

η^1 - and η^2 -benzene coordination in $[\text{Ag}(\text{C}_6\text{D}_6)_3\text{BF}_4]^1$ Andrei S. Batsanov, Simon P. Crabtree, Judith A.K. Howard, Christian W. Lehmann,
Melvyn Kilner **Department of Chemistry, University of Durham, Durham, DH1 3LE, UK*

Received 16 December 1996

Abstract

The title complex with one η^2 and two η^1 deuterobenzene and one monodentate BF_4 ligands was isolated as a by-product in the reaction between $[(\text{dppe})\text{RhCl}]_2$ and EtCl in C_6D_6 , in the presence of AgBF_4 and its X-ray crystal structure determined. © 1998 Elsevier Science S.A.

Keywords: Silver; Deuterobenzene π -coordination; Crystal structure

1. Introduction

The complexes of silver(I) with one [1] or two [2,3] π -coordinated benzene ligands have been known for a long time, but η -coordination of $\text{Ag}(\text{I})$ with *three* benzene rings simultaneously has never been observed before, unless the rings were incorporated into a cyclophane macrocycle [4–8]. Herein we report the single-crystal X-ray structural characterisation of the first “un-supported” tris-benzene silver complex, $[(\text{C}_6\text{D}_6)_3\text{-Ag}(\text{BF}_4)]$ (**1**), which was obtained by serendipity in an attempted reaction of $[(\text{dppe})\text{RhCl}]_2$ (**2**) [9] with EtCl in deuterobenzene, AgBF_4 being added to facilitate the elimination of chloride ion.

2. Results and discussion

2 (50 mg) was placed in an NMR tube equipped with a Young’s cap; C_6D_6 (0.75 ml) was added by vacuum distillation. The sample was freeze-thaw degassed and EtCl was introduced as a gas to 1 atm, and the tube was sealed. No reaction occurred, even on heating to 60°C . AgBF_4 (excess) was added to the mixture under nitrogen. The reaction quickly changed colour from orange to deep red to colourless. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum

of the resulting colourless solution (δ 71.7 ppm, br d, $^1J_{\text{Rh-P}}$ 170 Hz) was indicative of a single (unidentified) rhodium complex, distinct from **2** (δ 73.2 ppm, $^1J_{\text{Rh-P}}$ 198 Hz) [9]. Large rectangular colourless crystals of **1**, formed on slow evaporation of the solvent, are stable if stored under the mother liquor, but out of solution they decompose instantly losing C_6D_6 even in an inert atmosphere. It is noteworthy that the crystals dissolve readily in the perfluoropolyether oil used to exclude air during the X-ray experiment.

The crystal structure of **1** is built of discrete molecules (Fig. 1, Table 1). The silver atom coordinates one deuterobenzene ring in a η^2 and two others in η^1 fashion. The benzene rings (i, ii and iii, see the figure) are essentially planar and form dihedral angles i/ii 49.5° , i/iii 92.4° and ii/iii 51.7° . The $\text{Ag}-\text{C}$ bonds are not exactly perpendicular to the ring planes, but tilted outward (i.e. towards the deuterium atoms) by 7° (i), 7° (ii) and 9° (iii). Thermal ellipsoids of the carbon atoms indicate either a very substantial in-plane libration of the ring or (more likely at low temperature) a static disorder; therefore the $\text{C}-\text{C}$ bond distances are of too low accuracy to give insight into the bonding pattern.

The tetrafluoroborate moiety is coordinated via a single fluorine atom and the rest of the moiety is disordered between two orientations (A and B) with approximately equal occupancies. The overall environment of the Ag atom is trigonal-bipyramidal (with one apical position occupied by F(1) and the opposite one void) rather than tetrahedral. The envelopment of the

* Corresponding author.

¹ Dedicated to Professor Ken Wade on the occasion of his 65th birthday.

Ag atom by the benzene ligands in **1** is in striking contrast to the [2.2.2]paracyclophane [4–8] and deltaphane [5] complexes, where the silver atom does not enter the molecular cavity.

The mode of silver(I)–benzene coordination has long been a matter of theoretical [10,11] and experimental [1–8] inquiry. If the silver atom acts purely as an electron acceptor, its most favourable position would be in the direction of the filled $p\pi$ orbital of the carbon atom (η^1 coordination). If back donation from Ag d orbitals into the π^* orbital of the aromatic ring is significant, then the best overlap is achieved with the silver atom equidistant between two ring carbons (η^2 coordination). The latter coordination was predicted theoretically [10,11], while both were observed in X-ray crystal structures. Apparently, the energy difference between the two types of bonding is rather small, as minor differences in the nature of aromatic and/or acido ligands or even in crystal packing can tilt the balance, e.g. between tris- η^2 [4–6] and tris- η^1 [5] coordination in cyclophane complexes. The coexistence of both types of coordination of the *same* silver atom in **1** and in $\{\eta^1\text{-Ph}(\text{Bu}')\text{C}=\text{C}(\text{Bu}')\text{Ph-}\eta^2\}\text{Ag}(\text{O}_3\text{SCF}_3)$ (**3**) [12] confirms this conclusion.

In **1**, the Ag–C distances are shorter for the η^1 than for η^2 ligands (average 2.48(1) vs. 2.53(1) Å, respectively). A similar effect has been observed in [2.2.2]cyclophane complexes with tris(η^2 -benzene)AgX coordination (X = monodentate ClO_4 , O_3SCF_3 , SbF_6) [4–8] where the *average* Ag–C distance vary from 2.53 to 2.60 Å, compared to 2.43 Å in (deltaphane)AgOSO₂CF₃ with tris(η^1 -benzene) coordination. However, in **3** the Ag–C(η^2 -phenyl) (2.510(5) and 2.583(5) Å) and Ag–C(η^1 -phenyl) (2.579(4) Å) distances are comparable. Apparently, the relatively weak

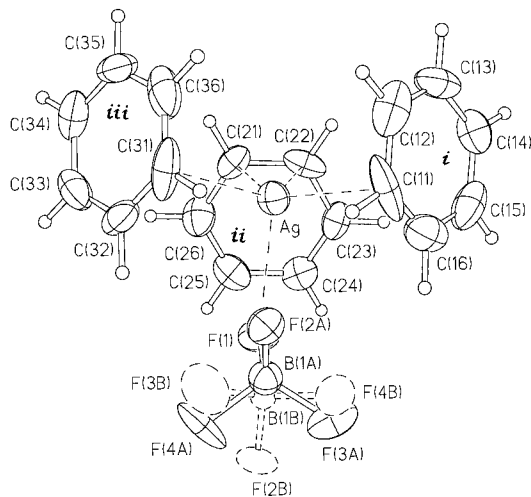


Fig. 1. Molecular structure of **1**, showing 50% probability ellipsoids and the two positions A (solid) and B (dashed) of the disordered BF_4 moiety.

Table 1
Bond distances (Å) and angles (°) in molecule **1**

Ag–C(11)	2.480(14)	Ag–C(31)	2.487(13)
Ag–F(1)	2.488(8)	Ag–C(22)	2.525(12)
Ag–C(21)	2.536(12)	C(11)–C(16)	1.32(3)
C(11)–C(12)	1.37(3)	C(12)–C(13)	1.37(2)
C(13)–C(14)	1.36(2)	C(14)–C(15)	1.36(3)
C(15)–C(16)	1.37(2)	C(21)–C(26)	1.36(2)
C(21)–C(22)	1.39(2)	C(22)–C(23)	1.38(2)
C(23)–C(24)	1.36(2)	C(24)–C(25)	1.38(2)
C(25)–C(26)	1.38(2)	C(31)–C(36)	1.34(2)
C(31)–C(32)	1.36(3)	C(32)–C(33)	1.37(2)
C(33)–C(34)	1.37(2)	C(34)–C(35)	1.35(2)
C(35)–C(36)	1.37(2)	F(1)–B(1B)	1.42(3)
F(1)–B(1A)	1.44(3)	B(1A)–F(2A)	1.38(2)
B(1A)–F(3A)	1.38(2)	B(1A)–F(4A)	1.38(2)
B(1B)–F(3B)	1.36(2)	B(1B)–F(2B)	1.36(2)
B(1B)–F(4B)	1.38(2)		
C(11)–Ag–C(31)	100.4(6)	C(11)–Ag–F(1)	99.4(6)
C(31)–Ag–F(1)	97.6(5)	C(11)–Ag–X ^a	126.5(4)
C(31)–Ag–X ^a	122.0(4)	F(1)–Ag–X ^a	105.0(4)
C(16)–C(11)–C(12)	120(1)	C(16)–C(11)–Ag	94(1)
C(12)–C(11)–Ag	94(1)	C(13)–C(12)–C(11)	119(2)
C(14)–C(13)–C(12)	121(2)	C(15)–C(14)–C(13)	120(1)
C(14)–C(15)–C(16)	118(2)	C(11)–C(16)–C(15)	123(2)
C(26)–C(21)–C(22)	120(1)	C(26)–C(21)–Ag	104.2(8)
C(22)–C(21)–Ag	73.6(7)	C(23)–C(22)–C(21)	119(1)
C(23)–C(22)–Ag	103.4(8)	C(21)–C(22)–Ag	74.5(7)
C(24)–C(23)–C(22)	121(1)	C(23)–C(24)–C(25)	119.5(13)
C(24)–C(25)–C(26)	120(1)	C(21)–C(26)–C(25)	121(1)
C(36)–C(31)–C(32)	121(2)	C(36)–C(31)–Ag	96.4(9)
C(32)–C(31)–Ag	92.3(11)	C(31)–C(32)–C(33)	120(2)
C(32)–C(33)–C(34)	119(2)	C(35)–C(34)–C(33)	119(1)
C(34)–C(35)–C(36)	122(2)	C(31)–C(36)–C(35)	119(2)
B(1B)–F(1)–Ag	132(1)	B(1A)–F(1)–Ag	114.5(9)
F(2A)–B(1A)–F(3A)	113(2)	F(2A)–B(1A)–F(4A)	112(2)
F(3A)–B(1A)–F(4A)	112(3)	F(2A)–B(1A)–F(1)	108(2)
F(3A)–B(1A)–F(1)	107(2)	F(4A)–B(1A)–F(1)	105(2)
F(3B)–B(1B)–F(2B)	112(2)	F(3B)–B(1B)–F(4B)	111(3)
F(2B)–B(1B)–F(4B)	108(2)	F(3B)–B(1B)–F(1)	109(2)
F(2B)–B(1B)–F(1)	108(2)	F(4B)–B(1B)–F(1)	108(2)

^aX is the midpoint of the C(21)–C(22) bond.

silver–arene bonding can be easily distorted by steric effects of rigid polyarene ligands.

3. Experimental section

The X-ray diffraction experiment was carried out at $T = 150$ K on a Siemens 3-circle diffractometer with a CCD area detector, using graphite-monochromated $\text{Mo-K}\alpha$ radiation, $\lambda = 0.71073$ Å. *Crystal data:* $\text{C}_{18}\text{D}_{18}\text{AgBF}_4$, $M = 447.1$, orthorhombic, space group $\text{Pca}2_1$ (No. 29), $a = 16.549(1)$, $b = 8.373(1)$, $c = 12.498(1)$ Å, $V = 1731.8(3)$ Å³ (from 512 setting reflections with $10 < \theta < 23^\circ$), $Z = 4$, $D_c = 1.71$ g cm⁻³, $F(000) = 856$, $\mu = 12.0$ cm⁻¹, crystal size $0.2 \times 0.1 \times 0.1$ mm. 7155 data with $2\theta \leq 51.5^\circ$ were collected in ω scan mode (0.3° steps); of these 2248 data were unique ($R_{\text{int}} = 0.077$) and 1609 ‘‘observed’’ with $I \geq 2\sigma(I)$.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) in **1**

	x	y	z	U_{eq}^a
Ag	1214.9(4)	2536.9(9)	2487(3)	36.9(2)
C(11)	2513(11)	3168(15)	3386(20)	72(5)
C(12)	2152(8)	3973(20)	4217(16)	63(5)
C(13)	2096(8)	5608(19)	4158(14)	55(4)
C(14)	2384(9)	6413(14)	3288(14)	47(3)
C(15)	2739(7)	5597(19)	2473(20)	63(4)
C(16)	2802(7)	3971(21)	2562(21)	63(4)
C(21)	-75(7)	3853(15)	1835(11)	42(3)
C(22)	514(8)	5042(16)	1852(11)	45(4)
C(23)	917(6)	5413(13)	917(14)	44(3)
C(24)	736(7)	4655(15)	-19(12)	43(3)
C(25)	162(8)	3469(17)	-25(12)	53(4)
C(26)	-245(7)	3088(16)	905(14)	53(3)
C(31)	818(8)	78(17)	3473(17)	62(5)
C(32)	462(9)	-560(14)	2594(20)	64(5)
C(33)	-356(8)	-452(14)	2459(18)	55(3)
C(34)	-810(8)	278(16)	3236(14)	54(4)
C(35)	-437(12)	918(16)	4092(16)	73(6)
C(36)	380(13)	813(20)	4228(15)	75(5)
F(1)	1743(3)	1214(7)	848(7)	50(2)
B(1A)	2391(18)	106(30)	1036(17)	37(9)
F(2A)	2458(8)	-130(16)	2122(10)	46(4)
F(3A)	3077(10)	766(42)	597(18)	52(7)
F(4A)	2166(12)	-1275(18)	514(18)	60(6)
B(1B)	2376(16)	100(28)	687(16)	22(7)
F(2B)	2459(9)	-149(17)	-386(10)	40(4)
F(3B)	2201(14)	-1273(19)	1226(18)	71(6)
F(4B)	3083(9)	766(43)	1067(18)	53(7)

$$^a U_{\text{eq}} = 1/3 \sum a_{ij} \mathbf{a}_{ij}$$

The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares against F^2 of 2206 data (Ag, F, C atoms anisotropic, B isotropic, H ‘‘riding’’, the geometries of the two orientations of the BF_3 moiety restrained to similarity, 243 variables, 31 restraints) using SHELXTL software [13]. The refinement converged at $wR(F^2, \text{all data}) = 0.170$, goodness-of-fit 1.14, $R(F, \text{obs. data}) = 0.049$; residual electron density features $\Delta \rho_{\text{max}} = 0.42$, $\Delta \rho_{\text{min}} = -0.71$

$\text{e}\text{\AA}^{-3}$. The absolute configuration was determined by refining the Flack [14] parameter, which converged to $-0.01(13)$, its ideal value being 0 for the correct and +1 for the inverted absolute configuration. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2. Lists of the hydrogen atoms coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre or can be obtained from the authors on request.

Acknowledgements

We thank E.P.S.R.C. for financial support (A.S.B. and S.P.C.) and I.C.I. Acrylics for sponsoring a CASE studentship (S.P.C.).

References

- [1] R.W. Turner, E.L. Amma, *J. Am. Chem. Soc.* 88 (1966) 3243.
- [2] E.A. Hall, E.L. Amma, *J. Chem. Soc. Chem. Commun.* (1968) 622.
- [3] I.F. Taylor Jr., E.A. Hall, E.L. Amma, *J. Am. Chem. Soc.* 91 (1969) 5745.
- [4] C. Cohen-Addad, P. Baret, P. Chautemps, J.-L. Pierre, *Acta Crystallogr. C* 39 (1983) 1346.
- [5] H.C. Kang, A.W. Hanson, B. Eaton, V. Boekelheide, *J. Am. Chem. Soc.* 107 (1985) 1979.
- [6] F.R. Heitzler, H. Hopf, P.G. Jones, P. Bubenitschek, *Chem. Ber.* 128 (1995) 1079.
- [7] P.G. Jones, P. Bubenitschek, F.R. Heitzler, H. Hopf, *Acta Crystallogr. C* 52 (1996) 1380.
- [8] P.G. Jones, F.R. Heitzler, H. Hopf, *Acta Crystallogr. C* 52 (1996) 1384.
- [9] D.P. Fairlie, B. Bosnich, *Organometallics* 7 (1988) 936.
- [10] M.J.S. Dewar, *Bull. Soc. Chim. France* 18 (1951) C79.
- [11] R.S. Mulliken, *J. Am. Chem. Soc.* 74 (1952) 811.
- [12] J.E. Gano, G. Subramanian, R. Birnbaum, *J. Org. Chem.* 55 (1990) 4760.
- [13] G.M. Sheldrick, SHELXTL, Version 5/VMS, Siemens Analytical X-Ray Instruments Inc., Madison, WI, USA, 1995.
- [14] H.D. Flack, *Acta Crystallogr. A* 39 (1983) 876.