

The 16-electron dithiolene complexes (*p*-cymene) $M[S_2C_2(B_{10}H_{10})]$ ($M = Ru, Os$) containing both η^6 -(*p*-cymene) and η^2 -(*ortho*-carborane-dithiolate): adduct formation with Lewis bases, and X-ray crystal structures of (*p*-cymene)- $Ru[S_2C_2(B_{10}H_{10})](L)$ ($L = PPh_3$) and $\{(p\text{-cymene})\text{-}Ru[S_2C_2(B_{10}H_{10})]\}_2(\mu\text{-}LL)$ ($LL = Ph_2PCH_2CH_2PPh_2$ and N_2H_4)

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Abstract

The reaction of the η^6 -arene complexes $[(p\text{-cymene})MCl_2]_2$ ($M = Ru, Os$; *p*-cymene = 4-isopropyl-toluene) with dilithium 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate (**a**) leads to the new 16e dithiolene complexes (*p*-cymene) $M[S_2C_2(B_{10}H_{10})]$ ($M = Ru$ (**1**), Os (**1A**)). Addition of monodentate Lewis bases (L) to **1** gives 18e dithiolate complexes of the type (*p*-cymene) $Ru[S_2C_2(B_{10}H_{10})](L)$ ($L = PPh_3$ (**2**), $P(OMe)_3$ (**3**), NH_3 (**4**), NC_5H_5 (**5**), CO (**6**), CN^tBu (**7**), SEt_2 (**8**), SC_4H_8 (**9**), CN^- (**10**) and SCN^- (**11**)), whereas bidentate bridging Lewis bases (LL) give centrosymmetric binuclear analogues, $\{(p\text{-cymene})Ru[S_2C_2(B_{10}H_{10})]\}_2(LL)$ ($LL = Ph_2PCH_2CH_2PPh_2$ (**12**), N_2H_4 (**13**) and 4,4'-dipyridine (**14**)). The stability of the Lewis base adducts depends on the nature of the ligating atom and decreases in the order $C > P > N > S > O$. The adducts were characterized by their 1H -, ^{13}C - and ^{11}B -NMR spectra, and X-ray crystal structures were determined for **2**, **12** and **13**. The phosphane ligands in **2** and **12** cause stronger folding of the planar dithiolene ring RuS_2C_2 in **1** along the $S\cdots S$ vector (by 25.6° in **2** and 21.0° in **12**) than the hydrazine ligand in **13** (7.5°). © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Osmium; *p*-Cymene complexes; *ortho*-Carborane-dithiolato complexes; X-ray

1. Introduction

The voluminous and chemically robust chelate ligand 1,2-dicarba-*closo*-dodecaborane-1,2-dithiolate (*ortho*-carborane dithiolate) has been repeatedly used in coordination compounds, and complexes of Mo [1], Re [1], Co [2], Ni [2,3], Pd [1,4], Pt [5] and — in particular — Au [6–9] have been characterized. However, only a few organometallic complexes are known, in general half-sandwich cyclopentadienyl or pentamethylcyclopentadienyl metal compounds with $CpMo$ [1], $CpCo$ [10] and Cp^*Rh [11] moiety. Among them, the 16-electron di-

thiolene complexes $CpCo[S_2C_2(B_{10}H_{10})]$ [10] and $Cp^*Rh[S_2C_2(B_{10}H_{10})]$ [11] are of particular interest because they contain an almost planar pseudoaromatic metallacycle MC_2S_2 ; two diselenolene analogues, $Cp^*M[Se_2C_2(B_{10}H_{10})]$ ($M = Rh$ [11], Ir [12]) have also been described. We now extend the series of 16-electron dithiolenes to the η^6 -arene complexes (*p*-cymene)- $M[S_2C_2(B_{10}H_{10})]$ ($M = Ru$ (**1**), Os (**1A**), *p*-cymene = 4-isopropyl-toluene). The 16-electron complexes take up Lewis bases to give coordinatively saturated 18-electron adducts, in which the dihedral angle MS_2/S_2C_2 at the $S\cdots S$ vector is apparently smaller than 180° . In the present paper, we describe a series of adducts of **1** with selected two-electron ligands; in three typical cases the molecular structure has been confirmed by X-ray structure analyses.

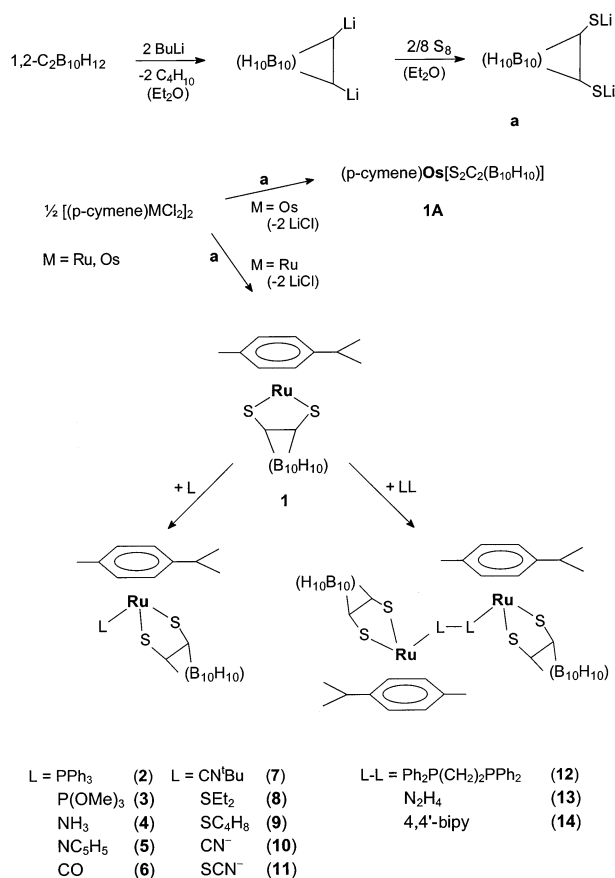
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2. Results and discussion

2.1. Syntheses

The dilithiated *o*-carborane dithiolate $\text{Li}_2[\text{S}_2\text{C}_2\text{-(B}_{10}\text{H}_{10})]$ (**a**) is conveniently prepared by insertion of



Scheme 1.

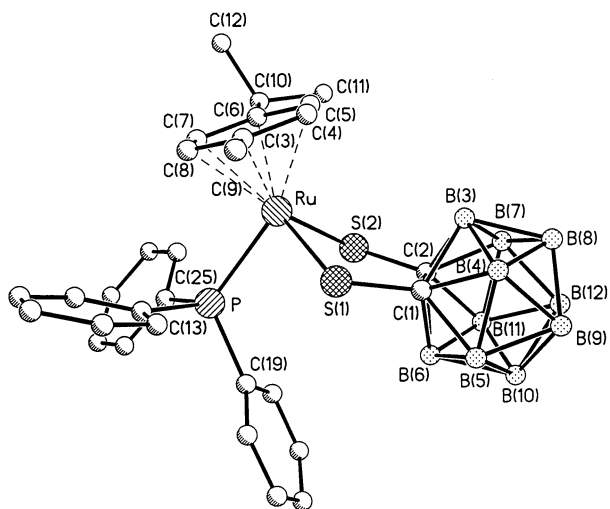


Fig. 1. Molecular structure of $(p\text{-cymene})\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})](\text{PPh}_3)$ (**2**) (hydrogen atoms are omitted for clarity).

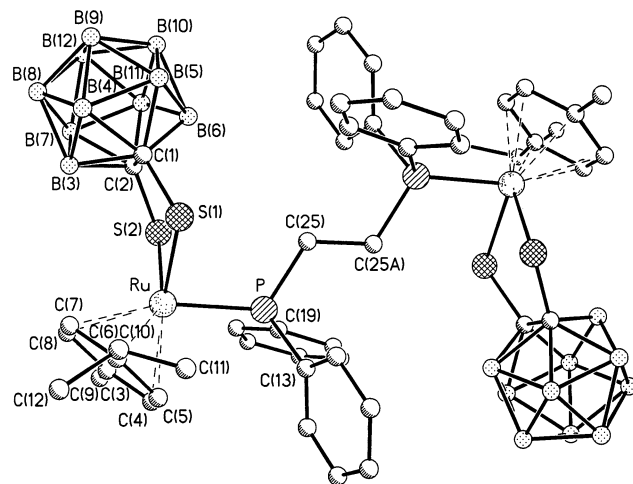


Fig. 2. Molecular structure of $\{(p\text{-cymene})\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (**12**) (hydrogen atoms are omitted for clarity).

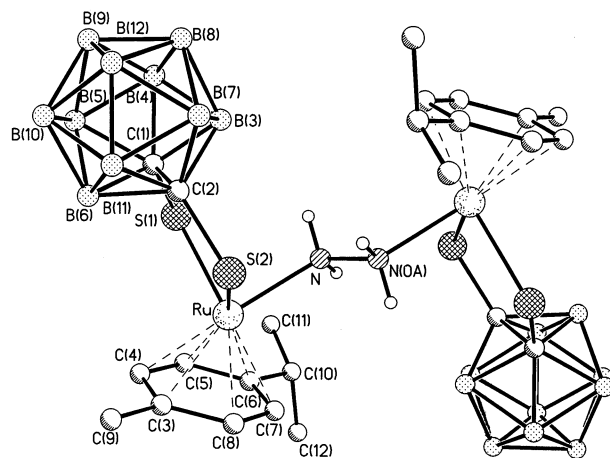


Fig. 3. Molecular structure of $\{(p\text{-cymene})\text{Ru}[\text{S}_2\text{C}_2(\text{B}_{10}\text{H}_{10})]\}_2(\mu\text{-N}_2\text{H}_4)$ (**13**) (hydrogen atoms are omitted for clarity except at N_2H_4).

sulfur into the C–Li bonds of the dilithiated *o*-carborane (Scheme 1). Stoichiometric reaction of **a** with the binuclear $\eta^6\text{-(}p\text{-cymene)}$ complexes $[(\text{Me-C}_6\text{H}_4\text{-Pr})\text{-MCl}_2]_2$ (M = Ru, Os) in THF solution leads in a straightforward way to the 16-electron complexes **1** and **1A** which are thermally stable up to 200°C.

Both the ^1H - and the ^{13}C -NMR data of **1** and **1A** are consistent with the monomeric, coordinatively unsaturated 16-electron structure. The electron impact mass spectra (EI-MS) show the mononuclear molecular ion as the parent peak and very little fragmentation. It is known that metalladithiolene 16-electron half-sandwich complexes can dimerize in order to reach the coordinatively saturated 18-electron configuration, if the steric situation allows it. Thus, a monomer–dimer equilibrium has been reported for the benzene–1,2-dithiolato complexes $\text{CpCo}[\text{S}_2\text{C}_6\text{H}_4]$ [13] and $(p\text{-cymene})\text{-Ru}[\text{S}_2\text{C}_6\text{H}_4]$ [14,15], although the X-ray structure

analysis of $(C_6Me_6)Ru[S_2C_6H_4]$ indicates a monomer [14]. Dimeric structures have also been characterized for ferrocene-1,1'-dithiolato and -diselenolato complexes such as $Cp^*Ir[(EC_5H_4)_2Fe]$ ($E = S, Se$) [16] in the solid state. However, in the case of the bulky *ortho*-carborane-dithiolate ligand, the dimerization appears to be excluded for steric reasons [10].

The 16-electron complexes **1** and **1A** react with Lewis bases (L) to give 18-electron adducts in which the pseudoaromatic metalladithiolene structure is more or less disturbed. This leads to bending of the originally planar MS_2C_2 ring along the S...S vector, as was shown by X-ray structure analysis in the case of the comparable adduct formation of the iridadiselenolene complex $Cp^*Ir[SeC_2(B_{10}H_{10})]$ with trimethylphosphane [12].

A series of adducts was prepared starting from the blue ruthenium complex **1** and various two-electron ligands with phosphorus (**2**, **3**, **12**), nitrogen (**4**, **5**, **13**, **14**), carbon (**6**, **7**), and sulfur (**8**, **9**) as ligating atoms (Scheme 1). Attempts to isolate adducts with oxygen-ligands (e.g. 4-picoline-*N*-oxide, dimethylsulfoxide) under comparable conditions were unsuccessful, although

reversible adduct formation clearly takes place in CH_2Cl_2 solution, as indicated by the color change from blue to brown-red. The sulfur ligands (diethylsulfide and tetrahydrothiophene) give brown-red adducts (**8**, **9**) which can be isolated, but the color of their CH_2Cl_2 solution is blue due to **1** unless an excess of the sulfide ligand is added. The more volatile dimethylsulfide easily evaporates from its solid adduct, and the blue powder of **1** remains back. The anionic adduct of **1** with thiocyanate (**11**) could only be studied in the presence of an excess of NaSCN in the NMR tube in CD_3CN solution.

The 18-electron adducts $(p\text{-cymene})Ru[S_2C_2(B_{10}H_{10})](L)$ (with labile ligands $L = NH_3$ (**4**), NC_5H_5 (**5**), SEt_2 (**8**), SC_4H_8 (**9**)) can be considered as the coordinatively stabilized derivatives of the 16-electron complex **1** which is easily reformed under vacuum or in solution. In a similar manner, the 16-electron 1,2-dithiolate complex $(C_6Me_6)Ru[S_2C_6H_4]$ [14] undergoes reversible adduct formation, and the chiral 16-electron hydrogenation catalyst $(p\text{-cymene})Ru[HN-CH(Ph)CH(Ph)-NSO_2C_6H_4-p-CH_3]$ may also be generated from suitable 18-electron precursors [17].

Table 1
Characterization

Complex	Yield	IR (KBr) $\nu(B,H)$ [cm^{-1}]	<i>Hetero-NMR</i>		NMR-solvent
			$\delta(^{11}B)$	Ligand L	
<i>(p</i> -Cymene)- $Ru[S_2C_2(B_{10}H_{10})]$ (1)	56% dec. 205°C	2613, 2589, 2578, 2549	−6.4, −7.5, −9.2		$CDCl_3$
<i>(p</i> -Cymene)- $Os[S_2C_2(B_{10}H_{10})]$ (1A)	80% dec. 210°C	2613, 2592, 2580, 2562	−5.5, −7.4, −8.6		$CDCl_3$
<i>(p</i> -Cymene) $Ru[S_2C_2(B_{10}H_{10})](L)$					
$L = PPh_3$ (2)	89% dec. 196°C	2592, 2576, 2561	−5.3, −7.0, −9.1, −11.3	33.2 (^{31}P)	CD_2Cl_2
$P(OMe)_3$ (3)	95% dec. 147°C	2599, 2586, 2574, 2563, 2553	−1.1, −5.9, −9.5, −10.6	137.4 (^{31}P)	$CDCl_3$
NH_3 (4)	56% dec. > 110°C	2586, 3333 and 3306 (NH_3)	−8.1, −9.9, −11.9		$CDCl_3$
Pyridine (5)	66% dec. 178°C	2569	−6.7, −8.7, −11.6		$CDCl_3$
CO (6)	100% dec. 130°C	2632, 2587, 2560 2012 (CO)	−1.9, −4.0, −5.4, −7.0, −8.6, −9.7, −11.6	194.8 (^{13}C)	CD_2Cl_2
$C\equiv N^tBu$ (7)	90%	2563 2148 (CN^tBu)	−5.6, −7.3, −8.7, −9.8, −11.7	30.8, 58.2 (^{13}C)	$CDCl_3$
SEt_2 (8)	>90%	2622, 2592, 2564, 2542	−7.3, −9.3, −11.4		$CDCl_3$
SC_4H_8 (9)	>90%	2578, 2557	−7.2, −9.2, −11.3		$CDCl_3$
CN^- (10)	83%	2576, 2080 (CN^-)	−2.6, −7.7, −9.4, −11.8, −13.0		CD_3CN
SCN^- (11) ^a			−2.9, −7.4, −9.1, −11.2, −13.1	101.5 (^{13}C)	CD_3CN
$LL = Ph_2P(CH_2)_2PPh_2$ (12)	92% dec. 225°C	2585, 2556	−6.2, −11.1 (br)	35.6 (^{31}P)	CD_2Cl_2
N_2H_4 (13)	66% dec. 155°C	2583, 3315 and 3219 (NH)	−6.4, −8.0, −9.5, −11.2		$CDCl_3$
4,4'-Bipyridine (14)	90% dec. 220°C	2634, 2576	−7.1, −9.5, −11.8		CD_2Cl_2

^a NMR tube experiment.

Table 2
¹H- and ¹³C-NMR data

Compound	¹ H-NMR				L	¹³ C-NMR				Carborane	L
	<i>p</i> -Cymene					<i>p</i> -Cymene					
	CH ₃	CHMe ₂ ^a	C ₆ H ₄			CH ₃	CHMe ₂	C ₆ H ₄ ^{a,g}			
<i>p</i> -Cymene ^b	2.53s	1.46d(6.9) 3.08sp(6.9)	7.32s			20.9	24.1	126.3, 129.0 {135.1, 145.8}			
1 ^b	2.18s	1.14d(7.0) 2.57sp(6.9)	5.54s	33.7		20.2	23.1	79.4, 81.3 {93.88, 104.1}	93.7		
1A ^b	2.37s	1.27d(6.9) 2.55sp(6.9)	5.92, 5.93 (AA'BB')			20.7	23.4	72.5, 74.9 {87.6, 97.5}	95.9		
2 ^c	2.08s	1.14d(7.0)	5.19, 5.22	7.4m		17.5	23.1	92.8d[5.5], 95.5d[5.5]	93.7	128.2, 130.5	
3 ^b	2.13s	2.52sp(7.0) 1.11d(6.9)	(AA'BB') 5.49d(6.3)	3.70d		17.9	22.6	{104.2s, 114.2s} 93.78, 93.86 93.90, 94.03	92.7	134.6, 135.2 54.2[7.9]	
4 ^b		2.76sp(6.9)	5.62d(6.3)	(³ <i>J</i> (P,H) 10.8 Hz)			30.5	{110.9d[5.4], 113.5}			
4 ^b	2.06s	1.06d(7.0) 2.57sp(7.0)	5.00d(6.0) 5.21d(6.0)	n.o.		18.3	22.6	83.9, 86.6 30.7 {100.5, 106.5}	94.1		
5 ^b	2.02s	1.17d(7.0) 2.54sp(7.0)	5.17d(6.0) 5.28d(6.0)	7.28 7.73 8.82		18.6	22.65 30.7	83.4, 84.4 {~99(?), 106.1}	93.8	124.3 137.3 153.8 194.8	
6 ^c	2.27s	1.22d(7.0) 2.73sp(6.9)	5.78d(6.5) 6.01d(6.5)			18.9	23.2	96.7, 99.3 32.3 {119.9, 123.5}	91.6		
7 ^b	2.18s	1.17d(6.9) 2.58d(6.9)	5.31(6.1) 5.50(6.1)	1.51s		18.1	22.95	90.3, 92.5 31.65 {111.9, 114.5}	93.3	30.8, 58.2	
8 ^b	2.17s	1.23d(7.0) 2.65sp(7.0)	5.46s	1.22t 2.57q (7.3)		19.9	23.0	80.3, 82.4 31.6 {94.9, 105.3}	94.0	14.6(CH ₃) 26.2(CH ₂)	
9 ^b	2.18s	1.22d(7.0) 2.68sp(7.0)	5.44(6.2) 5.46(6.2) (AA'BB')	1.96m 2.84m		19.7	22.7	81.4, 83.1 30.8 {not observed}	94.0	30.8, 31.5	
10 ^d	2.03s	1.14d(6.9) 2.69sp(6.9)	5.05d(6.0) 5.30d(6.0)			18.0	23.0	88.1, 89.3 31.8 {108.4, 108.8}	97.8	n.o. (138.9 free CN [−])	
11 ^{d e}	1.99	1.10d(6.9)	4.98d(6.0)			18.2	22.6	85.3, 87.1	97.7	n.o. (133.4 free SCN [−])	
12 ^c	1.86	2.62sp(6.9) 0.57d(6.6)br 2.40sp(6.9)	5.24d(6.0) 5.09br 5.22br	2.56br 7.4m		17.2	31.2 21.4br 30.1	{100.8, 107.1} 92.4br, 96.1br {100.6, 113.7}	94.3	18.8(C ₂ H ₄) 129.1, 129.2 131.1, 132.3	
13 ^b	2.20s	1.21d(7.0) 2.83sp(7.0)	5.17d(5.8) 5.42d(5.8)	n.o.		18.6	22.8	83.5, 85.5 30.8 {101.5, 107.8}	93.8		
14 ^c	2.10s	1.22d(7.0) 2.56sp(7.0)	5.46s	7.58d(6.0) 8.82d(6.0)	^f						

^a Coupling constants *J*(H,H) in parentheses, *J*(P,C) in square brackets; d = doublet, sp = septet; n.o. = not observed.^b In CDCl₃ solution.^c In CD₂Cl₂ solution.^d In CD₃CN solution.^e NMR tube experiment.^f Not observed due to low solubility in CD₂Cl₂.^g The ¹³C signals of the *p*-cymene carbon atoms without hydrogen are given in curly brackets; the carbon bearing the isopropyl substituent appears at lower field.

As expected, the ammonia complex **4** tends to lose NH₃ unless kept under an atmosphere of ammonia, both in the solid state and in solution. The hydrazine complex **13** is binuclear and more stable than **4**. The higher stability of the binuclear products **12**–**14** is

apparently due to their low solubility. The yellow adduct with pyridine (**5**) gives a green solution in CH₂Cl₂, indicating an equilibrium between **5** and the blue starting compound **1**. The binuclear 4,4'-bipyridine complex **14** precipitates from CH₂Cl₂ as a yellow powder,

whereas the supernatant, bright green solution contains a mixture of the yellow product **14** and the blue starting complex **1**. If methanol is used as a solvent, a brown solution of **14** is formed in the case of LL = 4,4'-bipy. The chelate ligand 2,2'-bipy did not react with **1** under comparable conditions.

The addition reactions of **1** with various Lewis bases indicate a qualitative order of decreasing stability according to the ligating atom $L = C > P > N > S > O$. The EI mass spectra of all addition compounds **2–14**

Table 3
Selected bond lengths [pm] and angles [°]

	2 (L = PPh ₃)	12 (LL = Ph ₂ P(CH ₂) ₂ PPh ₂)	13 (LL = N ₂ H ₄)
<i>Bond distances</i>			
Ru–P	235.0(1)	233.31(9)	
Ru–N			218.8(2)
Ru–S(1)	238.9(1)	240.25(10)	237.85(9)
Ru–S(2)	239.5(1)	239.30(12)	237.55(10)
Ru–C(3)	226.1(4)	226.6(4)	224.7(3)
Ru–C(4)	225.7(4)	222.2(4)	220.4(3)
Ru–C(5)	226.3(4)	224.7(4)	221.4(3)
Ru–C(6)	229.9(3)	227.4(4)	223.5(3)
Ru–C(7)	224.9(3)	226.1(4)	220.4(3)
Ru–C(8)	224.6(3)	224.4(4)	221.5(3)
Ru–Z ^a	177.0	175.4	170.8
S(1)–C(1)	178.9(3)	179.8(4)	178.6(3)
S(2)–C(2)	178.6(3)	177.6(4)	178.5(3)
C(1)–C(2)	164.0(5)	165.1(6)	166.7(6)
C(1)–B(3)	172.1(5)	172.7(7)	172.0(4)
C(1)–B(4)	171.8(5)	172.5(6)	171.5(5)
C(1)–B(5)	172.0(4)	171.8(6)	172.1(4)
C(1)–B(6)	174.6(6)	172.9(6)	173.0(5)
C(2)–B(3)	173.1(7)	172.8(6)	171.6(5)
C(2)–B(6)	174.6(6)	173.9(7)	173.0(5)
C(2)–B(7)	173.1(5)	172.5(7)	171.0(5)
C(2)–B(11)	173.5(5)	172.0(6)	171.2(5)
C(25)–C(25A)		152.5(7)	
N–N(0A)			146.4(5)
<i>Bond angles</i>			
S(1)–Ru–S(2)	86.6(1)	85.57(4)	89.84(3)
S(1)–Ru–P	87.1(1)	92.01(3)	
S(1)–Ru–N			84.34(7)
S(2)–Ru–P	90.5(1)	86.34(4)	
S(2)–Ru–N			86.14(8)
Z–Ru–P	127.7	127.4	
Z–Ru–N			130.0
Z–Ru–S(1)	124.6	124.7	125.6
Z–Ru–S(2)	127.4	127.9	127.0
Ru–S(1)–C(1)	105.8(1)	105.08(14)	106.49(12)
Ru–S(2)–C(2)	105.4(1)	106.02(15)	106.51(13)
Ru–P–C(25)		114.62(12)	
Ru–N–N(0A)			121.4(3)
S(1)–C(1)–C(2)	116.9(2)	116.9(2)	118.2(2)
S(2)–C(2)–C(1)	117.7(2)	116.5(3)	118.3(2)
P–C(25)–C(25A)		117.4(4)	

^a Z is the center of the *p*-cymene ring (C₃–C₈). The ring carbon C(3) carries the methyl, C(8) the isopropyl substituent.

contain the educt **1** as the highest peak together with the ligand L, after dissociation of the adduct under high vacuum.

The ¹H- and ¹³C-NMR spectra of the complexes **1–14** show the expected patterns (Table 2). With respect to free *p*-cymene, the signals of the aromatic protons and of the arene ring carbon atoms are shifted upfield due to π -coordination. It appears that adduct **6** which contains the acceptor ligand L = CO has the ¹H and ¹³C signals of the aromatic part of *p*-cymene at lowest fields. The ¹³C carborane signal can be recognized among the *p*-cymene signal manifold because it is broadened slightly as a result of partial relaxation of the scalar ¹³C–¹¹B spin–spin coupling. The $\delta(^{13}\text{C})$ values observed for the two equivalent carborane carbons in the [S₂C₂(B₁₀H₁₀)] ligand of the neutral ruthenium complexes **2–9** and **12**, **13** remain within a narrow range (between 91 and 95 ppm in CDCl₃ or CD₂Cl₂ solution); the high-field end (91.6) is represented by the carbonyl complex **6**.

2.2. X-ray structure determinations

The molecular structures of the mononuclear complex **2** and the binuclear analogues **12** and **13** are given in Figs. 1–3; characteristic bond lengths and angles are compared in Table 3. The complexes under study possess a (*p*-cymene)–ruthenium half-sandwich tripod structure in which two legs are sulfur atoms from the *o*-carborane dithiolato chelate ligand and the third leg is either P or N.

The binuclear complexes **12** and **13** are centrosymmetric with the inversion center in the middle of the C–C or N–N single bond. The dihedral angle S(1)RuS(2)/S(1)C(1)C(2)S(2) is expected to be 180° in the 16-electron educt **1**, in analogy to the structurally characterized compounds Cp*Co[S₂C₂(B₁₀H₁₀)] [10] and Cp*Ir[Se₂C₂(B₁₀H₁₀)] [12]. This angle at the S··S vector is reduced to 154.4° in the adduct (**2**) with PPh₃ and to 159.0° in the adduct (**12**) with Ph₂PCH₂CH₂PPh₂ (cf. Cp*Rh[S₂C₂(B₁₀H₁₀)](PMe₃) (155.1°) [11], Cp*Ir[Se₂C₂(B₁₀H₁₀)](PMe₃) (156.1°) [12]). However, the dihedral angle at the S··S vector is 172.5° in the adduct (**13**) with hydrazine. The Ru–P (or Ru–N) bond is nearly perpendicular to the S(1)RuS(2) plane (**2**: 87.0°, **12**: 85.7° and **13**: 83.2°).

The N–N distance (146.4(5) pm) in the binuclear hydrazine complex **13** corresponds closely to the analogous distance in {(C₆Me₆)Ru[S₂C₆H₄]}₂(μ -N₂H₄) (145.4(8) pm) [18] and is similar to the values in related hydrazine-bridged ruthenium complexes [cf. 18]. The hydrogen atoms in **13** were localized, and then refined according to the riding model with fixed isotropic temperature factors.

Table 4
Crystal structure determinations

	2	12	13
Empirical formula	C ₃₀ H ₃₉ B ₁₀ PRuS ₂	C ₅₀ H ₇₃ B ₂₀ P ₂ Ru ₂ S ₄ · 2CH ₂ Cl ₂	C ₂₄ H ₅₂ B ₂₀ N ₂ Ru ₂ S ₄
Crystal shape	Dark red prism	Brown irregular	Red platelet
Crystal dimensions (mm)	0.25 × 0.18 × 0.12	0.30 × 0.18 × 0.12	0.30 × 0.18 × 0.08
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Lattice parameters			
<i>a</i> (pm)	1159.2(2)	1073.37(11)	1035.35(9)
<i>b</i> (pm)	2965.6(3)	1163.07(10)	1095.89(11)
<i>c</i> (pm)	1102.6(2)	1552.02(14)	1130.86(9)
α (°)		93.064(7)	77.438(7)
β (°)	117.03(2)	106.573(7)	73.650(7)
γ (°)		112.205(8)	78.805(8)
<i>V</i> (10 ⁶ pm ³); <i>Z</i> ; <i>F</i> (000)	3378.4(9); 4; 1440	1690.7(3); 1; 726	1189.58(18); 1; 546
Absorption coefficient (mm ^{−1})	0.657	0.810	1.061
Diffractometer	Siemens P4(Mo–K α , λ = 71.073 pm; graphite monochromator)		
Scan range [2 θ ; °]; mode	3–55; ω	3–55; ω	3–55; ω
Measured reflections	9465	8948	4122
Independent reflections	7753	7702	4001
Observed reflections	6572(<i>F</i> > 2 σ (<i>F</i>))	6273(<i>I</i> > 2 σ (<i>I</i>))	3654(<i>I</i> > 2 σ (<i>I</i>))
Solution and refinement	SHELXTL-PLUS <i>V</i> . 4.2 (against <i>F</i>)	SHELXTL-PLUS <i>V</i> . 5.1 (against <i>F</i> ²)	SHELXTL-PLUS <i>V</i> . 5.1 (against <i>F</i> ²)
Absorption correction	Empirical (ψ -scan)	Empirical (ψ -scan)	Empirical (ψ -scan)
Min./max. transmission factors	0.4571/0.5179	0.5503/0.9645	0.3684/0.4621
Refined parameters	398	397	263
<i>R</i> values	0.044/0.037 (<i>R</i> / <i>wR</i> ; <i>w</i> ^{−1} = σ^2 (<i>F</i>))	0.140/0.059 (<i>wR</i> ₂ / <i>R</i> ₁)	0.094/0.038 (<i>wR</i> ₂ / <i>R</i> ₁)
Max./min. residual electron density (e 10 ^{−6} pm ^{−3})	0.56/−1.30	2.18/−1.26	1.04/−1.48

3. Experimental

The reactions were carried out under argon in carefully dried solvents. The starting materials Li₂[S₂C₂-(B₁₀H₁₀)] (**a**) [11], [(*p*-cymene)RuCl₂]₂ [19] and [(*p*-cymene)OsCl₂]₂ [20] were prepared according to literature procedures.

Instrumentation: IR spectra: Perkin–Elmer, 983 G. Mass spectra: VARIAN MAT CH7, direct inlet (70 eV). NMR-spectra: Bruker ARX 250 and DRX 500; chemical shifts are given with respect to CHCl₃–CDCl₃ (δ (¹H) = 7.24; δ (¹³C) = 77.0), CHDCl₂–CD₂Cl₂ (δ (¹H) = 5.33; δ (¹³C) = 53.8), external Et₂O–BF₃ (δ (¹¹B) = 0 for Ξ (¹¹B) = 32.083971 MHz), and external 85% aq. H₃PO₄ (δ (³¹P) = 0 for Ξ (³¹P) = 40.480747 MHz).

3.1. (*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)] (**1**)

o-Carborane, C₂B₁₀H₁₂ (144 mg, 1 mmol), was dissolved in 40 ml of diethylether and lithiated by addition of 1.4 ml (2.2 mmol) of the commercially available 1.6 M hexane solution of *n*-butyllithium. The addition of 70 mg (2.2 mmol) sulfur gave a colorless solution of Li₂[S₂C₂(B₁₀H₁₀)] (**a**). Then a solution of 306 mg (0.5 mmol) [(*p*-cymene)RuCl₂]₂ in 120 ml THF was added. The color of the Et₂O–THF solution immediately

changed from orange to blue. The solvents were removed under reduced pressure and the residue was purified by column chromatography on silica. Elution with hexane–CH₂Cl₂ (2:1) produced a blue zone from which 250 mg (56%) **1** were isolated. Dec. > 205°C. EI-MS: *m/z* 442 (100%, M⁺; correct isotope pattern).

3.2. (*p*-Cymene)Os[S₂C₂(B₁₀H₁₀)] (**1A**)

The osmium analogue of **1** was prepared starting from 144 mg (1 mmol) *o*-carborane and 395 mg (0.5 mmol) [(*p*-cymene)OsCl₂]₂ in Et₂O–THF, as described above in Section 3.1. The violet osmium complex was isolated in about 80% yield (425 mg). Dec. > 210°C. EI-MS: *m/z* 531 (100%, M⁺; correct isotope pattern).

3.3. General procedure to prepare the adducts (*p*-cymene)Ru[S₂C₂(B₁₀H₁₀)](*L*); *L* = triphenylphosphane (**2**), trimethylphosphite (**3**), pyridine (**5**), *tert*-butyl isocyanide (**7**), diethyl sulfide (**8**), tetrahydrothiophene (**9**)

The two-electron ligand *L* (0.5 mmol) was added to a solution containing 133 mg (0.3 mmol) of the blue

16-electron dithiolene complex (*p*-cymene)Ru[S₂C₂-(B₁₀H₁₀)] (**1**) in 20 ml CH₂Cl₂. The color changed immediately, indicating adduct formation. The solvent CH₂Cl₂ was evaporated and the residue washed with hexane to remove excess L (yield: 80–90%). Recrystallization from hexane–CH₂Cl₂ mixtures gave the desired adduct (*p*-cymene)Ru[S₂C₂(B₁₀H₁₀)](L) in yields of 80–90% (Table 1).

3.4. (*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)](NH₃) (**4**)

Ammonia gas was bubbled through the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH₂Cl₂, causing an immediate color change to brown–red. A hexane layer was placed on top of the brown–red solution and the reaction tube kept under an atmosphere of NH₃ at room temperature. After 1 week the red crystals of **4** were isolated, yield 52 mg (56%). Elemental analysis C₁₂H₂₇B₁₀NRuS₂ (458.55), Anal. Calc. C, 31.34; H, 5.91; N, 3.05, found C, 30.85; H, 6.04; N, 3.35%.

3.5. (*p*-Cymene)Ru[S₂C₂(B₁₀H₁₀)](CO) (**6**)

In contact with CO the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH₂Cl₂ turned yellow. The yellow product **6** was isolated in nearly quantitative yield.

3.6. K{(p-Cymene)Ru[S₂C₂(B₁₀H₁₀)]}(CN) (**10**)

An excess of KCN (20 mg, 0.3 mmol) was added to the solution of 90 mg (0.2 mmol) **1** in 20 ml of methanol. The deep brown slurry was brought to dryness under reduced pressure and the residue redissolved in CH₂Cl₂. Filtration gave a yellow solution which contained **10**.

3.7. Binuclear adducts {(p-cymene)Ru[S₂C₂-(B₁₀H₁₀)]}₂(μ-LL) (LL = 1,2-bis(diphenyl-phosphino)-ethane (**4**), 4,4'-bipyridine (**14**))

The bidentate bridging ligand LL (0.1 mmol) was added to the blue solution of 90 mg (0.2 mmol) **1** (in 20 ml of dichloromethane for **4** and in 20 ml of methanol for **14**). The product was washed with hexane and (in the case of **14**) with methanol. The yields are around 90%.

3.8. {(p-Cymene)Ru[S₂C₂(B₁₀H₁₀)]}₂(N₂H₄) (**13**)

Hydrazine hydrate, N₂H₄·H₂O (0.1 ml, 2.1 mmol) was added to the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH₂Cl₂. The resulting brown–red mixture was dried by the addition of anhydrous Na₂SO₄. Filtration

of the suspension gave an orange solution, over which a layer of hexane was placed carefully. After 1 week at room temperature the orange crystals which had been formed were harvested. Yield 60 mg (66%). Elemental analysis C₂₄H₅₂B₂₀N₂Ru₂S₄ (915.32), Anal. Calc. C, 31.49; H, 5.73; N, 3.06, found C, 30.80; H, 5.45; N, 3.09%.

3.9. X-ray crystallography

The intensity data for all three complexes were collected on a Siemens P4 diffractometer using Mo–K_α radiation (λ = 71.073 pm, graphite monochromator) at room temperature (296 K). Crystals suitable for X-ray structure determination were sealed in glass capillaries under argon. The refinement of the structures was carried out against *F* in the case of **2**, and against *F*² in the cases of **12** and **13**. All hydrogen atoms were placed in calculated positions and refined isotropically applying the riding model with fixed temperature factors (0.08 Å²). A summary of the refinement parameters is given in Table 4.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper (**2**, **12** and **13**) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 136420 (**2**), CCDC 136419 (**12**) and CCDC 136418 (**13**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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