Journal of Organometallic Chemistry 561 (1998) 13–18

Synthesis and reactivity of the ligand 1,2-bis(pyridine-2-ylthio)-1,2-dicarba-*closo*-dodecaborane. Crystal structure of $[Ag\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}(PPh_3)]OTf$

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Received 22 August 1997; received in revised form 11 February 1998

Abstract

A new *o*-carborane disubstituted ligand containing pyridinethiolate groups, $1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$, has been synthesised and its reactivity toward silver and gold studied. Thus, the reaction of AgOTf (OTf = trifluoromethanesulfonate) with $1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ in the molar ratio 1:1 or 1:2 affords the cationic three-coordinate silver(I) derivative $[Ag(OTf)\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}]$ or the four-coordinate one $[Ag\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2]OTf$, respectively. Other three-coordinate silver(I) complexes of stoichiometry $[Ag\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}L]$ OTf (L = tertiary phosphines or triphenylarsine) have been synthesised by reaction of [Ag(OTf)L] with the carborane derivative. The complex $[Au_2(PPh_3)_2\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}](OTf)_2$ has also been prepared by reaction of the ligand with $[Au(OTf)(PPh_3)]$ (molar ratio 1:2). The crystal structure of $[Ag\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}(PPh_3)]OTf$ has been established by X-ray diffraction studies. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Silver(I); Gold(I); *o*-Carborane; Pyridinethiolate

1. Introduction

The chemistry concerned with *o*-carborane derivatives has been widely studied because of their potential applications [1]. These result from their high boron content (preparation of tumour-seeking drugs for boron neutron capture therapy [2]) or as a consequence of the specific properties of carborane clusters as their remarkable thermal and chemical stability, which make then suitable for the synthesis of polymers for high temperature [3], neutron shielding purposes ([1]b) or for firing to form ceramics related to boron carbide [4].

Other properties of the carborane, such as their rigid backbones, have allowed the synthesis of complexes that exhibit novel structures. Some examples of this behaviour are the gold complex $[Au_4\{1,2\text{-}(PPh_2)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}_2(1,2\text{-}S_2\text{-}1,2\text{-}C_2B_{10}H_{10})_2]$ [5], in which two of the gold atoms exhibit an unusual tetrahedral geometry whereas the other two present linear geometries, or the silver derivative $[Ag_4(\mu^3\text{-}1\text{-}S\text{-}1,2\text{-}C_2B_{10}H_{11})_2(OTf)_2(PPh_3)_4]$, which presents an unprecedented structure in the chemistry of silver thiolates [6]. Furthermore, partially degraded *o*-carborane derivatives have provided interesting structures. Partially degraded thioether derivatives have been used for the modulation in hydride–ruthenium bonds [7], whereas in gold chemistry the partially degraded diphosphine $[7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ has been used in the synthesis of the cluster $[Au_4\{7,8\text{-}(PPh_2)_2\text{-}7,8\text{-}C_2B_9H_{10}\}_2\text{-}(AsPh_3)_2]$ [8].

This facts prompt us in the preparation of different ligands of *o*-carborane in order to study their reactivity, as well as the possible formation of unusual structures. Here we report on the synthesis of a new ligand that has two pyridinethiolate groups attached to the carbon

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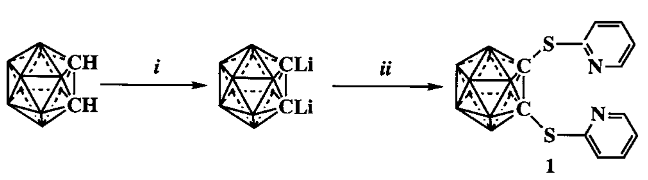
PII S0022-328X(98)00501-4



Scheme 1. (i) 2 Li^{n}Bu, (ii) 2 $C_{10}H_8N_2S_2$.

atoms of the *o*-carborane, 1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$, and the first results of its reactivity.

2. Results and discussion

2.1. Synthesis of the ligand 1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$

We have synthesised the new carborane derivative by addition of $C_{10}H_8N_2S_2$ (2,2′-dithiopyridine) to a solution of 1,2-Li_2-1,2-$C_2B_{10}H_{10}$ in diethyl ether in the molar ratio 2:1. After work up, the new ligand 1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) can be isolated in high yield (Scheme 1).

Compound **1** is a moisture- and air-stable pale yellow solid. It behaves as non-conductor in acetone solutions. In its IR spectrum, the B–H stretching modes [9] appear as a broad absorption centred at 2618 cm^{-1} and those due to ν(CN) [10] at 1574 cm^{-1}.

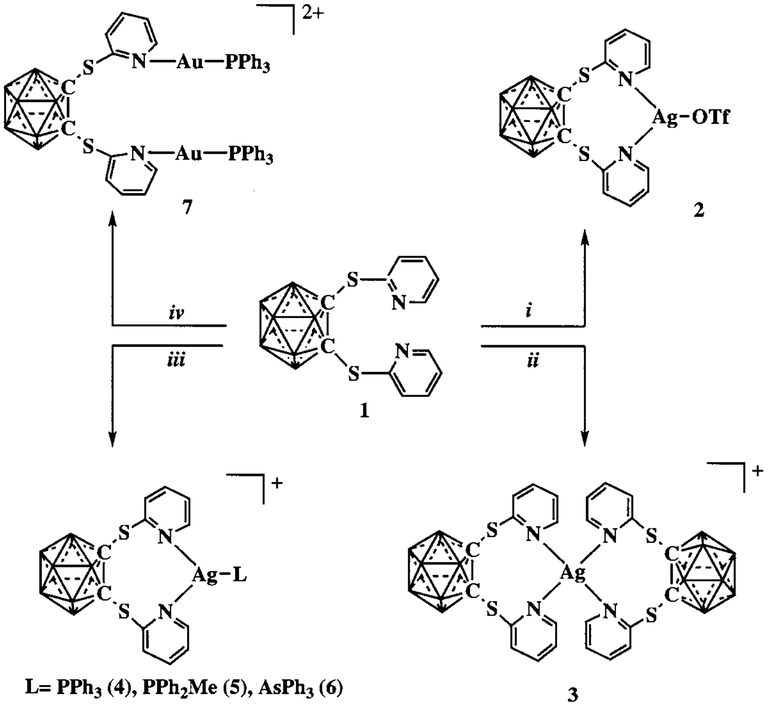
The ^{1}H-NMR spectrum of **1** shows the equivalence of the two pyridinethiolate groups. Although four signals are expected for the four different hydrogen atoms, the spectrum displays only three resonances as two of them are overlapped. One of the signals consists of two doublets; whereas the other two are broad multiplets.

The molecular peak $[M]^+$ [$m/z = 363$ (100%)] is present in the positive ion liquid secondary ion mass spectrum (LSIMS) of this ligand with coincident-calculated and experimental isotopic distributions.

2.2. Reactivity of 1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$

We have studied the reactivity of 1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$ (**1**) with silver and gold complexes. The coordination of the ligand to the metallic centre takes place through the nitrogen atom, as is evidenced by the crystal structure of one of the complexes. Thus, the treatment of **1** with AgOTf (OTf = trifluoromethanesulfonate) in molar ratios 1:1 or 1:2 affords the three-coordinate complex [Ag(OTf){1,2-$(C_5H_4NS)_2$-1,2-C_2B_{10}-H_{10}}] (**2**) or the four-coordinate one [Ag{1,2-$(C_5H_4NS)_2$-1,2-$C_2B_{10}H_{10}$}$_2$]OTf (**3**), respectively (Scheme 2).

Acetone solutions of complexes **2** and **3** behave as 1:1 electrolytes. In the case of compound **2** this is due to the lability of the OTf ligand. The solid IR spectra of these derivatives present the ν(BH) absorptions at 2615 (**2**) and 2579 (**3**) cm^{-1}, respectively; those corresponding to the ν(CN) vibration appear at 1583 (**2**) and 1578 (**3**) cm^{-1}, whereas those assigned to the OTf ligand [11] are different for both compounds. For complex **3**, the bands correspond to a non-coordinated anion [$\nu_{as}(SO_3) = 1268$, $\nu_s(CF_3) = 1224$, $\nu_{as}(CF_3) = 1151$,



Scheme 2. (i) AgOTf, (ii) 1/2 AgOTf, (iii) [Ag(OTf)L], (iv) 2 [Au(OTf)(PPh$_3$)].

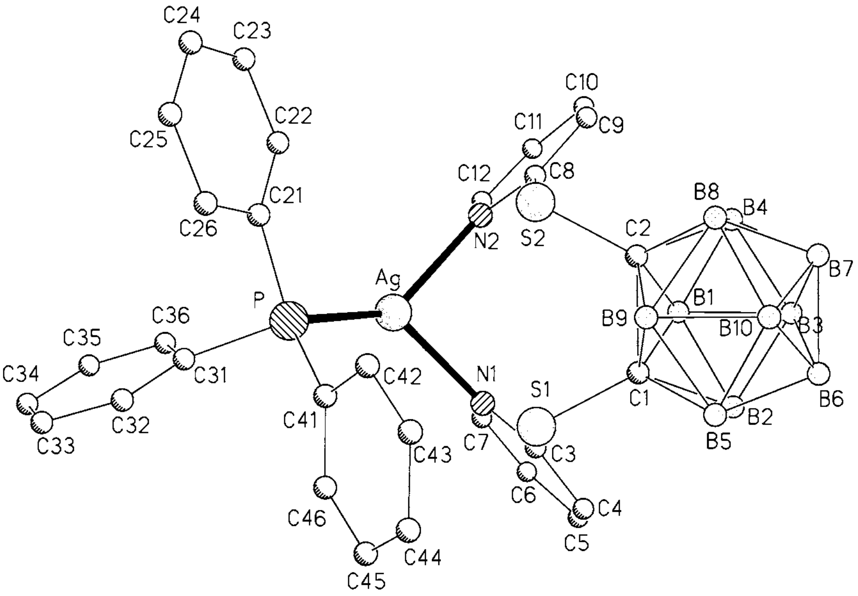


Fig. 1. Structure of the cation of complex **4** in the crystal with the atom numbering scheme. H atoms are omitted for clarity; radii are arbitrary.

$\nu_s(SO_3)$ 1032 cm^{-1}], whereas for complex **2**, they correspond to a covalent anion [$\nu_{as}(SO_3) = 1272$ and 1243, $\nu_s(CF_3) = 1224$, $\nu_{as}(CF_3) = 1178$, $\nu_s(SO_3)$ 1028 cm^{-1}].

In their ^{1}H-NMR spectra, the resonances observed for the hydrogen atoms of the pyridinethiolate groups appear displaced upfield compared with the free ligand. The spectrum of **2** consist of four signals, but in the case of complex **3** only three resonances appear.

In the LSIMS$^+$ mass spectra of both complexes, the most intense peak corresponds to the fragment $[Ag\{(C_5H_4NS)_2C_2B_{10}H_{10}\}]^+$ [$m/z = 470$]. For complex **3** the peak assigned to $[M{-}OTf]^+$ [$m/z = 833$ (3%)] is also present.

Displacement of the OTf anion in silver complexes [Ag(OTf)L] by **1** affords the three-coordinate complexes $[Ag\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}L]OTf$ [L = PPh$_3$ (**4**), PPh$_2$Me (**5**), AsPh$_3$ (**6**)].

The $^{31}P\{^1H\}$-NMR spectra of complexes **4** and **5** display a broad resonance. When the spectra were recorded at −55°C, the signal splits into two doublets that correspond to the coupling of the phosphine phosphorus with the silver nuclei ^{107}Ag and ^{109}Ag. The ^{1}H-NMR spectra of these complexes exhibit broad signals for the pyridinethiolate and phenyl protons. In the spectrum of complex **5** a doublet is present that is assigned to the methyl protons of the phosphine.

The LSIMS$^+$ mass spectra of **4**–**6** exhibit $m/z = 732$ (27%, **4**), 671 (20%, **5**) and 777 (4%, **6**) for the cation molecular peaks, $[Ag\{(C_5H_4NS)_2C_2B_{10}H_{10}\}L]^+$; although, those corresponding to $[AgL]^+$ are the most intense ones.

The reaction of [Au(OTf)(PPh$_3$)] and $1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}$ in molar ratio 2:1 affords the complex $[Au_2\{1,2\text{-}(C_5H_4NS)_2\text{-}1,2\text{-}C_2B_{10}H_{10}\}(PPh_3)_2](OTf)_2$ (**7**). The IR spectrum of this product displays the absorptions corresponding to the ν(BH) frequencies, as well as those assigned to the ν(CN) vibrations at 2614 and 1583 cm^{-1}, respectively.

The $^{31}P\{^1H\}$-NMR spectrum shows a broad singlet for the two phosphorus atoms. In the ^{1}H-NMR spectrum, the hydrogen atoms of the phenyl, carborane (BH) and pyridinethiolate groups appear as broad resonances.

In the LSIMS$^+$ mass spectrum, the peak $[M{-}2OTf]^+$ does not appear but that corresponding to $[Au\{(C_5H_4NS)_2C_2B_{10}H_{10}\}(PPh_3)]^+$ is present [$m/z = 822$ (28%)]; although the most intense peaks are those assigned to $[Au(PPh_3)]^+$ and $[Au(PPh_3)_2]^+$ ($m/z = 459$ (100%) and 721 (87%)), respectively.

*2.3. Crystal structure determination of complex **4***

The molecular structure of the cation of complex **4** is shown in Fig. 1. Selected bond lengths and angles are presented in Table 1 and atomic coordinates in Table 2. It contains a silver atom bonded to one phosphorus and to two nitrogen atoms, corresponding to the triphenylphosphine and carborane derivative, respectively. There are not many examples of silver derivatives with this type of coordination, as far as we are aware only the complexes $[IrAg(\eta^5\text{-}C_5Me_5)(pz)_3(PPh_3)]$ [12] and $[Ag\{P(C_6H_4Me\text{-}4)_3\}\{BPh_2(pz)_2\}]$ [13] (pz = pyrazolyl) have been reported; although the latter has a pseudo-three-coordination for the silver atom. The geometry for complex **4** is distorted from the trigonal planar, mainly because the restricted bite angle of the carborane ligand, N(1)–Ag–N(2) = 84.26(8)°. Consequently, the others are wider than the ideal 120°, N(1)–Ag–P = 134.10(6)° and N(2)–Ag–P = 136.43(6)°. The silver atom lies 0.29 Å out of the plane formed by the

P, N(1) and N(2) atoms. The Ag–N distances, 2.345(2) and 2.350(2) Å, are longer to those found in the complex [IrAg(η^5-C_5Me_5)$(pz)_3(PPh_3)$] (2.211(4) and 2.205(3) Å) [12] or the heterotetranuclear derivative [$Au_2Ag_2\{\mu$-$(PPh_2)_2N\}_2(OClO_3)_2(PPh_3)_2$] (2.239(4) Å) [14], which have trigonal silver atoms, but are in between the values obtained for the complex [Ag{P(C_6H_4Me-4)$_3$}{$BPh_2(pz)_2$}] (2.194(4) and 2.411(4) Å) [13]. However, they are also comparable with those in the tetrahedral compounds [Ag(dppf)(phen)]ClO_4 (2.343(3) and 2.361(3) Å) [15] or [Ag{$(PPh_2)_2C_2B_{10}$-H_{10}}(phen)]ClO_4 (2.312(5) and 2.333(5) Å) [16]. The Ag–P bond length of 2.3832(7) Å is of the same order as that in [IrAg(η^5-C_5Me_5)$(pz)_3(PPh_3)$] (2.341(1) Å) or the shortest in [Ag(dppf)(PPh_3)]ClO_4 (2.4244–2.4802(12) Å).

3. Experimental

IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C and H analyses

Table 1
Selected bond lengths (Å) and angles (°) for complex **4**

Bond lengths (Å)			
Ag–N(1)	2.345(2)	Ag–N(2)	2.350(2)
Ag–P	2.3832(7)	P–C(31)	1.822(3)
P–C(41)	1.825(3)	P–C(21)	1.829(3)
S(1)–C(1)	1.777(3)	S(1)–C(3)	1.793(3)
S(2)–C(2)	1.780(3)	S(2)–C(8)	1.797(3)
N(1)–C(3)	1.343(4)	N(1)–C(7)	1.347(4)
N(2)–C(12)	1.340(3)	N(2)–C(8)	1.348(4)
C(1)–C(2)	1.813(4)	C(3)–C(4)	1.393(4)
C(4)–C(5)	1.387(4)	C(5)–C(6)	1.382(5)
C(6)–C(7)	1.388(4)	C(8)–C(9)	1.379(4)
C(9)–C(10)	1.384(4)	C(10)–C(11)	1.370(4)
C(11)–C(12)	1.394(4)		
Bond angles (°)			
N(1)–Ag–N(2)	84.26(8)	N(1)–Ag–P	134.10(6)
N(2)–Ag–P	136.43(6)	C(31)–P–C(41)	105.29(13)
C(31)–P–C(21)	100.50(6)	C(41)–P–C(21)	107.97(14)
C(31)–P–Ag	117.67(10)	C(41)–P–Ag	110.06(9)
C(21)–P–Ag	114.43(9)	C(1)–S(1)–C(3)	103.73(13)
C(2)–S(2)–C(8)	103.39(13)	C(3)–N(1)–C(7)	117.7(3)
C(3)–N(1)–Ag	119.1(2)	C(7)–N(1)–Ag	123.0(2)
C(12)–N(2)–C(8)	116.5(2)	C(12)–N(2)–Ag	123.8(2)
C(8)–N(2)–Ag	119.6(2)	B(5)–C(1)–S(1)	119.0(2)
B(2)–C(1)–S(1)	125.9(2)	B(9)–C(1)–S(1)	112.1(2)
B(1)–C(1)–S(1)	122.3(2)	S(1)–C(1)–C(2)	118.3(2)
B(4)–C(2)–S(2)	126.1(2)	B(8)–C(2)–S(2)	119.2(2)
B(9)–C(2)–S(2)	111.9(2)	B(1)–C(2)–S(2)	122.1(2)
S(2)–C(2)–C(1)	118.0(2)	N(1)–C(3)–C(4)	123.7(3)
N(1)–C(3)–S(1)	115.4(2)	C(4)–C(3)–S(1)	120.8(3)
C(5)–C(4)–C(3)	117.6(3)	C(6)–C(5)–C(4)	119.3(3)
C(5)–C(6)–C(7)	119.4(3)	N(1)–C(7)–C(6)	122.1(3)
N(2)–C(8)–C(9)	123.7(3)	N(2)–C(8)–S(2)	114.7(2)
C(9)–C(8)–S(2)	121.6(2)	C(8)–C(9)–C(10)	118.4(3)
C(11)–C(10)–C(9)	119.2(3)	C(10)–C(11)–C(12)	118.6(3)
N(2)–C(12)–C(11)	123.3(3)		

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4**

	x	y	z	U_{eq}
Ag	2451(1)	2424(1)	6482(1)	25(1)
P	3791(1)	2560(1)	7304(1)	21(1)
S(1)	1982(1)	557(1)	7302(1)	28(1)
S(2)	2975(1)	690(1)	5464(1)	25(1)
N(1)	1083(2)	1939(2)	6746(1)	23(1)
N(2)	1994(2)	2072(2)	5098(1)	22(1)
C(1)	1844(2)	−320(2)	6589(2)	22(1)
C(2)	2359(2)	−254(2)	5635(2)	21(1)
C(3)	1005(2)	1165(2)	7113(2)	26(1)
C(4)	243(2)	864(2)	7391(2)	34(1)
C(5)	−484(2)	1373(2)	7230(2)	39(1)
C(6)	−421(2)	2158(2)	6827(2)	37(1)
C(7)	372(2)	2430(2)	6608(2)	32(1)
C(8)	2263(2)	1328(2)	4771(2)	22(1)
C(9)	2053(2)	1081(2)	3958(2)	28(1)
C(10)	1467(2)	1581(2)	3471(2)	33(1)
C(11)	1151(2)	2322(2)	3798(2)	30(1)
C(12)	1443(2)	2554(2)	4608(2)	27(1)
B(1)	1253(2)	−221(2)	5637(2)	22(1)
B(2)	959(2)	−958(2)	6430(2)	26(1)
B(3)	919(2)	−1301(2)	5374(2)	26(1)
B(4)	1791(2)	−848(2)	4897(2)	24(1)
B(5)	1941(2)	−1350(2)	6955(2)	30(1)
B(6)	1354(2)	−2008(2)	6195(2)	30(1)
B(7)	1858(2)	−1936(2)	5259(2)	29(1)
B(8)	2762(2)	−1245(2)	5428(2)	26(1)
B(9)	2798(2)	−843(2)	6470(2)	27(1)
B(10)	2503(2)	−1946(2)	6233(2)	31(1)
C(21)	4729(2)	2547(2)	6711(2)	24(1)
C(22)	4606(2)	2766(2)	5878(2)	32(1)
C(23)	5298(2)	2914(2)	5422(2)	39(1)
C(24)	6126(2)	2807(2)	5794(2)	38(1)
C(25)	6262(2)	2561(2)	6618(2)	36(1)
C(26)	5569(2)	2444(2)	7079(2)	29(1)
C(31)	3987(2)	3556(2)	7898(2)	21(1)
C(32)	4554(2)	3616(2)	8613(2)	29(1)
C(33)	4716(2)	4412(2)	9001(2)	32(1)
C(34)	4310(2)	5153(2)	8685(2)	30(1)
C(35)	3746(2)	5105(2)	7977(2)	30(1)
C(36)	3591(2)	4310(2)	7586(2)	27(1)
C(41)	3913(2)	1685(2)	8066(2)	22(1)
C(42)	4359(2)	935(2)	7934(2)	34(1)
C(43)	4340(2)	236(2)	8480(2)	47(1)
C(44)	3857(2)	286(2)	9153(2)	40(1)
C(45)	3397(2)	1026(2)	9282(2)	32(1)
C(46)	3426(2)	1720(1)	8743(1)	27(1)
S(3)	1517(1)	−5256(2)	6206(2)	42(1)
O(1)	1960(2)	−4631(2)	6744(2)	78(1)
O(2)	671(2)	−5474(2)	6406(2)	60(1)
O(3)	2026(2)	−6003(2)	5995(1)	45(1)
C(100)	1339(3)	−4694(2)	5218(3)	51(1)
F(1)	810(2)	−4018(1)	5262(2)	67(1)
F(2)	1002(2)	−5218(2)	4625(1)	72(1)
F(3)	2073(2)	−4391(2)	4977(2)	95(1)

U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor.

were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H, external) and 85% H_3PO_4 (^{31}P, external). *o*-Carborane (Dexsil Chemical) and $C_{10}H_8N_2S_2$ (Aldrich) were analytical reagent grade and used as-given. The starting materials [Ag(OTf)L] were prepared by reaction of Ag(OTf) and the ligand L in dichloromethane. [Au(OTf)(PPh_3)] was obtained from [AuCl(PPh_3)] [17] and Ag(OTf) in dichloromethane.

3.1. 1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$ (**1**)

To a solution of 1,2-$C_2B_{10}H_{10}$ (2.88 g, 20 mmol) in diethyl ether (100 cm^3) at 0°C, and under nitrogen atmosphere Li^nBu (8 cm^3, 2.5 M) was added. After stirring for 30 min, $C_{10}H_8N_2S_2$ (4.40 g, 40 mmol) was added. The mixture was warmed to r.t. and washed with water (3 × 40 cm^3). The organic phase was threated with $MgSO_4$, and after 30 min the $MgSO_4$ was filtered off. Concentration of the solution and addition of hexane afforded bright yellow crystals of **1**. Yield, 75%. Anal. Calc. for $C_{12}H_{18}B_{10}N_2S_2$: C, 39.75; H, 5.05; N, 7.7; S, 17.15. Found: C, 39.45; H, 4.8; N, 7.55; S, 17.7. $\Lambda_M = 3\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR: $\delta = 8.62$ (dd, 1H), 7.72 (m, br, 2H), 7.32 (m, br, 1H).

3.2. [Ag(OTf){1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$}] (**2**)

To a solution of 1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$ (0.036 g, 0.1 mmol) in dichloromethane (20 cm^3) a solution of AgOTf (0.1 mmol, 0.025 g) in Et_2O (10 cm^3) was added. The mixture was stirred for 30 min and the solution concentrated to ca. 5 cm^3. Addition of hexane (10 cm^3) gave complex **2** as a white solid. Yield, 78%. Anal. Calc. for $C_{13}H_{18}AgB_{10}F_3N_2OS_3$: C, 25.2; H, 2.9; N, 4.5; S, 15.5. Found: C, 24.9; H, 3.2; N, 4.3; S, 15.2. $\Lambda_M = 91\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 8.74 (dd, 1H), 7.93 (td, 1H), 7.71 (d, 1H), 7.55 (td, 1H).

3.3. [Ag{1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$}$_2$]OTf (**3**)

To a solution of 1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$ (0.072 g, 0.2 mmol) in dichloromethane (20 cm^3), a solution of AgOTf (0.1 mmol, 0.050 g) in Et_2O (10 cm^3) was added. The mixture was stirred for 30 min and the solution concentrated to ca. 5 cm^3. Addition of hexane (10 cm^3) gave complex **3** as a white solid. Yield, 69%. Anal. Calc. for $C_{25}H_{36}AgB_{20}F_3N_4O_3S_5$: C, 30.95; H, 3.7; N, 5.7; S, 16.0. Found: C, 30.45; H, 3.2; N, 5.3; S, 15.5. $\Lambda_M = 134\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 8.85 (d, 1H), 7.92 (m, br, 2 H), 7.55 (m, br, 1H).

3.4. [Ag{1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$}L]OTf [L = PPh_3 (**4**), PPh_2Me (**5**), $AsPh_3$ (**6**)]

To a solution of 1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$ (0.036 g, 0.1 mmol) in dichloromethane (30 cm^3), [Ag(OTf)L] was added (0.1 mmol; 0.052 g, L = PPh_3; 0.046 g, L = PPh_2Me; 0.056 g, L = $AsPh_3$). The solution was stirred for 30 min and concentrated to ca. 5 cm^3. Addition of diethyl ether (10 cm^3) gave complexes **4**–**6** as white solids. **4**: yield 65%. Anal. Calc. for $C_{31}H_{33}AgB_{10}F_3N_2O_3PS_3$: C, 42.2; H, 3.8; N, 3.2; S, 11.0. Found: C, 42.65; H, 3.75; N, 2.65; S, 10.4. $\Lambda_M = 94\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 9.38 (d, 1H), 7.92 (t, 1H), 7.70 (t, 1H), 7.76 (d, 1H), 7.3–7.5 (m, br, 15H). $^{31}P\{^1H\}$-NMR, δ: 12.9 (2 d, $J\ ^{109}AgP = 712.3$, $J\ ^{107}AgP = 619.4$ Hz). **5**: yield 50%. Anal. Calc. for $C_{26}H_{31}AgB_{10}F_3N_2O_3PS_3$: C, 38.1; H, 3.8; N, 3.4; S,11.75. Found: C, 38.05; H, 3.8; N, 3.2; S, 11.5. $\Lambda_M = 112\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 9.20 (d, 1H), 7.8 (t, 1H), 7.69 (d, 1H), 7.54 (t, 1H), 7.2–7.5 (m, br, 10H), 1.96 (d, J (PH) = 6.3 Hz). $^{31}P\{^1H\}$-NMR, δ: −6.6 (dd, $J\ ^{109}AgP = 732.4$, $J\ ^{107}AgP = 633.8$ Hz). **6**: yield 52%. Anal. Calc. for $C_{31}H_{33}AgB_{10}F_3N_2O_3S_3$: C, 40.2; H, 3.6; N, 3.0; S,10.45. Found: C, 40.65; H, 3.7; N, 2.5; S, 9.6. $\Lambda_M = 114\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 7.3–7.5 (m, br, 15H), 7.92 (m, br, 1H), 7.73 (m, br, 2H), 7.67 (m, br, 1H).

3.5. [Au_2{1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$}(PPh_3)$_2$](OTf)$_2$ (**7**)

To a solution of [Au(OTf)(PPh_3)] (0.062 g, 0.1 mmol) in dichloromethane (20 cm^3), 1,2-(C_5H_4NS)$_2$-1,2-$C_2B_{10}H_{10}$ (0.036 g, 0.1 mmol) was added. The mixture was stirred for 30 min. Concentration of solvent to ca. 5 cm^3 and addition of hexane (10 cm^3) afforded complex **7** as a white solid. Yield, 70%. Anal. Calc. for $C_{50}H_{66}Au_2B_{10}F_6N_2O_6P_2S_2$: C, 38.0; H, 3.1; N, 1.75; S, 8.1. Found: C, 38.5; H, 2.65; N, 1.8; S, 7.8. $\Lambda_M = 138\ \Omega^{-1}\,cm^2\,mol^{-1}$. ^1H-NMR, δ: 7.3–7.5 (m, br, 30H), 8.99 (m, br 1H), 8.35 (m, br, 2H), 7.96 (m, br, 1H). $^{31}P\{^1H\}$-NMR, δ: 34.6 (s, br).

3.6. Crystal structure determination of complex **4**

3.6.1. Crystal data

4: $C_{31}H_{33}AgB_{10}F_3N_2O_3PS_3$, $M_r = 881.71$, monoclinic, space group $P2_1/c$, $a = 15.647(1)$, $b = 15.411(1)$, $c = 16.190(1)$ Å, $\beta = 95.439(7)°$, $V = 3886.4(4)$ Å^3, $Z = 4$, $D_{calc} = 1.507$ Mg m^{-3}, λ(Mo–K$_\alpha$) = 0.71073 Å, $\mu = 0.772$ mm^{-1}, $F(000) = 1776$, $T = -100$°C.

3.6.2. Data collection and reduction

Single crystals were obtained by slow diffusion of hexane into a dichloromethane solution of complex **4**. A colourless prism $0.40 \times 0.30 \times 0.25$ mm was used to collect 9388 intensities to $2\theta_{max}$ 50° (Siemens P4 diffractometer, monochromated Mo–K_{α} radiation) of which 6836 were independent ($R_{int} = 0.030$). Cell constants were refined from 2θ values of 75 reflections in the range 10–25°. An absorption correction was applied on the basis of Ψ-scans (transmission factors 0.750–0.831).

3.6.3. Structure solution and refinement

Structure was solved by direct methods and refined on F^2 using the program SHELXL-93 [18]. All non-hydrogen atoms were refined anisotropically. Refinement proceeded to wR (F^2) 0.0634 for 6830 reflections and 487 parameters. Conventional $R(F)$ 0.0299; $S(F^2)$ 0.857; $\Delta\rho = 0.568$ e Å^{-3}.

4. Supplementary material available

Full details of the crystal structure determination can be ordered from Fachinformationszentrun Karlsruhe, 76344 Eggenstein-Leopoldshafen, under the depositary number CSD-407191.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (No. PB94-0079) for financial support.

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