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Reactivity of the anion 7,8-(ethane-1′,2′-dithiolato-*SS*′)-*nido*-undecaborate. Molecular structure of [7,8-(ethane-1′,2′-dithiolato-*SS*′)-dicarba-*nido*-undecaborate]bis(triphenylphosphine)rhodium(I)

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Abstract

The reactivity of the anion 7,8-(ethane-1′,2′-dithiolato-*SS*′)-dicarba-nido-undecaborate is reported. It reacts easily with salts of transition metals, replaces phosphines in complexes where these are ligands, and stabilizes low oxidation states. The molecular structure of 1,4-dithiabutane-7′,8′-dicarbaundecaborate(12)bis(triphenylphosphine)rhodium(I) has been resolved. The compound crystallizes in space group $P\bar{1}$ with 2 formula units per cell. The cell dimensions are $a = 10.165(2)$, $b = 14.665(3)$, $c = 14.951(3)$ Å with $\alpha = 81.21(4)$, $\beta = 87.68(4)$ and $\gamma = 72.20°$.

Introduction

The coordination chemistry of thioethers is currently the subject of intensive investigations, especially focused on the stabilization of metal centers in unusual oxidation states [1] and its potential similarity to that of phosphines, particularly in relation to catalytically active phosphine complexes. The polythiaethers 1,4,7-trithiacyclononane (9S3) [2–5], 1,4,7,10,13,16-hexathiacyclooctadecane (18S6) [6–8] and their expanded homologues 12S3 [9] and 24S6 [10], have received considerable attention in recent years. On the other hand, the coordination chemistry of the anion 7,8-dicarba-*nido*-undecaborate and its alkylderivatives has been thoroughly studied, especially by Hawthorne and coworkers [11–14]. These carborane compounds either present a h^5 (C_2B_3) coordination to metal as in $(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ [15] or *exo-nido* coordination as in *exo-nido*-$[(PPh_3)_2Rh][7,8\text{-}\mu\text{-}(CH_2)_3\text{-}7,8\text{-}C_2B_9H_{10}]$ [16]. However, the way this C_2B_3 open face would behave if two sulfur atoms were directly connected to the carbons was unknown.

In preceding papers we have reported the syntheses and structural characterization of several ligands which are derivatives of the 7,8-dicarbaundecaborate(10) anion [17–19] and have sulfur atoms directly connected to the carbons of the carborane.

Here we wish to report primary results on the reactivity of the 7,8-(ethane-1′,2′-dithiolato-*SS*′)-dicarba-*nido*-undecaborate anion (L) [12] and the molecular structure of [7,8-(ethane-1′,2′-dithiolato-*SS*′)-dicarba-*nido*-undecaborate]bis(triphenylphosphine)-rhodium(I).

Experimental

1,2-Dicarba-*closo*-dodecaborane was purchased from Dexil Chemical Corporation and sublimed before use. 1,2-Dimercapto-1,2-dicarba-*closo*-dodecaborane was synthesized according to the method described by Smith *et al.* [20].

All other reagents were Fluka or Aldrich analytical reagent grade and were used as supplied. Solvents were purified and dried before use. All reactions were carried out under a dinitrogen atmosphere.

$RhL(PPh_3)_2$

$RhCl(PPh_3)_3$ (200 mg; 0.216 mmol) was added to a solution of $[NMe_4]L$ (64 mg; 0.216 mmol) in degassed butanol (30 ml) under nitrogen. The mixture was brought to reflux for 1.5 h to yield a yellow–orange solid, which was recrystallized from acetone. Yield 149 mg (81%). IR spectrum (KBr): ν(B–H) = 2531,

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2551 cm^{-1}. *Anal.* Calc. for $C_{40}H_{44}B_9RhP_2S_2$: C, 56.45; H, 5.21. Found: C, 57.1; H, 5.1%.

[NMe$_4$][NiCl$_2$L]

$NiCl_2{\cdot}6H_2O$ (70 mg; 0.295 mmol) was added to a solution of [NMe_4]L (88 mg; 0.295 mmol) in degassed ethanol (30 ml) under nitrogen. The mixture was brought to reflux for 4 h to yield a brown–red solid. This was chromatographed (silica/acetone) to yield a pure sample. Yield 88 mg (70%). IR spectrum (KBr): ν(B–H) = 2530 cm^{-1}. ^{1}H NMR (d$_6$-acetone, ppm) 3.43 $(CH_3)_4N$, 2.84 (CH_2). *Anal.* Calc. for $C_8H_{26}B_9Cl_2NNiS_2$: C, 22.49; H, 6.13; N, 3.28. Found: C, 22.8; H, 6.2; N, 3.2%.

[NMe$_4$]$_2$[Cu$_2$Cl$_2$L$_2$]

$CuCl_2{\cdot}2H_2O$ (115 mg; 0.673 mmol) was added to a solution of [NMe_4]L (200 mg; 0.671 mmol) in degassed ethanol (40 ml). A green precipitate separated which dissolved on refluxing. Almost immediately, the solution became colourless. Upon concentration a white solid separated, which was filtered and washed with diethylether. Yield 163 mg (61%). IR spectrum (KBr): ν(B–H) = 2527 cm^{-1}. *Anal.* Calc. for $C_8H_{26}B_9ClCuNS_2$: C, 24.22; H, 6.61; N, 3.53. Found: C, 24.6; H, 6.7; N, 3.4%.

Data collection and reduction

Yellow crystals of $C_{40}H_{43}B_9P_2RhS_2$ were grown from acetone. Crystal data are summarized in Table 1. A prismatic crystal with dimensions 0.20 × 0.30 × 0.5 mm was chosen. Parameters were refined from 25 reflections in the range $10 < 2\theta < 25$. An Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation was used. Intensity variation of one standard reflection was 3.84%. A total of 7648 reflections was collected giving 7339 unique reflections. The number of unobserved reflections was 3685 with $I < 2.5\sigma(I)$.

TABLE 1. Crystal data and details of data collection

Molecular formula	$C_{40}H_{44}B_9S_2P_2Rh$
Crystal system	triclinic
a (Å)	10.165(2)
b (Å)	14.665(3)
c (Å)	14.951(3)
α (°)	81.21(4)
β (°)	87.68(4)
γ (°)	72.20(3)
Space group	$P\bar{1}$
V (Å^3)	2097
D_c (g cm^{-3})	1.35
Z	2
Crystal dimensions (mm)	0.20 × 0.30 × 0.50
Radiation	Mo Kα (λ = 0.70926 Å)
Absorption coefficient (cm^{-1})	5.99
2θ limits	$4 < 2\theta < 50$
Collection range, ±h, ±k, l	±11, ±17, 16
No. unique reflections	7339
No. unobserved reflections, $I < 2.5\sigma(I)$	3685
R	0.0608
R_w	0.063

The crystal structure was determined by Random phase refinement using the Ω tangent formula [21, 22]. The H atoms bound to B atoms were found in Δ Fourier maps; the remaining ones at calculated positions. The benzene rings were handled as rigid fragments with a global isotropic temperature factor during the refinement. The remaining non-H atoms were refined anisotropically. The positional parameters of the H atoms bonded to B atoms were also refined. Least-squares refinement using a Shelx program [23] gave $R = 0.0608$ and $R_w = 0.063$ (weighting scheme: $w = 0.972/(\sigma^2(F + 0.0031F^2))$). Final $(\Delta/\sigma)_{max} = 0.48$. Maximum and minimum heights in final ΔF map: 0.83, −0.31 e/Å^3. Atomic scattering factors were taken from the International Tables for Crystallography [24].

Results and discussion

The [7,8-(ethane-1′,2′-dithiolato-*SS*′)-dicarba-*nido*-undecaborate] anion contains two competing sites, the cluster's open face and the two thioether groups. In the absence of the two sulfur elements a h^5 rhodium coordination to the C_2B_3 open face or an *exo-nido* coordination would be expected upon reaction of the Wilkinson's catalyst with a 7,8-dicarba-*nido*-undecaborate derivative.

Upon reaction of $RhCl(PPh_3)_3$ with the tetramethylammonium salt of [7,8-(ethane-1′,2′-dithiolato-*SS*′)dicarba-*nido*-undecaborate]([NMe_4]L), in refluxing ethanol, a yellow–orange solid was obtained, which after recrystallization in acetone yielded orange crystals of the composition $RhL(PPh_3)_2$. The IR spectrum displayed ν(B–H)* absorptions at 2531–2551 cm^{-1}, which are in the correct range for

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*The position of the B–H band in the IR spectrum is highly significant when studying 1,2-dicarba-*closo*-dodecaborane or 7,8-dicarba-*nido*-undecaborate derivatives. With few exceptions if ν(B–H) is < 2550 cm^{-1} the cluster is partially degraded, on the contrary if ν(B–H) is > 2550 the cluster is a *closo* compound. the most frequently observed values are < 2540 cm^{-1} for partially degraded (*nido*) and > 2570 for *closo* (see refs. 17–19). When a metal occupies the vacant position in a 7,8-dicarba-*nido*-undecaborate derivative the ν(B–H) usually is observed at the borderline between the *closo* and *nido* compound, e.g. $(PPh_3)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ displays two bands in the range 2565–2555.

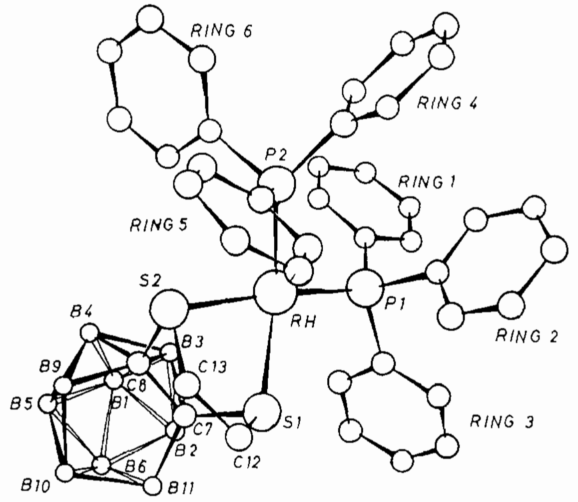

Fig. 1. Molecular structure of Rh(PPh$_3$)$_2$L.

TABLE 2. Final refined atomic coordinates (×10^4) and equivalent temperature factors (Å^2)

	x/a	y/b	z/c	B_{eq}
Rh	9761(1)	1893(0)	2581(0)	2.9
S1	10308(2)	659(1)	3840(1)	3.2
S2	9954(2)	490(1)	1923(1)	3.6
P1	9835(2)	3101(1)	3316(1)	3.0
P2	8691(2)	2789(1)	1305(1)	3.1
B1	14321(12)	−788(8)	2739(9)	5.2
B2	13408(12)	−511(8)	3743(8)	4.6
B3	12785(11)	189(7)	2700(7)	3.9
B4	13109(12)	−598(8)	1870(9)	4.7
B5	13855(12)	−1778(8)	2395(10)	5.5
B6	14014(13)	−1743(7)	3584(10)	5.4
C7	11695(8)	−260(5)	3424(6)	3.5
C8	11544(8)	−312(6)	2420(6)	3.7
B9	12080(13)	−1400(8)	2145(9)	4.7
B10	12718(13)	−2176(8)	3179(9)	5.0
B11	12325(11)	−1324(7)	4010(8)	4.0
C12	8948(9)	126(7)	3666(6)	4.3
C13	8847(9)	−33(6)	2695(6)	3.9
H2	13621(79)	−284(55)	4383(56)	4.0
H3	12527(77)	998(55)	2590(51)	4.0
H4	13201(79)	−295(55)	1191(57)	4.0
H5	14630(81)	−2321(56)	1989(52)	4.0
H6	14829(82)	−2310(57)	3929(53)	4.0
H9	11575(82)	−1589(56)	1672(56)	4.0
H10	12793(77)	−2872(58)	3355(52)	4.0
H11	12124(80)	−1423(55)	4704(56)	4.0

TABLE 3. Bond lengths (Å) with e.s.d.s in parentheses

S1–RH	2.357(2)
S2–RH	2.365(2)
P1–RH	2.244(2)
P2–RH	2.253(2)
C7–S1	1.793(8)
C12–S1	1.828(9)
C8–S2	1.793(8)
C13–S2	1.826(8)
C46–P1	1.841(6)
C56–P1	1.822(6)
C66–P1	1.828(5)
C76–P2	1.839(6)
C86–P2	1.834(6)
C96–P2	1.830(6)
B2–B1	1.767(18)
B3–B1	1.762(14)
B4–B1	1.758(18)
B5–B1	1.808(17)
B6–B1	1.830(17)
B3–B2	1.755(15)
B6–B2	1.771(15)
C7–B2	1.737(14)
B11–B2	1.847(16)
B4–B3	1.774(16)
C7–B3	1.721(13)
C8–B3	1.735(14)
B5–B4	1.737(16)
C8–B4	1.725(13)
B9–B4	1.794(16)
B6–B5	1.802(20)
B9–B5	1.755(17)
B10–B5	1.773(18)
B10–B6	1.788(17)
B11–B6	1.766(17)
C8–C7	1.530(12)
B11–C7	1.621(12)
B9–C8	1.633(13)
B10–B9	1.788(17)
B11–B10	1.842(16)
C13–C12	1.518(12)

a 7,8-dicarba-*nido*-undecaborate free cluster. In addition no signal attributable to ν(Rh–H)[*] (expected near 2100 cm^{-1}) was observed. These values did not support h^5 metal to carborane coordination, and as a consequence a thioether coordination was assumed, which was confirmed by X-ray diffraction analysis.

The structure of the metallocarborane complex has been determined by X-ray diffraction analysis and is shown in Fig. 1. Final atomic parameters are reported in Table 2. Selected distances and angles are reported in Tables 3 and 4, respectively. It is worth noticing the formally zwitterionic nature of this compound.

The Rh atom displays a nearly square-planar geometry with the two PPh$_3$, in a *cis* position. The remaining sites are occupied by the *exo*-cluster sulfur atoms. The ethylene group extends towards the cluster's open face, in such a way that the rhodium occupies the farthest possible position with respect to the cluster's open face, avoiding any possible interaction. The ligand's conformation is the expected one for the free ligand to reduce the sulfur lone

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[*] This signal would be expected if the Rh was h^5 coordinated to C$_2$B$_3$ due to the formation of a Rh–H bond.

TABLE 4. Selected bond angles with e.s.d.s in parentheses

S2–RH–S1	77.6(1)
P1–RH–S1	96.5(1)
P1–RH–S2	172.2(1)
P2–RH–S1	159.3(1)
P2–RH–S2	88.4(1)
P2–RH–P1	98.6(1)
C7–S1–RH	102.6(3)
C12–S1–RH	97.0(3)
C12–S1–C7	96.2(4)
C8–S2–RH	100.9(3)
C13–S2–RH	99.2(3)
C13–S2–C8	95.0(4)
C46–P1–RH	118.1(2)
C56–P1–RH	114.6(2)
C56–P1–C46	106.3(2)
C66–P1–RH	114.3(2)
C66–P1–C46	96.4(3)
C66–P1–C56	104.9(3)
C76–P2–RH	128.4(2)
C86–P2–RH	101.9(2)
C86–P2–C76	102.7(3)
C96–P2–RH	115.0(2)
C96–P2–C76	100.8(3)
C96–P2–C86	105.7(3)
B3–B1–B2	59.6(6)
B4–B1–B2	108.1(8)
B4–B1–B3	60.5(6)
B5–B1–B2	107.1(8)
B5–B1–B3	106.2(8)
B5–B1–B4	58.3(7)
B6–B1–B2	58.9(6)
B6–B1–B3	105.3(8)
B6–B1–B4	105.5(8)
B6–B1–B5	59.4(7)
B3–B2–B1	60.1(6)
B6–B2–B1	62.3(7)
B6–B2–B3	108.2(8)
C7–B2–B1	103.1(8)
C7–B2–B3	59.1(5)
C7–B2–B6	98.8(8)
B11–B2–B1	108.0(8)
B11–B2–B3	105.4(8)
B11–B2–B6	58.4(6)
B11–B2–C7	53.7(5)
B2–B3–B1	60.3(7)
B4–B3–B1	59.6(6)
B4–B3–B2	108.0(7)
C7–B3–B1	103.9(7)
C7–B3–B2	59.9(6)
C7–B3–B4	101.7(7)
C8–B3–B1	103.0(7)
C8–B3–B2	102.2(7)
C8–B3–B4	58.9(6)
C8–B3–C7	52.5(5)
B3–B4–B1	59.9(7)
B5–B4–B1	62.3(7)
B5–B4–B3	108.8(9)
C8–B4–B1	103.6(8)
C8–B4–B3	59.4(6)
C8–B4–B5	100.4(8)
B9–B4–B1	109.8(9)
B9–B4–B3	107.6(8)
B9–B4–B5	59.6(7)
B9–B4–C8	55.2(5)
B4–B5–B1	59.4(7)
B6–B5–B1	60.9(7)
B6–B5–B4	107.7(8)
B9–B5–B1	109.3(8)
B9–B5–B4	61.8(7)
B9–B5–B6	106.8(9)
B10–B5–B1	111.5(9)
B10–B5–B4	111.9(8)
B10–B5–B6	60.0(7)
B10–B5–B9	60.9(7)
B2–B6–B1	58.8(6)
B5–B6–B1	59.7(7)
B5–B6–B2	107.2(8)
B10–B6–B1	109.8(9)
B10–B6–B2	113.7(8)
B10–B6–B5	59.2(7)
B11–B6–B1	108.9(7)
B11–B6–B2	63.0(6)
B11–B6–B5	107.2(9)
B11–B6–B10	62.4(7)
B2–C7–S1	123.1(6)
B3–C7–S1	113.8(5)
B3–C7–B2	61.0(6)
C8–C7–S1	113.2(6)
C8–C7–B2	112.3(7)
C8–C7–B3	64.2(6)
B11–C7–S1	121.6(6)
B11–C7–B2	66.7(6)
B11–C7–B3	118.0(7)
B11–C7–C8	112.1(7)
B3–C8–S2	118.2(6)
B4–C8–S2	124.9(7)
B4–C8–B3	61.7(6)
C7–C8–S2	113.6(6)
C7–C8–B3	63.3(6)
C7–C8–B4	112.7(7)
B9–C8–S2	117.5(7)
B9–C8–B3	117.5(7)
B9–C8–B4	64.5(6)
B9–C8–C7	115.0(7)
B5–B9–B4	58.6(7)
C8–B9—B4	60.2(6)
C8–B9–B5	103.4(8)
B10–B9–B4	108.6(9)
B10–B9–B5	60.0(7)
B10–B9–C8	104.8(8)
B6–B10–B5	60.8(8)
B9–B10–B5	59.0(7)
B9–B10–B6	106.0(8)
B11–B10–B5	105.2(8)
B11–B10–B6	58.2(6)
B11–B10–B9	102.5(7)
B6–B11–B2	58.6(6)
C7–B11–B2	59.7(5)
C7–B11–B6	103.6(8)
B10–B11–B2	107.8(8)
B10–B11–B6	59.4(7)
B10–B11–C7	105.4(8)
C13–C12–S1	113.1(6)
C12–C13–S2	113.1(6)

pairs–π open face electrons interaction to an energy minimum. This suggests that the most stable ligand conformer establishes the ligand conformation in this complex.

$RhCl(PPh_3)_3$ is known as a good reagent to insert Rh on the C_2B_3 open face because oxidative-addition may occur leaving a Rh–H bond. With other metals basic conditions are needed to remove the ligand's open face proton.

The next reactions were carried out to test the ability of this *exo*-dithiacarborane ligand to react promptly with salts of transition metal ions. Copper(II) was used because we presumed that L would stabilize the readily accessible Cu(I) oxidation state and Ni(II) because we expected that the oxidation state would be maintained. In fact reaction of $[NMe_4]L$ with $CuCl_2$ in ethanol in the ratio Cu:L = 1:1 yields a Cu(I) complex of stoichiometry $[NMe_4]_2[Cu_2L_2Cl_2]$ while Ni(II) chloride reacted with $[NMe_4]L$ in ethanol, in the ratio Ni:L = 1:1 to give a solid of composition $[NMe_4][NiCl_2L]$. The IR spectrum (ν(B–H)) clearly indicated that the cluster had not been altered in either of the two cases and suggested a type of coordination similar to that found in $RhL(PPh_3)_2$.

These results prompted us to study further the reactivity of this and similar ligands, the results of which will be the object of future papers.

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