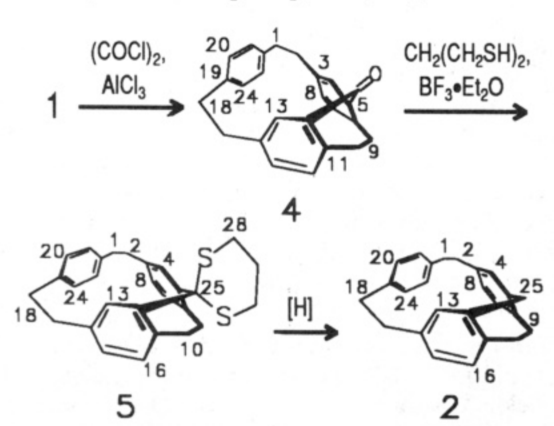


Figure 1. Crystal structure of 2. Hydrogen atoms are not shown.

Scheme I. Synthesis of 5,12-Methano[2.2.2]paracyclophane



Preparation and Characterization of Silver Perchlorate Complex. Slow recrystallization from dichloromethane–hexane of the solid obtained from evaporation of a solution of **2** and 1 equiv of silver perchlorate dichloromethane–toluene yielded **3**, an air- and light-stable solid of mp = 191–193 °C (this is coincidentally 6 °C within that of **2**). The ^{1}H-NMR spectrum of **3** showed downfield shifting of all signals from **2**, especially those from the aromatic protons (see Table I).

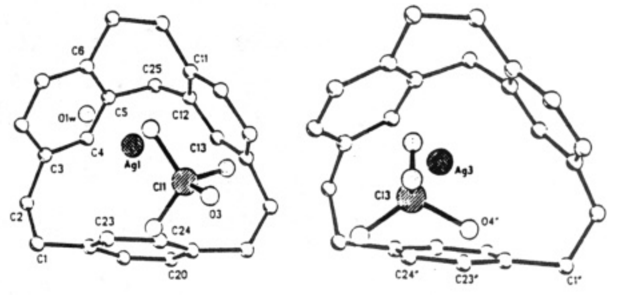
Table I. ^{1}H-NMR Chemical Shifts of Silver Complex 3 and Magnitudes of Shifting Relative to Ligand 2[a]

	H-4, H-13	H-7, H-16	H-8, H-15	H-20, H-21	H-23, H-24
δ_3	6.54	7.38	7.17	7.47	6.35
$\Delta\delta$, ppm	0.42	0.48	0.27	0.54	0.92

[a] Spectrum recorded from ca. 0.10 M solution in $CDCl_3$ at 200 MHz; shifts are relative to TMS.

The ^{1}H-NMR spectra of solutions of **2** containing less than 1.0 equiv of $AgClO_4$ exhibited resonances between those of **2** and **3**. Although 5-fold dilution of a 0.11 M solution of **3** caused a ca. 15-Hz upfield shifting of the signals of 4-H and 13-H (measurement frequency: 200 MHz), this magnitude is too small to have arisen from a rapid exchange[16] in the equilibrium described in eq 1, in contrast to the case of some other efficient silver ligands.[17] As a relative measure of its affinity for silver(I), the ^{1}H-NMR spectrum of **3** in the presence of 1 equiv of **1** was also recorded in $CDCl_3$. No downfield shifting of the absorptions of **2** was observed; the only silver(I) complex which could be detected was that of **1**.

$$\mathbf{2} + AgClO_4 \rightleftharpoons \mathbf{3} \qquad (1)$$



3a

3c

Figure 2. Structures of **3a** and **3c**. See Table II for bonding parameters. Hydrogen atoms are omitted for clarity.

Crystal Structure of Complex. An X-ray crystallographic analysis of **3**[18] was undertaken to determine the site of complexation and thereby gain insight into the influence of the geometry of **2** on the strength of its complexing abilities (see Figure 2). Three independent molecules of **3** occur per asymmetric unit: **3a–c**. In one of them, **3a**, the bonding of perchlorate to silver is replaced by the contact with a molecule of water, which in turn hydrogen bonds to perchlorate. In **3b** and **3c**, there is direct contact between silver and perchlorate. Complexation of Ag to the ligand in **3a–c** occurs on the C(5)–C(6), C(11)–C(12), and C(23)–C(24) bonds (Table II), although the corresponding Ag–C distances are not much less than those involving C(7) and C(16). The silver atom in **3c** is 0.13 Å outside the plane passing through the centers of the C(7)–C(8), C(15)–C(16), and C(20)–C(21) bonds; this distance in **3a** is 0.31 Å and 0.23 Å in **3b**. The ligand geometries of **3a** and **3b** are very similar. The dihedral angle between the planes of the aromatic rings which are attached to the methylene group in **3a** and **3b** is 87.1° (average value) and is 98.5° in **3c**. Ligand bond lengths in **3a–c** agree to within 0.03 Å with each other and with **2**.

Discussion

The synthesis of gram quantities of **2** rests on the outcome of the reaction of **1** with oxalyl chloride. The intramolecular Friedel–Crafts reactivity of the presumed[19] intermediate 4′-formyl[2.2.2]paracyclophanyl chloride (**6**) (Scheme II) is however, not surprising, since similar reactivity among other strongly electrophillic [2.2.2]paracyclophanyl systems is also known.[1,10]

The methylene bridge of **2** deforms the [2.2.2]paracyclophanyl cavity, changing the form of the juxtaposition of the planes of the aromatic nuclei from an equilateral triangle to a roughly isoceles triangle having a right angle

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[16] Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: New York, 1983; p 208.

[17] Gano, J. E.; Subramaniam, G.; Birnbaum, R. *J. Org. Chem.* **1990**, *55*, 4760.

[18] X-ray measurements for **3**: see ref 14. Crystal data: $C_{25}H_{24.667}$-$AgClO_{4.333}$, FW = 537.1, space group $P2_1/c$, $a = 9.731(4)$, $b = 35.020(12)$, $c = 19.018(7)$ Å, $\beta = 98.68(3)°$, $Z = 12$, $D_{calc} = 1.670$ g cm^{-3}, $6 < 2\theta < 50°$, $R = 0.0726$ for 8660 unique absorption-corrected reflections with $F > 4\sigma(F)$.

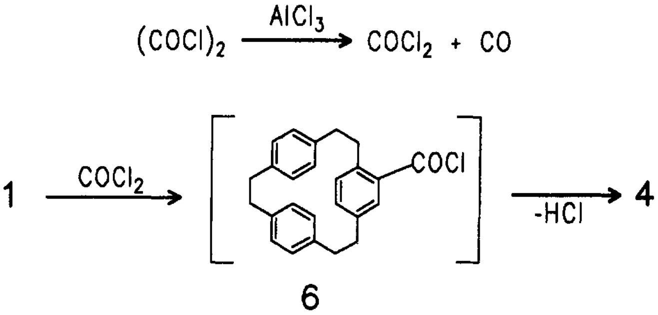
[19] Norbert, M. E.; Fishel, D. L. *Org. Synth.* **1983**, *61*, 8.

Table II. Closest Silver Contacts in 3[a]

	C(5)	C(6)	C(7)	C(11)	C(12)	C(16)	C(23)	C(24)	Ag–O
3a	3.00	2.98	3.18	2.63	2.89	2.72	2.51	2.55	2.30[b]
3b	2.84	2.76	2.95	2.59	2.83	2.84	2.49	2.59	2.43[c]
3c	2.74	2.72	3.04	2.71	2.79	3.03	2.48	2.49	2.39[c]

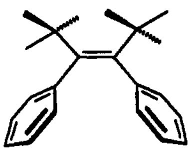
[a] Distances accurate to ±0.01 Å. [b] Oxygen of water. [c] Oxygen of perchlorate.

Scheme II. Proposed Mechanism for Formation of 5,12-Methano[2.2.2]paracyclophan-25-one



between the planes of the 2-fold bridged aromatic rings. The conformations of **2** and **3** are very similar; minor differences can be accounted for by the accommodation of the metal cation along the side of the cavity. All of the shortest silver–carbon distances for **3a–c** are within the limits seen in classical silver–aromatic complexes[3,20] and the silver(I) complexes[4,15] of **1**. Mildly exceptional in this regard is **3a**, for which the distances to C(5)–C(7) and C(12) are ca. 0.1–0.2 Å greater than those in **3b** and **3c**. This, as well as the lopsided fit of silver into, and its greater displacement from, the cavity might be ascribed to the insertion of water into its bond with perchlorate.[4,17] Correspondingly, oxygen is ca. 0.1 Å closer to Ag in **3a** than in **3b** or **3c**. In **3c**, Ag is almost perfectly symmetrically bound on the plane bisecting the methylene bridge and is 0.18 Å closer to the cavity than in **3a**. The slight difference between the complexation geometries of **3b** and **3c** (see Table II) may be caused by crystal packing forces. Since the carbon atoms of **2** which are adjacent to the sites binding Ag also exhibit the greatest relative downfield shifting of their ^{1}H-NMR spectroscopic shifts (Table I), it stands to reason that the complexation geometry in the solid state must also predominate in solution.

The bonding pattern of **3** parallels that found in the silver(I) complexes of **1**, i.e. that the silver cation is centered between adjacent aromatic carbons and not localized around a single one. This bonding mode has been rationalized in terms of back-bonding from filled metal d-orbitals.[20] The competition experiment and the mildly concentration-dependent ^{1}H-NMR spectra of **3** both indicate that the silver(I) complexes of **1**[4,15] are significantly more stable than those of **2** (the insolubility of **2** and **3** in solvents in which silver(I) salts are adequately soluble prevents the determination of the stability constant of **3** under Benesi–Hildebrand conditions[21]). The stability of the Ag(I) complex of **2** is thus comparable to those of π-prismand type ligands showing a significant amount of localized silver–carbon bonding character, e.g. (*Z*)-2,2,5,5-tetramethyl-3,4-diphenylhex-3-ene (**7**)[17] or deltaphane (**8**)[4]. Hence, any stabilization of π-prismand complexes through this back-bonding must be subordinate to geometrical or steric[3] factors.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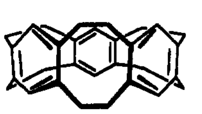
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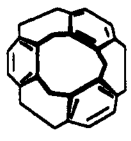
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An intriguing consequence of the metal bonding mode in **3** nonetheless is that although Ag is situated *outside* the cyclophane cavity, it binds to sites *within* it. The question of whether, either through elongation of the methylene bridge or through introduction of further bridges spanning the remaining aromatic nuclei of **1**, such as in **9**, silver would occupy a site *within* the cyclophane cavity is under investigation in our laboratory.[22]

Experimental Section

5,12-Methano[2.2.2]paracyclophan-25-one. To a stirred suspension of 4.0 g (30 mmol) of aluminum trichloride and 2.8 mL (32 mmol) of oxalyl chloride in 125 mL dichloromethane at 0 °C under nitrogen was added 5.0 g (16 mmol) of [2.2.2]paracyclophane in 300 mL of dichloromethane over 1 h. The rate of addition was controlled such that the temperature of the reaction mixture did not exceed 0 °C. The mixture was stirred an additional 15 min and quenched with 15 mL of ethanol. The reaction mixture was washed successively with 2 N hydrochloric acid, saturated aqueous sodium bicarbonate, and brine and dried with magnesium sulfate. Removal of the solvent from the crude product, followed by column chromatography (silica gel, dichloromethane) gave 3.54 g (10.5 mmol; 65%) of **4**: mp = 207–8 °C (lit.[10] 215 °C); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ = 31.40, 35.91, 37.48 (CH_2; C-1, C-2, C-9, C-10, C-17, C-18), 127.77, 127.97, 128.30, 129.94 (CH; C-4, C-7, C-8, C-13, C-15, C-16, C-20, C-21, C-23, C-24), 133.15, 136.98, 139.24, 143.27 (C; C-3, C-5, C-6, C-11, C-12, C-14, C-19, C-22), 205.80 (C, C-25).

5,12-Methano[2.2.2]paracyclophane. To a stirred mixture of 2.0 g (5.9 mmol) of **4** and 1.78 mL (17.7 mmol) of 1,3-propanedithiol in 20 mL of anhydrous chloroform at −5 °C under nitrogen was added 2.20 mL (17.9 mmol) of boron trifluoride etherate. The mixture was stirred at rt for 65 h, at which time it was quenched with water. The organic phase was separated and washed successively with 2 N sodium hydroxide, water, and brine and dried with magnesium sulfate. Removal of the solvent left 2.4 g (5.6 mmol) of crude dithioketal **5**, slightly contaminated with **4**, which was directly treated with 15 g of freshly prepared Raney nickel W2 in 100 mL of boiling ethanol under reflux for 3 h. After filtration of the reaction mixture from solids and removal of the solvent under reduced pressure, column chromatography (dichloromethane) gave 1.07 g (3.30 mmol, 56% from **4**) of **2** in the first fraction; mp = 185–187 °C (lit.[11] 189.5–190.5 °C); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 30.44, 36.59, 37.50 (CH_2, C-1, C-2, C-9, C-10, C-17, C-18), 39.97 (CH_2, C-25), 125.40, 127.44, 128.31, 129.14, 129.66, 129.98 (CH, C-4, C-7, C-8, C-13, C-15, C-16, C-20, C-21, C-23, C-24), 133.47, 137.15, 138.47, 141.66 (C, C-3, C-5, C-6, C-11, C-12, C-14, C-19, C-22). In a separate experiment, 0.50 g (1.5 mmol) of **4** was reacted under identical

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[20] Taylor, I. F., Jr.; Hall, E. A.; Amma, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 5745.

[21] Foster, R. *Molecular Complexes*; Crane, Russak and Co.: New York, 1972, Vol. 2, pp 107–172.

[22] The author has deposited atomic coordinates for **2** and **3** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

conditions. The crude **5** was purified by preparative TLC (dichloromethane) to give 0.44 g (1.0 mmol; 69%) of **5** and 0.08 g (0.24 mmol; 16%) of **4**. For **5**: mp = 201–4 °C; IR (KBr) ν = 1440 cm^{-1} (s), 815 (vs), 620 (s); EI-MS (70 eV) *m/z* (rel %) = 420 ($M^{+\bullet}$, 60), 354 (60), 321 (100); elemental analyses for C, H, and S within acceptable limits.

5,12-Methano[2.2.2]paracyclophane Silver Perchlorate. A solution of 32.4 mg (99.5 μmol) of **2** in anhydrous dichloromethane was mixed with a solution of 26 mg (130 μmol) silver perchlorate in anhydrous toluene. After removal of the solvent under reduced pressure, the residual solid was dissolved in dichloromethane, filtered through Celite, and recrystallized by slow evaporation from a dichloromethane–hexane solution: FAB-MS (NBA) *m/z* (%) = 431 (100), 432 (33), 433 (91), 434 (25), 435 (3) ($C_{25}H_{25}Ag^+$); IR (KBr) ν = 3033 cm^{-1} (w), 2855 (m), 1502 (m), 1493 (m), 1441 (m), 1419 (m), 1107 (vs), 1044 (s), 813 (s), 624 (s). Anal. Calcd for $C_{25}H_{24}AgClO_4\cdot{}^1/_3H_2O$: C 55.73, H 4.80. Found: C 55.52, H 4.76.

Competition Experiment. A solution of 21.1 mg (65.1 μmol) of **2** and 23 mg (110 μmol) of silver perchlorate was prepared in anhydrous THF. After removal of the solvent under reduced pressure and drying at 0.1 mbar, the residual solid was dissolved in $CDCl_3$, filtered through Celite to remove excess silver salt, and diluted to 1.0 mL. To this solution of **3** was added 20.3 mg (65.0 μmol) of **1**, and the ^{1}H-NMR spectrum of the solution was measured at 400 MHz after ca. 2 h at room temperature.

Acknowledgment. We thank Merck (Darmstadt) for their generous gift of [2.2.2]paracyclophane, the Deutsche Forschungsgemeinschaft for a research stipendium for F.R.H., and the Fonds der Chemischen Industrie for financial support. We are also grateful to Dr. H. M. Schiebel (MS), Prof. L. Ernst (NMR), and Mr. A. Weinkauf (X-ray) for technical advice. The X-ray program system "Siemens SHELXTL PLUS" was used.

Supplementary Material Available: Spectral characterization of **3** and **5** (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.