ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 598 (2000) 142–149

Journal of Organometallic Chemistry

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-cymene*)-Ru[$S_2C_2(B_{10}H_{10})$]}$_2$(μ-LL) (LL = $Ph_2PCH_2CH_2PPh_2$ and N_2H_4)

Max Herberhold *, Hong Yan, Wolfgang Milius

Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, D-95440 Bayreuth, Germany

Received 22 September 1999; received in revised form 29 October 1999

Abstract

The reaction of the η^6-arene complexes [(*p-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-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 ^{1}H-, ^{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···S vector (by 25.6° in **2** and 21.0° in **12**) than the hydrazine ligand in **13** (7.5°).

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*-dodecarborane-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 dithiolene 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···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.

* Corresponding author. Tel.: +49-921-552540; fax: +49-921-552157.

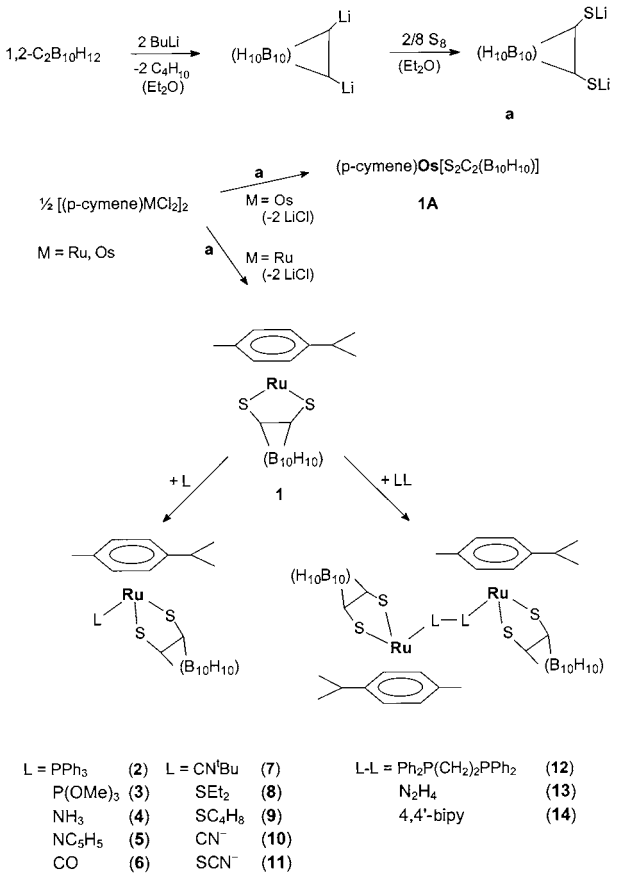
E-mail address: max.herberhold@uni-bayreuth.de (M. Herberhold)

0022-328X/00/$ - see front matter
PII: S0022-328X(99)00692-0

2. Results and discussion

2.1. Syntheses

The dilithiated *o*-carborane dithiolate $Li_2[S_2C_2(B_{10}H_{10})]$ (**a**) is conveniently prepared by insertion of sulfur into the C–Li bonds of the dilithiated *o*-carborane (Scheme 1). Stoichiometric reaction of **a** with the binuclear η^6-(*p-cymene*) complexes $[(Me–C_6H_4–^iPr)MCl_2]_2$ (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.



Scheme 1.

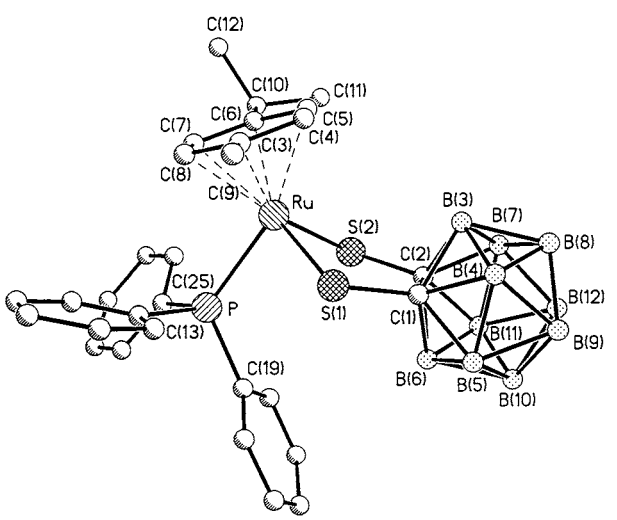


Fig. 1. Molecular structure of (*p-cymene*)$Ru[S_2C_2(B_{10}H_{10})](PPh_3)$ (**2**) (hydrogen atoms are omitted for clarity).

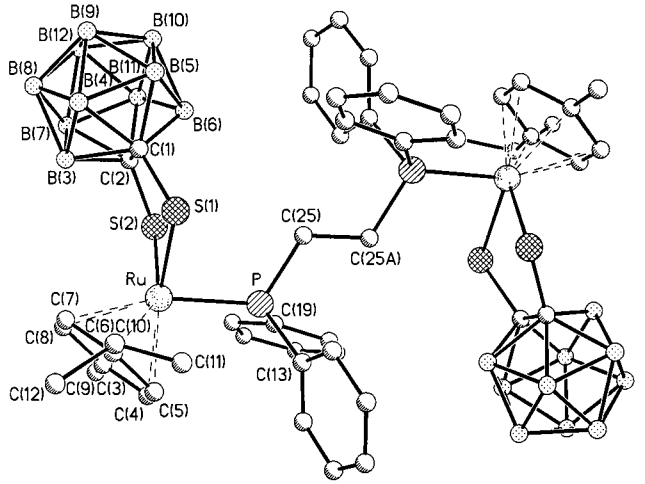


Fig. 2. Molecular structure of {(*p-cymene*)$Ru[S_2C_2(B_{10}H_{10})]\}_2(\mu$-$Ph_2PCH_2CH_2PPh_2$) (**12**) (hydrogen atoms are omitted for clarity).

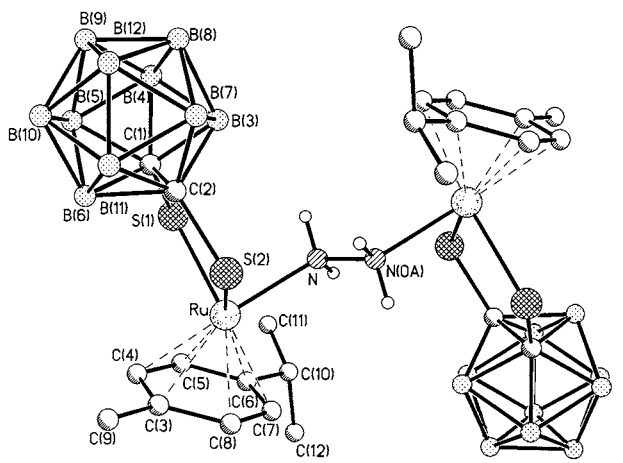


Fig. 3. Molecular structure of {(*p-cymene*)$Ru[S_2C_2(B_{10}H_{10})]\}_2(\mu$-$N_2H_4$) (**13**) (hydrogen atoms are omitted for clarity except at N_2H_4).

Both the ^{1}H- 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 $CpCo[S_2C_6H_4]$ [13] and (*p-cymene*)-$Ru[S_2C_6H_4]$ [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-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-cymene*)$Ru[HN–CH(Ph)CH(Ph)–NSO_2C_6H_4–p\text{-}CH_3]$ may also be generated from suitable 18-electron precursors [17].

Table 1
Characterization

Complex	Yield	IR (KBr) ν(B,H) [cm^{-1}]	*Hetero-NMR*		NMR-solvent
			$\delta(^{11}B)$	Ligand L	
(*p*-Cymene)-$Ru[S_2C_2(B_{10}H_{10})]$ (**1**)	56% dec. 205°C	2613, 2589, 2578, 2549	−6.4, −7.5, −9.2		$CDCl_3$
(*p*-Cymene)-$Os[S_2C_2(B_{10}H_{10})]$ (**1A**)	80% dec. 210°C	2613, 2592, 2580, 2562	−5.5, −7.4, −8.6		$CDCl_3$
(p-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≡N′Bu (**7**)	90%	2563 2148 (CN′Bu)	−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
^{1}H- and ^{13}C-NMR data

Compound	^{1}H-NMR				^{13}C-NMR				
	p-Cymene			L	*p*-Cymene			Carborane	L
	CH_3	$CHMe_2$ [a]	C_6H_4		CH_3	$CHMe_2$	C_6H_4 [a,g]		
p-Cymene [b]	2.53s	1.46d(6.9) 3.08sp(6.9)	7.32s		20.9	24.1 33.7	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 31.9	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 32.4	72.5, 74.9 {87.6, 97.5}	95.9	
2 [c]	2.08s	1.14d(7.0) 2.52sp(7.0)	5.19, 5.22 (AA′BB′)	7.4m	17.5	23.1 30.8	92.8d[5.5], 95.5d[5.5] {104.2s, 114.2s}	93.7	128.2, 130.5 134.6, 135.2
3 [b]	2.13s	1.11d(6.9) 2.76sp(6.9)	5.49d(6.3) 5.62d(6.3)	3.70d (^3J(P,H) 10.8 Hz)	17.9	22.6 30.5	93.78, 93,86 93.90, 94.03 {110.9d[5.4], 113.5}	92.7	54.2[7.9]
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 30.7	83.9, 86.6 {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
6 [c]	2.27s	1.22d(7.0) 2.73sp(6.9)	5.78d(6.5) 6.01d(6.5)		18.9	23.2 32.3	96.7, 99.3 {119.9, 123.5}	91.6	194.8
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 31.65	90.3, 92.5 {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 31.6	80.3, 82.4 {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 30.8	81.4, 83.1 {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 31.8	88.1, 89.3 {108.4, 108.8}	97.8	n.o. (138.9 free CN^-)
11 [d,e]	1.99	1.10d(6.9) 2.62sp(6.9)	4.98d(6.0) 5.24d(6.0)		18.2	22.6 31.2	85.3, 87.1 {100.8, 107.1}	97.7	n.o. (133.4 free SCN^-)
12 [c]	1.86	0.57d(6.6)br 2.40sp(6.9)	5.09br 5.22br	2.56br 7.4m	17.2	21.4br 30.1	92.4br, 96.1br {100.6, 113.7}	94.3	18.8(C_2H_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 30.8	83.5, 85.5 {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 $CDCl_3$ solution.
[c] In CD_2Cl_2 solution.
[d] In CD_3CN solution.
[e] NMR tube experiment.
[f] Not observed due to low solubility in CD_2Cl_2.
[g] The ^{13}C 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 NH_3 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 CH_2Cl_2, indicating an equilibrium between **5** and the blue starting compound **1**. The binuclear 4,4′-bipyridine complex **14** precipitates from CH_2Cl_2 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** contain the educt **1** as the highest peak together with the ligand L, after dissociation of the adduct under high vacuum.

The ^{1}H- and ^{13}C-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 ^{1}H and ^{13}C signals of the aromatic part of *p-cymene* at lowest fields. The ^{13}C 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 ^{13}C-^{11}B spin–spin coupling. The $\delta(^{13}C)$ values observed for the two equivalent carborane carbons in the $[S_2C_2(B_{10}H_{10})]$ ligand of the neutral ruthenium complexes **2**–**9** and **12**, **13** remain within a narrow range (between 91 and 95 ppm in $CDCl_3$ or CD_2Cl_2 solution); the high-field end (91.6) is represented by the carbonyl complex **6**.

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

	2 (L = PPh_3)	**12** (LL = $Ph_2P(CH_2)_2PPh_2$)	**13** (LL = N_2H_4)
Bond distances			
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)
Bond angles			
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 (C_3–C_8). The ring carbon C(3) carries the methyl, C(8) the isopropyl substituent.

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 $Cp^*Co[S_2C_2(B_{10}H_{10})]$ [10] and $Cp^*Ir[Se_2C_2(B_{10}H_{10})]$ [12]. This angle at the S···S vector is reduced to 154.4° in the adduct (**2**) with PPh_3 and to 159.0° in the adduct (**12**) with Ph_2PCH_2-CH_2PPh_2 (cf. $Cp^*Rh[S_2C_2(B_{10}H_{10})](PMe_3)$ (155.1°) [11], $Cp^*Ir[Se_2C_2(B_{10}H_{10})](PMe_3)$ (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 $\{(C_6Me_6)Ru[S_2C_6H_4]\}_2(\mu\text{-}N_2H_4)$ (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	$C_{30}H_{39}B_{10}PRuS_2$	$C_{50}H_{72}B_{20}P_2Ru_2S_4 \cdot 2CH_2Cl_2$	$C_{24}H_{52}B_{20}N_2Ru_2S_4$
Crystal shape	Dark red prism	Brown irregular	Red platelet
Crystal dimensions (mm)	$0.25 \times 0.18 \times 0.12$	$0.30 \times 0.18 \times 0.12$	$0.30 \times 0.18 \times 0.08$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
Lattice parameters			
a (pm)	1159.2(2)	1073.37(11)	1035.35(9)
b (pm)	2965.6(3)	1163.07(10)	1095.89(11)
c (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)
V (10^6 pm^3); Z; $F(000)$	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, $\lambda = 71.073$ pm; graphite monochromator)		
Scan range [2θ; °]; mode	3–55; ω	3–55; ω	3–55; ω
Measured reflections	9465	8948	4122
Independent reflections	7753	7702	4001
Observed reflections	6572($F > 2\sigma(F)$)	6273($I > 2\sigma(I)$)	3654($I > 2\sigma(I)$)
Solution and refinement	SHELXTL-PLUS *V*. 4.2 (against F)	SHELXTL-PLUS *V*. 5.1 (against F^2)	SHELXTL-PLUS *V*. 5.1 (against F^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
R values	0.044/0.037 (R/wR; $w^{-1} = \sigma^2(F)$)	0.140/0.059 (wR_2/R_1)	0.094/0.038 (wR_2/R_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 $Li_2[S_2C_2(B_{10}H_{10})]$ (**a**) [11], $[(p\text{-}cymene)RuCl_2]_2$ [19] and $[(p\text{-}cymene)OsCl_2]_2$ [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 $CHCl_3$–$CDCl_3$ ($\delta(^1H) = 7.24$; $\delta(^{13}C) = 77.0$), $CHDCl_2$–CD_2Cl_2 ($\delta(^1H) = 5.33$; $\delta(^{13}C) = 53.8$), external Et_2O–BF_3 ($\delta(^{11}B) = 0$ for $\Xi(^{11}B) = 32.083971$ MHz), and external 85% aq. H_3PO_4 ($\delta(^{31}P) = 0$ for $\Xi(^{31}P) = 40.480747$ MHz).

3.1. (p-Cymene)Ru[$S_2C_2(B_{10}H_{10})$] (1)

o-Carborane, $C_2B_{10}H_{12}$ (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 $Li_2[S_2C_2(B_{10}H_{10})]$ (**a**). Then a solution of 306 mg (0.5 mmol) $[(p\text{-}cymene)RuCl_2]_2$ in 120 ml THF was added. The color of the Et_2O–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–CH_2Cl_2 (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[$S_2C_2(B_{10}H_{10})$] (1A)

The osmium analogue of **1** was prepared starting from 144 mg (1 mmol) *o*-carborane and 395 mg (0.5 mmol) $[(p\text{-}cymene)OsCl_2]_2$ in Et_2O–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[$S_2C_2(B_{10}H_{10})$](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[S_2C_2-($B_{10}H_{10}$)] (**1**) in 20 ml CH_2Cl_2. The color changed immediately, indicating adduct formation. The solvent CH_2Cl_2 was evaporated and the residue washed with hexane to remove excess L (yield: 80–90%). Recrystallization from hexane–CH_2Cl_2 mixtures gave the desired adduct (*p-cymene*)Ru[$S_2C_2(B_{10}H_{10})$](L) in yields of 80–90% (Table 1).

3.4. (p-Cymene)Ru[$S_2C_2(B_{10}H_{10})$](NH_3) (4)

Ammonia gas was bubbled through the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH_2Cl_2, 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 NH_3 at room temperature. After 1 week the red crystals of **4** were isolated, yield 52 mg (56%). Elemental analysis $C_{12}H_{27}B_{10}NRuS_2$ (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[$S_2C_2(B_{10}H_{10})$](CO) (6)

In contact with CO the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH_2Cl_2 turned yellow. The yellow product **6** was isolated in nearly quantitative yield.

3.6. K{(p-Cymene)Ru[$S_2C_2(B_{10}H_{10})$]}(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 CH_2Cl_2. Filtration gave a yellow solution which contained **10**.

3.7. Binuclear adducts {(p-cymene)Ru[S_2C_2-($B_{10}H_{10}$)]}$_2$(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[$S_2C_2(B_{10}H_{10})$]}$_2$(N_2H_4) (13)

Hydrazine hydrate, $N_2H_4 \cdot H_2O$ (0.1 ml, 2.1 mmol) was added to the blue solution of 90 mg (0.2 mmol) **1** in 20 ml CH_2Cl_2. The resulting brown–red mixture was dried by the addition of anhydrous Na_2SO_4. 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 $C_{24}H_{52}B_{20}N_2Ru_2S_4$ (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 ($\lambda = 71.073$ 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 Å^2). 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).

Acknowledgements

Support of this work by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Professor B. Wrackmeyer, Bayreuth, for helpful discussions.

References

[1] J.D. McKinney, H. Chen, T.A. Hamor, K. Paxton, C.J. Jones, J. Chem. Soc. Dalton Trans. (1998) 2163.
[2] H.D. Smith Jr., M.A. Robinson, S. Papetti, Inorg. Chem. 6 (1967) 1014.
[3] H.D. Smith Jr., J.C. Obenland, S. Papetti, Inorg. Chem. 5 (1966) 1013.
[4] J.G. Contreras, L.M. Silva-Trivino, M.E. Solis, J. Coord. Chem. 14 (1986) 309.
[5] K. Base, M.W. Grinstaff, Inorg. Chem. 37 (1998) 1432.
[6] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Chem. Soc. Chem. Commun. (1993) 1696.

[7] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Chem. Soc. Dalton Trans. (1997) 1099.
[8] O. Crespo, M.C. Gimeno, P.G. Jones, B. Ahrens, A. Laguna, Inorg. Chem. 36 (1997) 495.
[9] O. Crespo, M.C. Gimeno, P.G. Jones, A. Laguna, J. Organomet. Chem. 547 (1999) 89.
[10] D.-H. Kim, J. Ko, K. Park, S. Cho, S.O. Kang, Organometallics 18 (1999) 2738.
[11] M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, J. Organomet. Chem. 587 (1999) 252.
[12] M. Herberhold, G.-X. Jin, H. Yan, W. Milius, B. Wrackmeyer, Eur. J. Inorg. Chem. 5 (1999) 873.
[13] E.J. Miller, T.B. Brill, A.L. Rheingold, W.C. Fultz, J. Am. Chem. Soc. 105 (1983) 7580.
[14] K. Mashima, H. Kaneyoshi, S. Kaneko, A. Mikami, K. Tani, A. Nakamura, Organometallics 16 (1997) 1016.
[15] A. Hörnig, U. Englert, U. Kölle, J. Organomet. Chem. 464 (1994) C25.
[16] (a) M. Herberhold, G.-X. Jin, A.L. Rheingold, G.F. Sheats, Z. Naturforsch. 47b (1992) 1091. (b) M. Herberhold, G.-X. Jin, A.L. Rheingold, in preparation.
[17] (a) K.-J. Haack, S. Hashiguchi, A. Fujii, T. Ikariya, R. Noyori, Angew. Chem. 109 (1997) 297. (b) ibid., Angew. Chem. Int. Ed. Engl. 36 (1997) 285.
[18] K. Mashima, S. Kaneko, K. Tani, H. Kaneyoshi, A. Nakamura, J. Organomet. Chem. 545-546 (1997) 345.
[19] (a) M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233. (b) M.A. Bennett, T.-N. Huang, T.W. Matheson, A.K. Smith, Inorg. Synth. 21 (1982) 74.
[20] J.A. Cabeza, P. Maitlis, J. Chem. Soc. Dalton Trans. (1985) 573.