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Mixed Sandwich Carborane/Thiamacrocycle Compounds. Synthesis and Characterization of 1-Ph-3,3,3-[9]aneS$_3$-κ^3-*S,S′,S″*-3,1,2-*closo*-RuC$_2$B$_9$H$_{10}$ and 1,2-Ph$_2$-3,3,3-[9]aneS$_3$-κ^3-*S,S′,S″*-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$[†,‡]

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The reactions between [Ru([9]aneS$_3$)(MeCN)$_3$][CF$_3$SO$_3$]$_2$, a useful source of the [Ru{[9]aneS$_3$-κ^3-*S,S′,S″*}]$^{2+}$ fragment dication, and [Tl][TlC$_2$B$_9$H$_{10}$Ph] and [Tl][TlC$_2$B$_9$H$_9$Ph$_2$], respectively sources of the {C$_2$B$_9$H$_{10}$Ph}$^{2-}$ and {C$_2$B$_9$H$_9$Ph$_2$}$^{2-}$ fragment dianions, have afforded 1-Ph-3,3,3-[9]aneS$_3$-κ^3-*S,S′,S″*-3,1,2-*closo*-RuC$_2$B$_9$H$_{10}$, **1**, and 1,2-Ph$_2$-3,3,3-[9]aneS$_3$-κ^3-*S,S′,S″*-3,1,2-*pseudocloso*-RuC$_2$B$_9$H$_9$, **2**, the first reported examples of mixed thiamacrocyle/carborane compounds. Compounds **1** and **2** have been characterized by multinuclear (^{1}H, ^{11}B-{^{1}H}, and ^{13}C{^{1}H}) NMR spectroscopy, and by single-crystal X-ray diffraction studies. Compound **1** [space group $P\bar{1}$, $a = 10.3552(7)$ Å, $b = 13.7960(18)$ Å, $c = 15.9795(13)$ Å, $\alpha = 68.227(7)°$, $\beta = 82.983(5)°$, $\gamma = 82.496(7)°$, $R = 0.0377$ for 5893 observed data] is a *closo* metal carborane, based on an icosahedron, in which the [9]andS$_3$ ligand has effective C_3 symmetry. In solution at room temperature the macrocyclic ligand of **1** undergoes rapid rotation about an axis through the metal carborane polyhedron, and it is likely that the cage phenyl group is also spinning, the two fluxional processes operating in concert *via* a geared-type mechanism. Compound **2** [space group *Pbca*, $a = 16.771(3)$ Å, $b = 16.907(3)$ Å, $c = 17.757(4)$ Å, $R = 0.0397$ for 2946 observed data] is a *pseudocloso* metal carborane and has a polyhedral architecture characterized by C(1)···C(2) 2.504(7) Å and Ru(3)···B(6) 2.960(6) Å, as a consequence of intramolecular crowding between the phenyl cage substituents. Phenyl/thiamacrocycle intramolecular crowding affords the latter a conformation with effective C_s symmetry—indeed, the entire molecule is effectively mirror-symmetric. The weighted average ^{11}B chemical shift of **2** is δ +8.18 ppm, *ca.* 16 ppm to high frequency of that of **1**. By ^{1}H and ^{13}C{^{1}H} NMR spectroscopy it appears that the phenyl substituents of **2** spin at room temperature, but that the [9]aneS$_3$ ligand does not.

Introduction

The chemistry of transition metal sandwich compounds bearing carborane ligands is a well-developed area; although the first examples, [Fe(C$_2$B$_9$H$_{11}$)$_2$]$^-$, and [Fe(C$_2$B$_9$H$_{11}$)$_2$]$^{2-}$, were described by Hawthorne more than 30 years ago,[1a] carborane sandwich compounds (in the context of the present paper the word "carborane" refers exclusively to the *nido*-icosahedral {C$_2$B$_9$} fragment) are still relevant to the current literature.[1b,c] The chemistry of "traditional" mixed sandwich carborane compounds (*i.e.* carborane ligand and cyclopentadiene, arene or related ligand [*e.g.* tris(1-pyrazolyl)borate], sketched in Figure 1a) is both also well established and continues to attact attention.[2] Recent work in this group[3] has focused on aspects of the structures and chemistries of mixed sandwich carborane compounds of the type [(η-L)M(C$_2$B$_9$H$_9$PhR)] (L = Cp, Cp*, C$_9$H$_7$, C$_9$Me$_7$; M = Ir, Rh. L = C$_6$H$_6$, C$_6$H$_3$Me$_3$-1,3,5, C$_6$H$_4$-Me-1-^{i}Pr-4, C$_6$Me$_6$; M = Ru. R = H, Me, Ph). These are especially intriguing when R = Ph, as steric congestion forces the phenyl groups to lie essentially co-planar, levering the cage carbons apart and resulting in a *pseudocloso* structure.[3a,d−f]

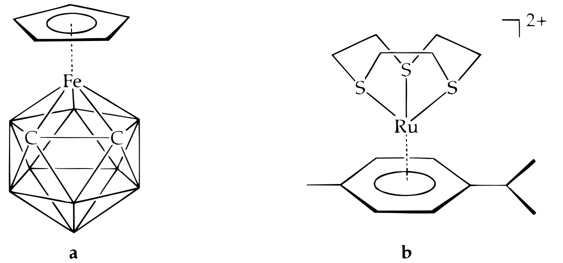

Figure 1. Typical "mixed sandwich" compounds, with (a) cyclopentadienyl and carborane ligands and (b) thiamacrocycle and arene ligands.

At the same time much current interest attends the chemistry of thiamacrocycles,[4] especially their coordination chemistry with transition elements. Particular attention has been paid to the ligand 1,4,7-trithiacyclononane ([9]aneS$_3$), which can be loosely compared with η-cyclopentadienide or η-arene ligands insofar as it occupies three facial sites of a metal coordination sphere

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[†] [9]aneS$_3$ = 1,4,7-trithiacyclononane.

[‡] Steric Effects in Heteroboranes. 13. For part 12 see ref 3f.

[⊗] Abstract published in *Advance ACS Abstracts*, June 15, 1996.

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and acts as a six-electron donor.[4,5] In common with metal carboranes, mixed sandwich compounds involving macrocyclic and arene or cyclopentadienyl ligands have also been reported, *e.g.* Figure 1b.[6]

In view of this it is surprising that, at least to our knowledge, no mixed thiamacrocycle/carborane sandwich compounds have been reported, although this appears to be a natural extension to the chemistry of both areas.

We report herein details of the synthesis, characterization and the solid state structures of two mixed sandwich macrocycle/carborane compounds bearing the tridentate, facially coordinating, thiamacrocycle [9]aneS_3 and the carborane fragments $\{C_2B_9H_{10}Ph\}$ and $\{C_2B_9H_9Ph_2\}$.

Experimental Section

1. Synthesis. General Procedures. All manipulations were carried out under a dry dinitrogen atmosphere, although both new compounds appear to be indefinitely air-stable in the solid state. The compounds [Tl][Tl$C_2B_9H_9Ph_2$],[3a] [Tl][Tl$C_2B_9H_{10}Ph$],[3d] and [Ru([9]aneS_3)(MeCN)$_3$][CF_3SO_3]$_2$[7] were prepared as described in the literature. MeOH and dmso (HPLC grade, Aldrich) were stored over 3 and 4 Å molecular sieves, respectively, and degassed prior to use. Diethyl ether was distilled under dinitrogen from Na/benzophenone immediately prior to use. The macrocycle [9]aneS_3 was used as supplied by Aldrich. ^{1}H NMR spectra were recorded on a Brüker AC 200 spectrometer. $^{11}B\{^{1}H\}$ and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Brüker DPX 400 spectrometer at 128.4 and 100.6 MHz respectively. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual protio solvent in the sample; $^{11}B\{^{1}H\}$ NMR spectra were referenced to $BF_3{\cdot}OEt_2$ (external). All NMR spectra were recorded from dmso-d_6 solutions at room temperature.

1-Ph-3,3,3-[9]aneS_3-κ^3-*S,S′,S″*-3,1,2-*closo*-Ru$C_2B_9H_{10}$ (1). [Ru([9]aneS_3)(MeCN)$_3$][CF_3SO_3]$_2$ (0.085 g, 0.12 mmol) and [Tl][Tl$C_2B_9H_{10}$Ph] (0.089 g, 0.14 mmol) were suspended in MeOH (10 cm^3) and heated to reflux for 3 h. The resulting supernatant liquid was removed *via* syringe and the brown solid remaining washed twice with MeOH and once with diethyl ether and then dried *in vacuo*. Recrystallization from dmso/MeOH afforded brown *plates* of diffraction quality; mass 0.033 g, yield 56%.

Anal. Calcd for $C_{14}H_{27}B_9S_3Ru$: C, 34.4; H, 5.5. Found: C, 32.2; H, 5.2 (incomplete combustion).

^{1}H NMR: δ 7.14−6.90 (m, 5 H, Ph), 4.57 (s br, 1 H, CH), 2.75 (m, 3 H, [9]aneS_3), 2.60 (m, 3 H, [9]aneS_3) (multiplet partially obscured by solvent peak) , 2.18 (m, 3 H, [9]aneS_3), 1.68 (m, 3 H, [9]aneS_3) ppm.

$^{11}B\{^{1}H\}$ NMR: δ 2.11 (1 B), −0.25 (1 B), −3.44 (1 B), −5.46 (1 B), −7.22 (1 B), −12.52 (3 B), −23.24 (1 B) ppm.

$^{13}C\{^{1}H\}$ NMR: δ 147.4 (1C, Ph), 128.0 (4C, Ph), 124.0 (1C, Ph), 36.0 (3C, [9]aneS_3), 31.5 (3C, [9]aneS_3) ppm.

1,2-Ph_2-3,3,3-[9]aneS_3-κ^3-*S,S′,S″*-3,1,2-*pseudocloso*-Ru$C_2B_9H_9$ (2). Similarly, [Ru([9]aneS_3)(MeCN)$_3$][CF_3SO_3]$_2$ (0.083 g, 0.12 mmol) and [Tl][Tl$C_2B_9H_9Ph_2$] (0.100 g, 0.14 mmol) were suspended in MeOH (10 cm^3) and heated to reflux for 3 h. The resulting supernatant liquid was removed *via* syringe, and the purple solid which remained was washed twice with MeOH and once with diethyl ether and then dried *in vacuo*. Recrystallization from dmso/MeOH afforded purple *blocks* of diffraction quality; mass 0.030 g, yield 46%.

Anal. Calcd for $C_{20}H_{31}B_9S_3Ru$: C, 42.4; H, 5.5. Found: C, 40.9, H, 5.1 (incomplete combustion).

Table 1. Crystallographic Data for Compounds **1** and **2**

	1	**2**
formula	$C_{14}H_{27}B_9S_3Ru$	$C_{20}H_{31}B_9S_3Ru$
fw	489.9	565.2
cryst dimens, mm	0.5 × 0.3 × 0.2	0.4 × 0.4 × 0.3
cryst syst	triclinic	othorhombic
space group	$P\bar{1}$	*Pbca*
a, Å	10.3552(7)	16.771(3)
b, Å	13.7960(18)	16.907(3)
c, Å	15.9795(13)	17.757(4)
α, deg	68.227(7)	90
β, deg	82.983(5)	90
γ, deg	82.496(7)	90
T, K	293	293
V, Å^3	2095.08	5034.95
Z	4	8
D_{calc}, g cm^{-3}	1.553	1.493
μ(Mo *K*α), mm^{-1}	1.04	0.88
F(000), e	992	2304
2*θ* range, deg	4 − 50	4 − 50
no. of unique data collcd	7245	4395
h range	−1 to 12	−1 to 19
k range	−15 to 15	−1 to 20
l range	−18 to 18	−1 to 21
R (all data)	0.0557	0.0770
no. of data obsd [$\lvert F_o\rvert > 4\sigma(\lvert F_o\rvert)$]	5893	2946
R (obsd data)[a]	0.0377	0.0397
wR_2[b]	0.0947	0.1138
S[c]	1.107	0.905
g_1	0.0340	0.0576
g_2	5.06	6.53
max residue, e Å^{-3}	+0.42	+0.47
min residue, e Å^{-3}	−0.45	−0.41

[a] $R = \sum\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\sum\lvert F_o\rvert$. [b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$ where n = number data and p = number of variables.

^{1}H NMR: δ 7.27 (d, 2H, *ortho* Ph), 7.14 (app t, 2H, *meta* Ph), 6.98 (t, 1H, *para* Ph), 2.85−2.27 (m, 8 H, [9]aneS_3), 2.10 (m, 2 H, [9]aneS_3), 1.12 (m, 2 H, [9]aneS_3) ppm.

$^{11}B\{^{1}H\}$ NMR: δ 28.5 (1 B), 18.0 (2B), 13.2 (1 B), 4.5 (2 B), 2.0 (2 B), −17.1 (1 B) ppm.

$^{13}C\{^{1}H\}$ NMR: δ 152.7 (1C, Ph), 128.0 (2C, Ph), 125.7 (2C, Ph), 124.6 (1C, Ph), 36.7 (2C, [9]aneS_3), 36.5 (2C, [9]aneS_3), 32.4 (2C, [9]aneS_3) ppm.

2. X-ray Crystallography. Intensity measurements on **1** and **2** were made by ω scans at room temperature using a Siemens P4 diffractometer with graphite-monochromated Mo *K*α X-radiation (λ_{bar} = 0.710 73 Å). Relevant crystallographic data are given in Table 1. Periodic remeasurement of three standard reflections revealed no crystal or electronic instability in either case. Intensity data were corrected for the effects of X-ray absorption by ψ-scans.

The structures were solved without difficulty by direct methods and refined by full-matrix least-squares, using SHELXTL.[8] In the case of compound **1** the C_{cage} atom not carrying the phenyl substituent, C(2), was unambiguously identified by a combination of interatomic distances and refined (as *B*) with isotropic thermal parameters. In both cases all H atoms were located. For **1** those attached to cage atoms were positionally refined, resulting in X−H 0.97(3)−1.15(3) Å, whereas for **2** B−H distances were constrained to a common value of 1.10(3) Å; for both determinations cage H atoms were refined with individual isotropic thermal parameters. Methylene-H and phenyl-H atoms were constrained to idealized positions (C−H = 0.97 and 0.93 Å respectively) and given isotropic displacement parameters riding at 1.2*U*(C). All non-H atoms were refined with anisotropic displacement parameters. In the final stages of refinement data were weighted such that $w^{-1} = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = [\max(F_o^2 \text{ or } 0) + 2F_c^2]/3$.

Positional parameters for compounds **1** and **2**, together with equivalent isotropic thermal parameters, are listed in Tables 2 and 3, respectively. Hydrogen atom coordinates and displacement parameters,

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Table 2. Atomic Coordinates ($\times 10^5$ Ru, S; $\times 10^4$ B, C) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

	x	*y*	*z*	*U*(eq)[a]
Ru(3)	84457(3)	2642(3)	20241(2)	21(1)
S(1)	81133(12)	14150(10)	5644(8)	30(1)
S(2)	65440(12)	11365(11)	24941(8)	32(1)
S(3)	70464(11)	−7790(10)	17806(8)	29(1)
C(1)	9241(4)	−659(4)	3327(3)	23(1)
C(2)	9562(5)	609(4)	2928(3)	29(1)
B(4)	9769(5)	−1170(4)	2487(4)	26(1)
B(5)	10687(5)	−1435(4)	3444(4)	27(1)
B(6)	10526(5)	−320(5)	3728(4)	31(1)
B(7)	10285(6)	1002(5)	1843(4)	34(1)
B(8)	10491(5)	−167(5)	1537(4)	30(1)
B(9)	11505(5)	−1122(5)	2344(4)	29(1)
B(10)	11939(5)	−580(5)	3107(4)	30(1)
B(11)	11199(6)	716(5)	2811(4)	32(1)
B(12)	11813(5)	216(5)	1948(4)	30(1)
C(31)	8157(4)	−1046(4)	4055(3)	27(1)
C(32)	7627(5)	−487(5)	4599(4)	41(1)
C(33)	6603(6)	−845(7)	5249(4)	57(2)
C(34)	6108(6)	−1752(6)	5356(4)	59(2)
C(35)	6615(6)	−2325(6)	4831(4)	52(2)
C(36)	7639(5)	−1976(4)	4178(3)	37(1)
C(21)	7078(6)	2501(4)	745(4)	40(1)
C(22)	5965(6)	2170(5)	1473(4)	41(1)
C(23)	5313(5)	213(5)	2740(4)	40(1)
C(24)	5366(5)	−301(5)	2056(4)	39(1)
C(25)	7063(6)	−310(4)	547(3)	37(1)
C(26)	6962(5)	863(4)	113(3)	36(1)
Ru(3′)	88302(3)	52164(3)	21068(2)	22(1)
S(1′)	107467(11)	57960(9)	12489(8)	28(1)
S(2′)	96663(12)	55131(11)	32927(8)	32(1)
S(3′)	99846(12)	35625(10)	26320(8)	31(1)
C(1′)	6800(4)	5003(4)	2647(3)	25(1)
C(2′)	7088(5)	6268(4)	2168(3)	29(1)
B(4′)	7323(5)	4407(5)	1853(4)	28(1)
B(5′)	5621(6)	4780(5)	2085(4)	35(1)
B(6′)	5482(5)	5948(5)	2293(4)	32(1)
B(7′)	7807(6)	6591(5)	1081(4)	31(1)
B(8′)	7936(6)	5374(5)	841(4)	29(1)
B(9′)	6301(6)	5022(5)	959(4)	34(1)
B(10′)	5188(6)	5985(5)	1231(4)	33(1)
B(11′)	6098(6)	6930(5)	1320(4)	33(1)
B(12′)	6602(6)	6370(5)	480(4)	33(1)
C(31′)	6736(4)	4439(4)	3652(3)	30(1)
C(32′)	6616(5)	4963(5)	4249(4)	43(1)
C(33′)	6602(6)	4413(6)	5173(4)	54(2)
C(34′)	6695(6)	3348(6)	5513(4)	55(2)
C(35′)	6813(6)	2816(6)	4932(4)	56(2)
C(36′)	6834(5)	3346(5)	4000(4)	40(1)
C(21′)	11325(5)	6548(4)	1829(4)	33(1)
C(22′)	11265(5)	6018(4)	2843(4)	37(1)
C(23′)	10158(6)	4198(5)	4073(4)	41(1)
C(24′)	10852(5)	3488(5)	3600(4)	42(1)
C(25′)	11362(5)	3659(4)	1777(4)	34(1)
C(26′)	11990(5)	4658(4)	1503(4)	33(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates ($\times 10^5$ Ru, S; $\times 10^4$ B, C) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2**

	x	*y*	*z*	*U*(eq)[a]
Ru(3)	88981(2)	21104(2)	41415(2)	25(1)
S(1)	95431(8)	9522(8)	46420(8)	38(1)
S(2)	89708(9)	26998(10)	53875(8)	48(1)
S(3)	101955(8)	26380(9)	40245(9)	44(1)
C(1)	7713(3)	1606(3)	4136(3)	30(1)
C(2)	8672(3)	1558(3)	3056(3)	29(1)
B(4)	7676(4)	2562(4)	4256(4)	35(1)
B(5)	6974(3)	1993(4)	3689(4)	40(2)
B(6)	7667(3)	1345(4)	3194(4)	35(1)
B(7)	8831(4)	2505(4)	2965(3)	38(1)
B(8)	8271(4)	3133(4)	3608(4)	39(2)
B(9)	7222(4)	2984(4)	3418(5)	49(2)
B(10)	7152(4)	2229(4)	2750(4)	50(2)
B(11)	8099(4)	1945(4)	2432(4)	43(2)
B(12)	7900(5)	2947(4)	2669(4)	52(2)
C(21)	9474(5)	1069(4)	5650(3)	69(2)
C(22)	9534(6)	1891(5)	5943(4)	88(3)
C(23)	9675(5)	3418(5)	5327(4)	80(2)
C(24)	10230(6)	3424(6)	4718(6)	113(4)
C(25)	10887(4)	1903(5)	4397(6)	109(4)
C(26)	10595(4)	1119(4)	4468(5)	72(2)
C(101)	7520(3)	1007(3)	4729(3)	32(1)
C(102)	7492(4)	207(3)	4584(4)	53(2)
C(103)	7310(5)	−334(4)	5148(4)	69(2)
C(104)	7130(5)	−82(4)	5855(4)	67(2)
C(105)	7142(4)	713(4)	6019(3)	59(2)
C(106)	7349(4)	1246(4)	5464(3)	47(2)
C(201)	9213(3)	912(3)	2805(3)	33(1)
C(202)	9967(3)	1090(4)	2511(4)	55(2)
C(203)	10465(4)	497(4)	2268(4)	73(2)
C(204)	10248(4)	−288(4)	2313(4)	61(2)
C(205)	9511(4)	−473(4)	2593(3)	52(2)
C(206)	9015(3)	117(3)	2843(3)	42(1)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

non-hydrogen atom thermal parameters, and a full listing of interatomic distances and interbond angles (except those involving H atoms) are available as Supporting Information.

Results and Discussion

Reflux of a methanolic solution of the recently reported complex [Ru{[9]aneS_3-κ^3-*S*,*S*′,*S*″}(NCMe)$_3$][CF_3SO_3]$_2$,[7] prepared from [RuCl_2{[9]aneS_3-κ^3-*S*,*S*′,*S*″}(dmso)][CF_3SO_3] and [Ag][CF_3SO_3] (dmso = dimethyl sulfoxide), with a slight excess of the thallium salts [Tl][Tl$C_2B_9H_{10}$Ph] and [Tl][Tl$C_2B_9H_9Ph_2$] (effectively [7-Ph-7,8-*nido*-$C_2B_9H_{10}$]$^{2-}$ and [7,8-Ph_2-7,8-*nido*-$C_2B_9H_9$]$^{2-}$), results in the precipitation of the first examples of mixed sandwich carborane/thiamacrocycle compounds 1-Ph-3,3,3-[9]aneS_3-κ^3-*S*,*S*′,*S*″-3,1,2-*closo*-Ru$C_2B_9H_{10}$, **1**, and 1,2-Ph_2-3,3,3-[9]aneS_3-κ^3-*S*,*S*′,*S*″-3,1,2-*pseudocloso*-Ru$C_2B_9H_9$, **2**, respectively, in moderate yield. Although both **1** and **2** were initially characterized by multinuclear (^{1}H, ^{11}B, and ^{13}C) NMR spectroscopies, the spectra, particularly in the context of the fluxionality of **1** and the partial fluxionality of **2** in solution, are best related to the respective molecular structures established crystallographically. Discussion of the NMR data is therefore deferred until after the results of the appropriate diffraction study have been presented. Recrystallization of both compounds **1** and **2** from dmso/methanol afforded brown plates and purple blocks, respectively, which were suitable for single-crystal X-ray diffraction studies.

Two independent molecules of compound **1** crystallize in the asymmetric fraction of the unit cell. The molecule is chiral, but the space group is centrosymmetric with equal numbers of molecules of each hand. Figure 2 shows similar views of both crystallographically-independent molecules and demonstrates the atomic numbering scheme. Table 4 lists selected interatomic distances (except those involving H atoms) and interbond angles determined. There is no chemically significant difference between the two independent molecules, so for convenience parameters are discussed for the molecule involving Ru(3) only, with data in square brackets representing differences in respect of the molecule involving Ru(3′).

The {RuC_2B_9} portion of the molecule has the *closo* icosahedral structure anticipated by empirical electron counting rules.[9] The mean Ru−B and Ru−C distances, 2.217 and 2.181 [2.226 and 2.183] Å are marginally longer than those, 2.205 and 2.169 Å, respectively, in the related species 1-Ph-3-(mes)-

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(9) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

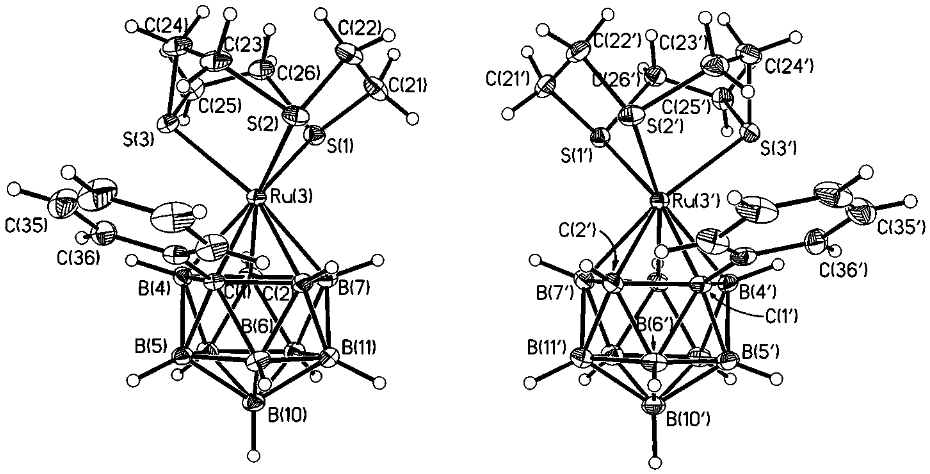

Figure 2. Crystallographically-independent molecules of compound **1**. Thermal elipsoids were drawn at the 30% probability level. H atoms have an artificial radius of 0.1 Å for clarity. The phenyl ring was numbered cyclically. H atoms of the phenyl carborane ligand carry the same number as the atom to which they are attached.

3,1,2-*closo*-$RuC_2B_9H_{10}$[3d] (mes = $C_6H_3Me_3$-1,3,5), but the pattern of distances is similar, with Ru−C(1) > Ru−C(2) and Ru−B(8) the longest Ru−B. Within the carborane ligand the relative lengths of the connectivities are as expected, with C(1)−C(2) 1.688(7) [1.677(7)] Å, C−B 1.702(7)−1.742(7) [1.702(7)−1.751(7)] Å, and B−B 1.740(8)−1.832(9) [1.741(8)−1.841(8)] Å. The conformation of the phenyl substituent (θ), defined[3d] as the modulus of the average C_{cage}−C_{cage}−C−C torsion angle, is 71.0(4) [74.4(4)]°, in excellent accord with that recently measured in the parent carborane 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (65−70°) both in the gaseous phase[10] and in two crystalline modifications.[10,11] The closest intramolecular approach between carborane and [9]aneS_3 ligands involves the *endo*-H atom bound to C(23) which lies only 2.82 [2.74] Å above the phenyl ring plane. Figure 3, a space-filling representation of compound **1**, shows that this contact is just at the van der Waals sum.

In compound **1** the {Ru[9]aneS_3} fragment has near C_3 symmetry with the sulfur atoms coordinated to Ru(3) in tris-*endo*dentate fashion and staggered conformations about the C−C bonds. Although Ru−S distances and S−Ru−S angles are broadly similar to those previously observed in {Ru^{II}[9]aneS_3} fragments,[5b,7,12] close inspection reveals that Ru−S(2) is significantly the longest, and presumably the weakest, such bond. In that Ru−S(2) lies effectively *cis* to cage carbon atoms and consequently effectively *trans* to cage boron atoms, its relative weakness can be ascribed to the differeing *trans* influences of C_{cage} and B_{cage} in such systems established by previous structural studies.[2a,3d,13] The [9]aneS_3 ligand displays staggered conformations about all three C−C bonds, with S−C−C−S torsion angles of 47.3(5), 46.4(5), and 47.8(5) [-47.7(5), −46.5(5), and −48.1(5)]°.

The $^{11}B\{^1H\}$ NMR spectrum of compound **1** is fully consistent with the crystallographically-determined molecular structure, there being seven signals of relative integration 1:1:1:1:1:3:1 (high frequency to low frequency), the penultimate signal representing a triple coincidence. The range of ^{11}B chemical shifts, +2.1 to −23.2 ppm, is fully consistent with a metal carborane compound with a *closo* structure.[3b,e,f] The ^1H NMR spectrum displays the expected resonances due to the cage C−*H* atom and the aromatic protons of one phenyl group. However, only four multiplets, each with an integral equivalent to three protons, are observed between 2.8 and 1.6 ppm attributable to the thioether methylene groups [we ascribe the lowest frequency methylene signal to the *endo* protons bound to C(21), C(23) and C(25) as a consequence of the proximity ot the cage phenyl ring]. Moreover, the $^{13}C\{^1H\}$ NMR spectrum displays only two signals (36.0 and 31.5 ppm) due to the methylene carbon atoms. If the macrocycle were static [that is to say not spinning about the molecular axis from Ru(3) to B(10)], then six signals would be observed in the $^{13}C\{^1H\}$ NMR spectrum due to the reduction in symmetry imposed by the asymmetric carborane moiety. However, if rotation about this axis occurs at a rate which is faster than the NMR time scale only two signals of equal intensity would be expected, due to the equivalence of two sets of three carbon atoms (Figure 4). Such rotation is also fully consistent with the observation in the ^1H NMR spectrum of only four equal integral multiplets arising from the methylene groups of the [9]aneS_3 ligand, each of the two magnetically-inequivalent C atoms carrying non-interconverting *exo* and an *endo* protons.

Only three signals, in the ratio 1:4:1, are observed in the phenyl region of the $^{13}C\{^1H\}$ NMR spectrum of compound **1** at 100.6 MHz. Assuming that the central resonance represents a coincidence this observation is consistent with a rotation of the pendant phenyl group about the C(1)−C(31) bond which is rapid on the NMR time scale at room temperature (a static phenyl group would necessitate the assumption of a quadruply coincident resonance). We suggest that the clear fluxionality of the thioether ligand, and the likely fluxionality of the cage phenyl group, in **1** are correlated, the phenyl group locking into gaps [*e.g.* between S(3) and the *endo*-H atom on C(23)] in the van der Waals surface of the macrocycle in a geared type rotation.[14] All attempts to arrest this fluxionality have been frustrated by the insolubility of the compound in solvents other than dmso.

A perspective view of a single molecule of compound **2** is presented in Figure 5, and Table 5 lists selected interatomic distances and interbond angles determined. The molecule has near-mirror symmetry about the plane containing Ru(3), B(8), B(6), and B(10).

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Table 4. Selected Interatomic Distances (Å) and Interbond Angles (deg) for **1**

Ru(3)−C(1)	2.193(4)	Ru(3′)−C(1′)	2.186(4)
Ru(3)−C(2)	2.170(5)	Ru(3′)−C(2′)	2.179(5)
Ru(3)−B(4)	2.189(5)	Ru(3′)−B(4′)	2.190(5)
Ru(3)−B(7)	2.214(6)	Ru(3′)−B(7′)	2.236(5)
Ru(3)−B(8)	2.249(5)	Ru(3′)−B(8′)	2.252(5)
Ru(3)−S(1)	2.3207(12)	Ru(3′)−S(1′)	2.3224(12)
Ru(3)−S(3)	2.3280(13)	Ru(3′)−S(3′)	2.3349(13)
Ru(3)−S(2)	2.3623(12)	Ru(3′)−S(2′)	2.3616(13)
S(1)−C(21)	1.817(5)	S(1′)−C(21′)	1.818(5)
S(1)−C(26)	1.837(5)	S(1′)−C(26′)	1.847(5)
S(2)−C(22)	1.829(5)	S(2′)−C(22′)	1.838(5)
S(2)−C(23)	1.826(6)	S(2′)−C(23′)	1.828(6)
S(3)−C(25)	1.831(5)	S(3′)−C(25′)	1.833(5)
S(3)−C(24)	1.840(5)	S(3′)−C(24′)	1.845(6)
C(1)−C(31)	1.508(6)	C(1′)−C(31′)	1.499(6)
C(1)−C(2)	1.688(7)	C(1′)−C(2′)	1.677(7)
C(1)−B(5)	1.710(7)	C(1′)−B(5′)	1.721(7)
C(1)−B(6)	1.731(7)	C(1′)−B(6′)	1.750(7)
C(1)−B(4)	1.737(7)	C(1′)−B(4′)	1.751(7)
C(2)−B(11)	1.702(7)	C(2′)−B(11′)	1.702(7)
C(2)−B(7)	1.718(8)	C(2′)−B(7′)	1.722(8)
C(2)−B(6)	1.742(7)	C(2′)−B(6′)	1.745(7)
B(4)−B(9)	1.791(7)	B(4′)−B(9′)	1.766(7)
B(4)−B(8)	1.792(8)	B(4′)−B(8′)	1.780(8)
B(4)−B(5)	1.797(7)	B(4′)−B(5′)	1.803(8)
B(5)−B(6)	1.742(8)	B(5′)−B(6′)	1.748(9)
B(5)−B(10)	1.766(8)	B(5′)−B(10′)	1.761(8)
B(5)−B(9)	1.779(8)	B(5′)−B(9′)	1.776(8)
B(6)−B(10)	1.740(8)	B(6′)−B(10′)	1.741(8)
B(6)−B(11)	1.769(8)	B(6′)−B(11′)	1.756(8)
B(7)−B(12)	1.785(8)	B(7′)−B(12′)	1.783(8)
B(7)−B(11)	1.803(8)	B(7′)−B(11′)	1.802(8)
B(7)−B(8)	1.832(9)	B(7′)−B(8′)	1.841(8)
B(8)−B(9)	1.791(8)	B(8′)−B(9′)	1.791(8)
B(8)−B(12)	1.803(8)	B(8′)−B(12′)	1.799(8)
B(9)−B(12)	1.774(8)	B(9′)−B(12′)	1.783(9)
B(9)−B(10)	1.773(8)	B(9′)−B(10′)	1.786(9)
B(10)−B(11)	1.764(8)	B(10′)−B(11′)	1.760(8)
B(10)−B(12)	1.779(8)	B(10′)−B(12′)	1.780(8)
B(11)−B(12)	1.777(8)	B(11′)−B(12′)	1.778(9)
C(21)−C(22)	1.518(8)	C(21′)−C(22′)	1.508(8)
C(23)−C(24)	1.500(8)	C(23′)−C(24′)	1.511(8)
C(25)−C(26)	1.501(8)	C(25′)−C(26′)	1.495(7)

C(2′)−Ru(3′)−C(1′)	45.2(2)	C(2)−Ru(3)−C(1)	45.5(2)
C(1)−Ru(3)−B(4)	46.7(2)	C(1′)−Ru(3′)−B(4′)	47.2(2)
C(2)−Ru(3)−B(7)	46.1(2)	C(2′)−Ru(3′)−B(7′)	45.9(2)
B(4)−Ru(3)−B(8)	47.6(2)	B(4′)−Ru(3′)−B(8′)	47.2(2)
B(7)−Ru(3)−B(8)	48.5(2)	B(7′)−Ru(3′)−B(8′)	48.4(2)
S(1)−Ru(3)−S(3)	86.49(5)	S(1′)−Ru(3′)−S(3′)	86.37(4)
S(1)−Ru(3)−S(2)	86.81(5)	S(1′)−Ru(3′)−S(2′)	86.73(4)
S(3)−Ru(3)−S(2)	86.27(5)	S(3′)−Ru(3′)−S(2′)	85.99(5)
C(21)−S(1)−C(26)	100.8(3)	C(21′)−S(1′)−C(26′)	100.9(2)
C(21)−S(1)−Ru(3)	103.1(2)	C(21′)−S(1′)−Ru(3′)	103.0(2)
C(26)−S(1)−Ru(3)	107.4(2)	C(26′)−S(1′)−Ru(3′)	107.2(2)
C(22)−S(2)−C(23)	100.8(3)	C(22′)−S(2′)−C(23′)	101.2(3)
C(22)−S(2)−Ru(3)	106.3(2)	C(22′)−S(2′)−Ru(3′)	106.2(2)
C(23′)−S(2′)−Ru(3′)	104.0(2)	C(23)−S(2)−Ru(3)	103.5(2)
C(25)−S(3)−C(24)	99.8(3)	C(25′)−S(3′)−C(24′)	100.2(3)
C(25)−S(3)−Ru(3)	103.5(2)	C(25′)−S(3′)−Ru(3′)	103.5(2)
C(24)−S(3)−Ru(3)	107.4(2)	C(24′)−S(3′)−Ru(3′)	107.6(2)
C(22)−C(21)−S(1)	114.2(4)	C(22′)−C(21′)−S(1′)	114.2(4)
C(21)−C(22)−S(2)	111.1(4)	C(21′)−C(22′)−S(2′)	111.0(3)
C(24)−C(23)−S(2)	113.7(4)	C(24′)−C(23′)−S(2′)	113.1(4)
C(23)−C(24)−S(3)	111.8(4)	C(23′)−C(24′)−S(3′)	111.6(4)
C(26)−C(25)−S(3)	113.1(4)	C(26′)−C(25′)−S(3′)	113.0(4)
C(25)−C(26)−S(1)	110.7(4)	C(25′)−C(26′)−S(1′)	110.8(3)

It is immediately apparent that **2** is a *pseudocloso* metal carborane.[3a,e,f] Although in the parent carborane 1,2-Ph_2-1,2-*closo*-$C_2B_{10}H_{10}$[15] the phenyl rings adopt conformations defined by very low θ values (average θ for two crystallographically-independent molecules with no imposed symmetry is 5.5°) the phenyl groups in **2** are required to have high θ values [$\theta_{C(101-106)} = 53.4(4)$, $\theta_{C(201-206)} = 53.9(4)°$] by the steric demands of the [9]aneS_3 ligand, and the Ph···Ph repulsion thus generated results in stretching of the C(1)−C(2) connectivity to 2.504(7) Å. Figure 6, a space-filling representation of **2** in the same orientation as Figure 5, clearly shows touching phenyl rings even with C(1)···C(2) extended [H(102)···H(206) is 2.43 Å]. Prizing open the C(1)−C(2) connectivity is accompanied by a shortening of the the Ru(3)···B(6) distance, to 2.960(6) Å, the overall result being the formation of a nearly square C(1)-Ru(3)C(2)B(6) polyhedral face. Figure 7 contrasts key molecular parameters in this four-atom fragment of compound **1**

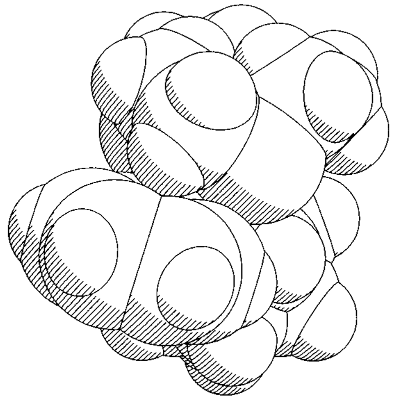

Figure 3. Space-filling representation of compound **1** [molecule containing Ru(3)]. van der Waals radii used (Å): S, 1.80; B, 1.70; H, 1.20; C(non-Ph), 1.70; C(Ph), 1.85.

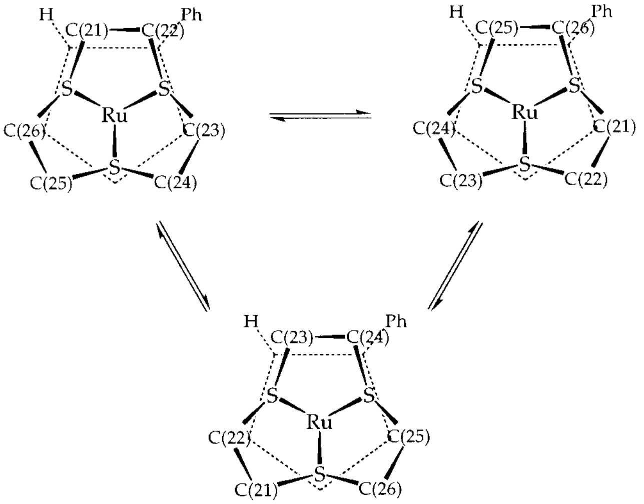

Figure 4. Rotation of the [9]aneS_3 ligand in compound **1**. Dashed lines indicate upper face of carborane ligand.

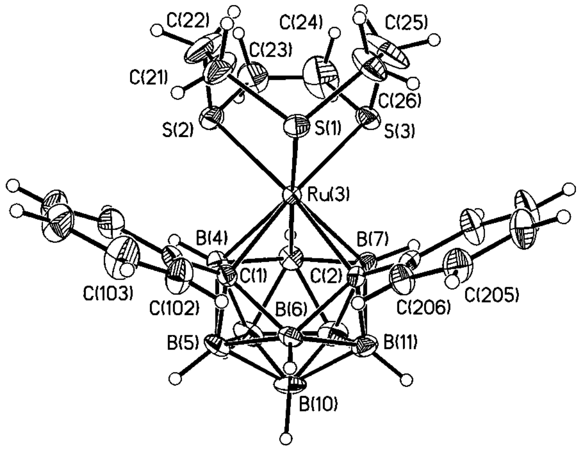

Figure 5. Perspective view of compound **2**. Construction and labeling conventions are as in Figure 2.

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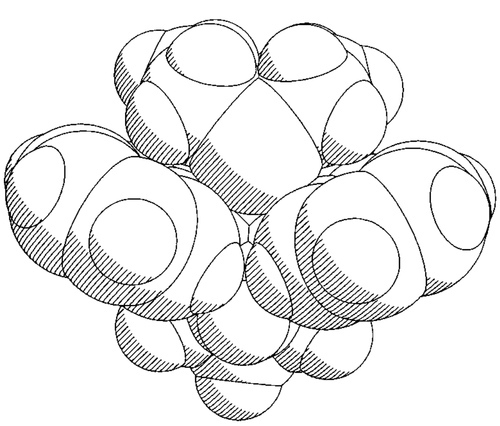

Figure 6. Space-filling representation of a single molecule of compound **2**. Radii are as in Figure 3.

Table 5. Selected Interatomic Distances (Å) and Interbond Angles (deg) for **2**

Ru(3)−C(1)	2.163(5)	Ru(3)−C(2)	2.175(5)
Ru(3)−B(7)	2.196(6)	Ru(3)−B(4)	2.197(6)
Ru(3)−B(8)	2.234(6)	Ru(3)−S(3)	2.3607(14)
Ru(3)−S(2)	2.365(2)	Ru(3)−S(1)	2.4072(14)
S(1)−C(21)	1.805(6)	S(1)−C(26)	1.813(6)
S(2)−C(22)	1.817(7)	S(2)−C(23)	1.823(7)
S(3)−C(24)	1.812(8)	S(3)−C(25)	1.824(7)
C(1)−C(101)	1.497(7)	C(1)−B(5)	1.610(7)
C(1)−B(4)	1.632(7)	C(1)−B(6)	1.730(8)
C(2)−C(201)	1.488(7)	C(2)−B(11)	1.606(8)
C(2)−B(7)	1.630(8)	C(2)−B(6)	1.741(7)
B(4)−B(8)	1.803(9)	B(4)−B(9)	1.816(9)
B(4)−B(5)	1.823(9)	B(5)−B(10)	1.741(10)
B(5)−B(9)	1.792(9)	B(5)−B(6)	1.822(9)
B(6)−B(11)	1.839(9)	B(6)−B(10)	1.898(9)
B(7)−B(12)	1.809(9)	B(7)−B(11)	1.815(9)
B(7)−B(8)	1.821(9)	B(8)−B(12)	1.807(10)
B(8)−B(9)	1.809(9)	B(9)−B(10)	1.747(11)
B(9)−B(12)	1.750(11)	B(10)−B(12)	1.752(10)
B(10)−B(11)	1.753(10)	B(11)−B(12)	1.776(10)
C(21)−C(22)	1.488(10)	C(23)−C(24)	1.426(10)
C(25)−C(26)	1.419(11)		

C(1)−Ru(3)−C(2)	70.5(2)	C(2)−Ru(3)−B(7)	43.8(2)
C(1)−Ru(3)−B(4)	44.0(2)	B(7)−Ru(3)−B(8)	48.5(2)
B(4)−Ru(3)−B(8)	48.0(2)	S(3)−Ru(3)−S(2)	84.41(5)
S(3)−Ru(3)−S(1)	85.74(5)	S(2)−Ru(3)−S(1)	85.18(5)
C(21)−S(1)−C(26)	102.4(4)	C(21)−S(1)−Ru(3)	104.4(2)
C(26)−S(1)−Ru(3)	104.4(2)	C(22)−S(2)−C(23)	101.3(4)
C(22)−S(2)−Ru(3)	107.7(2)	C(23)−S(2)−Ru(3)	104.1(2)
C(24)−S(3)−C(25)	103.5(5)	C(24)−S(3)−Ru(3)	104.3(3)
C(25)−S(3)−Ru(3)	107.2(3)	C(22)−C(21)−S(1)	116.4(5)
C(21)−C(22)−S(2)	113.1(5)	C(24)−C(23)−S(2)	118.2(5)
C(23)−C(24)−S(3)	119.3(6)	C(26)−C(25)−S(3)	116.7(5)
C(25)−C(26)−S(1)	119.7(5)		

(average of two crystallographically-independent molecules) with those in compound **2**.

Ru−S distances in **2** (one of *ca.* 2.41 Å, two of *ca.* 2.36 Å) are consistently *ca.* 0.04 Å longer than those in **1**, the longest, Ru(3)−S(1), again being to that sulfur atom which lies effectively *cis* to the cage carbon atoms. Both phenyl rings lie under and reasonably close to an *endo*-H atom of the [9]aneS$_3$ ligand [C(21)-H···C(101−106) plane = 2.84 Å, C(26)−H···C(201−206) plane = 2.97 Å]. Such interligand crowding affords the thiamacrocycle a conformation with *apparent* C_s (not C_3) symmetry, having torsion angles of opposite sign about C(25)−C(26), −29.6(6)°, and C(21)−C(22), 42.6(6)°, and a near-eclipsed conformation about C(23)−C(24), torsion angle 1.4(6)°. Note, however, that *U*(eq) values for C(24) and C(25) are relatively large; although this suggests partial disorder of these atoms, we were not able successfully to refine such a disorderd model.

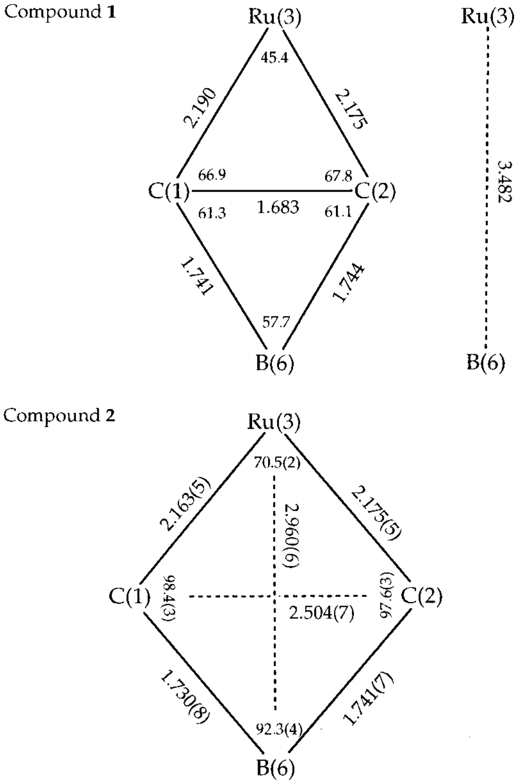

Figure 7. Geometrical details (Å and deg) in the faces defined by Ru(3), C(1), B(6) and C(2) in the *closo* compound **1** (average of two crystallographically-independent molecules) and the *pseudocloso* compound **2**.

Previously we observed *pseudocloso* metal carborane structures for 1,2-Ph$_2$-3-L-3,1,2-MC$_2$B$_9$ skeletons in which L is an η-bonded cyclic polyene ligand [M = Rh, L = Cp*[3a] (Cp* = η^5-C$_5$Me$_5$) and Indy*[3f] (Indy* = η^5-C$_9$Me$_7$); M = Ir, L = Cp*[3e]; M = Ru, L = η^6-C$_6$H$_6$, η^6-C$_6$Me$_6$ and η^6-C$_6$H$_4$(Me)^{i}Pr-1,4[3e]]. Compound **2** represents the first *pseudocloso* metal carborane in which the *exo*polyhedral ligand is simply σ-bonded to the M(3) vertex. In keeping with established *pseudocloso* metal carboranes the weighted average ^{11}B NMR chemical shift in **2**, +8.18 ppm, lies substantially to high frequency of that in the otherwise analogous compound **1**, −8.34 ppm. By analogy with the experimentally assigned (*via* ^{11}B COSY) spectrum of 1,2-Ph$_2$-3-Indy*-3,1,2-RhC$_2$B$_9$H$_9$,[3f] the specific ^{11}B NMR resonances of compound **2** are δ 25.5 [B(8)], 18.0 [B(5,11)], 13.2 [B(10)], 4.5 [B(4,7)], 2.0 [B(9,12)] and −17.1 [B(6)] ppm.

The ^{1}H NMR spectrum of **2** reveals resonances due to 10 methylene protons betwen 2.9 and 2.1 ppm, with a further, low frequency, resonance due to 2 protons at 1.12 ppm. We ascribe the last to the thiamacrocycle H atoms which lie above the cage phenyl rings. In the ^{13}C{^{1}H} NMR spectrum there are three equal intensity *C*H$_2$ resonances between 36.2 and 31.8 ppm, clearly consistent with the crystallographically determined structure of **2** and showing unequivocally that the [9]aneS$_3$ ligand is not rapidly rotating about the Ru(3)···B(10) axis.

Only three signals (integral-2 doublet, integral-2 apparent triplet and integral-1 triplet) are observed in the aromatic region of the ^{1}H spectrum, and there are only four resonances (1:2:2:1) between 152.7 and 124.6 ppm in the ^{13}C{^{1}H} spectrum. Although these patterns could result from coincident resonances arising from nonrotating phenyl groups (two coincidences in the ^{1}H spectrum and two in the ^{13}C spectrum), an alternative explanation is that the phenyl groups in **2** *are* spinning about the C$_{\text{cage}}$−C$_{\text{phenyl}}$ bonds in solution, in spite of the apparent crowding in Figure 6.

Thus the fluxionalities of **1** and **2** in solution appear to be different in that both polyhedral substituents spin in **1** while only the phenyl groups apparently spin in **2**. On the basis of the crowding between [9]aneS_3 ligand and phenyl groups revealed (Figure 6) in the crystallographic study of **2** it appears likely that substantial libration of the macrocycle about the metal···cage axis is necessary to allow the phenyl rings to rotate. Once again, further study of this system has been frustrated by the very low solubility of **2** in solvents other than dmso.

Conclusions

The first examples of mixed sandwich carborane/thiamacrocycle compounds have been synthesised and characterized, including molecular structure determinations. Compound **1** is a *closo* metal carborane with [9]aneS_3 substituents that are both fluxional in dmso solution at room temperature, whereas compound **2** is a *pseudocloso* metal carborane in which, in dmso at room temperature, the phenyl rings only appear to be spinning. These mixed-sandwich compounds presage a large family of similar species with potentially interesting structural and spectroscopic properties, and we are currently working to develop this area of metal carborane chemistry.

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Supporting Information Available: Tables of anisotropic displacement factors, hydrogen atom coordinates, and interatomic distances and angles for complexes **1** and **2** (16 pages). Ordering information is given on any current masthead page.

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