N,S-CHELATING AMINO-*ortho*-CARBORANETHIOLATE COMPLEXES OF RHODIUM AND IRIDIUM: SYNTHESIS AND REACTIVITY. X-RAY CRYSTAL STRUCTURES OF $(\eta^4\text{-}C_8H_{12})Rh[(NMe_2CH_2)SC_2B_{10}H_{10}]$ AND $(CO)_2Rh[(NMe_2CH_2)SC_2B_{10}H_{10}]$

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Received February 5, 1999
Accepted March 29, 1999

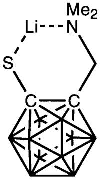
Dedicated to Dr Stanislav Heřmánek on the occasion of his 70th birthday.

The reaction of $[M(\mu\text{-}Cl)(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) with two equivalents of the lithium *ortho*-carboranethiolate derivative $LiCab^{N,S}$ **2** [$LiCab^{N,S}$ = *closo*-2-(dimethylaminomethyl)-1-(lithiumthiolato)-*ortho*-carborane] produced the four-coordinated metallacyclic compounds, $Cab^{N,S}M(cod)$ **3** (M = Rh **3a**, Ir **3b**), in which the metal atom was stabilized *via* intramolecular *N,S*-coordination. These new compounds have been isolated in high yields and characterized by IR and NMR spectroscopy. The structure consists of an amino-*ortho*-carboranethiolate fragment bonded to (cod)Rh(I) *via* nitrogen and sulfur, so as to give the metal a square-planar environment. Subsequent carbonylation reactions of **3a**, **3b** result in the quantitative formation of the corresponding (amino-*ortho*-carboranethiolato)(carbonyl)metal *N,S*-chelates $Cab^{N,S}M(CO)_2$ **4** (M = Rh **4a**, Ir **4b**). The metal carbonyl complexes **4a**, **4b** have been isolated and characterized by spectroscopic and compound **4a** also by X-ray diffraction techniques. The molecular structure of **4a** reveals that the rhodium atom is coordinated by nitrogen and sulfur atoms of the amino-*ortho*-carboranethiolate ligand, and two carbonyl ligands complete the coordination of the metal atom.

Key words: Boranes; Carboranes; *N,S*-Ligands; Chelates; Intramolecular *N,S*-coordination; Amino-*ortho*-carboranethiolate; Group 9 transition metals; Carbonylation.

In recent years, transition metal complexes with ligands containing dissimilar donor atoms such as nitrogen and sulfur have been widely investigated, primarily for their applications in the synthesis of early and late transition metal complexes[1]. Such ligands would be capable of forming strong bonds with early transition metals in their higher oxidation state through the nitrogen atom, while the sulfur atom would assist the formation of the metal complex by forming a stable bond to the late transition metal center.

Our work involves the use of an *ortho*-carboranethiolate ligand with a tertiary amine substituent which, through intramolecular coordination, can stabilize the metal center by blocking specific coordination sites. To understand the coordination behavior and reactivity of the *ortho*-carboranethiolate ligand with a potentially coordinating *N*-donor substituent, we have sythesized the corresponding lithium complex LiCab^{N,S} **2** and studied its reactivity toward group 9 transition metals. The *ortho*-carboranethiolate ligand described in this work having an *ortho*-substituent bearing amino group can generate a six-membered chelate ring on coordination through nitrogen and sulfur to a metal center.



LiCab^{N,S} **2**

Herein, we report the synthesis and characterization of *ortho*-carboranethiolate complexes of rhodium and iridium and their reactivity toward the carbonyl ligand.

EXPERIMENTAL

All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmosphere HE-493 dry box. THF was freshly distilled over potassium benzophenone. Ether and toluene were dried and distilled from sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH_2. ^{1}H, ^{11}B, and ^{13}C NMR spectra were recorded on a Varian Gemini 2000 spectrometer operating at 200.1, 64.2, and 50.3 MHz, respectively. All ^{11}B chemical shifts were referenced to $BF_3{\cdot}Et_2O$ (0.0 ppm) with a negative sign indicating an upfield shift. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). IR spectra were recorded on a Biorad FTS-165 spectrophotometer. High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. Decaborane and 1-dimethylaminoprop-2-yne were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without purification. The following starting materials were prepared according to literature procedures: HCab^N **1** (ref.[2]), [Rh(μ-Cl)(cod)]$_2$ (ref.[3]), and [Ir(μ-Cl)(cod)]$_2$ (ref.[4]).

Synthesis of Cab^{N,S}Rh(cod) **3a**

To HCab^N **1** (0.60 g, 3.0 mmol) dissolved in hexane (20 ml) at –10 °C was added a solution of BuLi in hexane (3 mmol). The resulting mixture was stirred for 12 h at room temperature. The white precipitate formed was separated from the solution by decantation. The solid LiCab^N was washed twice with 30 ml of pentane and dried *in vacuo*; yield 0.43 g (2.1 mmol, 70%). LiCab^N (0.21 g, 1.0 mmol) dissolved in THF (30 ml) was slowly added to a suspension of sublimed sulfur (0.035 g, 1.1 mmol) in THF (20 ml) at –78 °C. The solution was warmed to room temperature, and [Rh(μ-Cl)(cod)]$_2$ (0.247 g, 0.5 mmol) was added. The reaction mixture was then allowed to react at 0 °C for 1 h, and the solution was stirred for another 2 h at room temperature. The solution gradually turned dark brown, suggesting the formation of the *ortho*-carboranethiolato metal complex. The solution was reduced *in vacuo* to about half its original volume, and some insoluble material was removed by filtration. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of methylene chloride and then transferred to a column of silica gel. The crude residue was purified by column chromatography affording >95% pure complex as purple crystals. Yield: 0.31 g (0.69 mmol, 69%) of complex **3a**. ^{11}B NMR (64.2 MHz, ppm, C_6D_6): –4.7 (d, B_9, B_{12}, J_{BH} = 150 Hz); –7.8 (d, $B_{8,10}$, $B_{4,5}$, J_{BH} = 160 Hz); –9.2 (d, $B_{7,11}$, $B_{3,6}$, J_{BH} = 160 Hz). ^{1}H NMR (200.13 MHz, ppm, C_6D_6): 3.97 (br s, 4 H, =C**H** cod); 3.39 (s, 2 H, N-C$\mathbf{H}_2$); 2.64 (s, 6 H, N-C$\mathbf{H}_3$); 2.38 (br s, 4 H, C$\mathbf{H}_{exo}$ cod); 2.34 (br s, 4 H, C$\mathbf{H}_{endo}$ cod). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 84.92 (s, =CH cod); 72.16 (s, C_{cab}); 66.46 (s, N-CH_2); 49.93 (s, N-CH_3); 31.00 (s, CH_2 cod); 29.39 (s, CH_2 cod). Exact mass: for $^{12}C_{13}{}^1H_{30}{}^{11}B_{10}{}^{14}N_1{}^{32}S_1{}^{103}Rh_1$ calculated: 445.2085; found: 445.2090. Analysis: for $C_{13}H_{30}B_{10}NSRh$ (443.4) calculated: 35.21% C, 6.82% H, 3.16% N; found: 35.30% C, 6.89% H, 3.24% N. R_F 0.12 (TLC silica gel, hexane); m.p. 185–188 °C (dec.). IR (KBr pellet, cm^{-1}): ν(B–H) 2 589, ν(C=C cod) 2 180.

Synthesis of Cab^{N,S}Ir(cod) **3b**

A solution of freshly prepared LiCab^{N,S} **2** (0.21 g, 1.0 mmol) in THF (30 ml) was added over 1 h to a suspension of [Ir(μ-Cl)(cod)]$_2$ (0.34 g, 0.5 mmol) in toluene (20 ml) at –78 °C. The reaction mixture was stirred for 12 h at room temperature, after which the suspended solid was collected by filtration. The volume of the filtrate was reduced by evaporation in vacuum, and then this was allowed to stand at –20 °C for several days. Colorless crystals of **3b** were formed in 62% yield (0.33 g, 0.62 mmol). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): –5.8 (d, B_9, B_{12}, J_{BH} = 200 Hz); –9.4 (d, $B_{8,10}$, $B_{4,5}$, J_{BH} = 140 Hz); –12.1 (d, $B_{7,11}$, $B_{3,6}$, J_{BH} = 180 Hz). ^{1}H NMR (200.13 MHz, ppm, C_6D_6): 4.41 (br s, 4 H, =C**H** cod); 3.02 (br s, 4 H, C$\mathbf{H}_{exo}$ cod); 2.99 (s, 2 H, N-C$\mathbf{H}_2$); 2.32 (s, 6 H, N-C$\mathbf{H}_3$); 1.53 (br s, 4 H, C$\mathbf{H}_{endo}$ cod). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 80.60 (s, =CH cod); 70.10 (s, C_{cab}); 55.64 (s, N-CH_2); 47.29 (s, N-CH_3); 28.30 (s, CH_2 cod). Exact mass: for $^{12}C_{13}{}^1H_{30}{}^{11}B_{10}{}^{14}N_1{}^{32}S_1{}^{192}Ir_1$ calculated: 532.2659; found: 532.2662. Analysis: for $C_{13}H_{30}B_{10}IrNS$ (532.8) calculated: 29.31% C, 5.68% H, 2.63% N; found: 29.35% C, 5.71% H, 2.66% N. R_F 0.19 (TLC silica gel, hexane); m.p. 187–190 °C (dec.). IR (KBr pellet, cm^{-1}): ν(B–H) 2 599, ν(B–H) 2 561, ν(B–H) 2 533, ν(C=C cod) 2 184.

Synthesis of Cab^{N,S}Rh(CO)$_2$ **4a**

A solution of complex **3a** (0.09 g, 0.2 mmol) in toluene (20 ml) was treated with excess CO gas for 5 min at room temperature. The orange color of the solution quickly faded to give a yellow solution. The volatile substances were then removed *in vacuo*, and the resulting solid was extracted with CH_2Cl_2. Addition of hexane to the concentrated extract gave complex **4a** as yellow crystals. Yield: 0.07 g (0.18 mmol, 90%). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): –3.9 (d, B_9, B_{12}, J_{BH} = 190 Hz); –8.0 (d, $B_{8,10}$, $B_{4,5}$, J_{BH} = 150 Hz); –11.5 (d, $B_{7,11}$, $B_{3,6}$, J_{BH} = 160 Hz). ^{1}H NMR (200.13 MHz, ppm, C_6D_6): 3.52 (s, 2 H, N-C**H**$_2$); 3.02 (s, 3 H, N-C**H**$_3$); 2.99 (s, 3 H, N-C**H**$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 66.12 (s, N-CH_2); 54.36 (s, N-CH_3). Exact mass: for $^{12}C_7{}^1H_{18}{}^{11}B_{10}{}^{14}N_1{}^{16}O_2{}^{32}S_1{}^{103}Rh_1$ calculated: 393.1044; found: 393.1049. Analysis: for $C_7H_{18}B_{10}NO_2RhS$ (391.3) calculated: 21.49% C, 4.64% H, 3.58% N; found: 21.53% C, 4.67% H, 3.62% N. R_F 0.24 (TLC silica gel, hexane); m.p. 118–120 °C (dec.). IR (KBr pellet, cm^{-1}): ν(B–H) 2 590, ν(CO) 2 074, ν(CO) 2 013, ν(CO) 1 997, ν(CO) 1 963 w.

Synthesis of Cab^{N,S}Ir(CO)$_2$ **4b**

A solution of complex **3b** (0.11 g, 0.2 mmol) in toluene (20 ml) was treated with excess CO gas for 5 min at room temperature. The orange color of the solution quickly faded to give a yellow solution. The volatile substances were then removed *in vacuo*, and the resulting solid was extracted with CH_2Cl_2. Addition of hexane to the concentrated extract gave complex **4b** as yellow crystals. Yield: 0.09 g (0.19 mmol, 95%). ^{11}B NMR (64.2 MHz, ppm, C_6D_6): –3.4 (d, B_9, B_{12}, J_{BH} = 180 Hz); –7.1 (d, $B_{8,10}$, $B_{4,5}$, J_{BH} = 160 Hz); –13.5 (d, $B_{7,11}$, $B_{3,6}$, J_{BH} = 150 Hz). ^{1}H NMR (200.13 MHz, ppm, C_6D_6): 3.38 (d, 2 H, N-C**H**$_2$, J_{gem} = 13 Hz); 2.32 (s, 6 H, N-C**H**$_3$). ^{13}C{^{1}H} NMR (50.3 MHz, ppm, C_6D_6): 68.69 (s, N-CH_2); 52.54 (s, N-CH_3). Exact mass: for $^{12}C_7{}^1H_{18}{}^{11}B_{10}{}^{14}N_1{}^{16}O_2{}^{32}S_1{}^{192}Ir_1$ calculated: 483.1618; found: 483.1613. Analysis: for $C_7H_{18}B_{10}IrNO_2S$ (480.6) calculated: 17.49% C, 3.78% H, 2.91% N; found: 17.53% C, 3.82% H, 2.96% N. R_F 0.22 (TLC silica gel, hexane); m.p. 130–132 °C (dec.). IR (KBr pellet, cm^{-1}): ν(B–H) 2 588, ν(CO) 2 034.

X-Ray Crystallography

Suitable crystals of **3a** and **4a** were obtained by slow diffusion of hexane into a methylene chloride solution of the complexes at room temperature and were mounted on a glass fiber. Diffraction measurements were made on an Enraf CAD4 automated diffractometer with graphite-monochromated MoKα radiation. The unit cell was determined by using search, center, index and least-squares routines. The intensity data were corrected for Lorentz and polarization effects and for anisotropic decay. Empirical absorption corrections based on psi scans were also applied. Each structure was solved by the application of Patterson methods using the SHELXL86 program[5a] and least-squares refinement using SHELXL93 (ref.[5b]).

Compound **3a** crystallized in the orthorhombic crystal system. The space group *Pbca* (No. 61) was uniquely identified from the systematic absences in the intensity data. All nonhydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms, including those on the cage B–H group and the hydrogens of the cod ligand, were located and refined with isotropic thermal parameters. The final *R* value was 0.0368 with 4 013 ($I > 2\sigma I$) observed reflections and 247 parameters. Compound **4a** crystallized in the orthorhombic crystal system. The centrosymmetric space group *Pbca* (No. 61) was selected and was confirmed by the successful solution and refinement of the structure. Nonhydrogen atoms were anisotropically refined and hydrogen atoms were isotropically refined. The final *R* value was 0.0375 with 3 329 ($I > 2\sigma I$) observed reflections and 211 parameters. Crystallographic data and results are listed in Table I.

TABLE I
X-Ray crystallographic data and processing parameters for compounds **3a** and **4a**

Parameter	**3a**	**4a**
Formula	$B_{10}C_{13}H_{30}NRhS$	$B_{10}C_7H_{18}NO_2RhS$
Formula weight	443.45	391.29
Crystal class	orthorhombic	orthorhombic
Space group	*Pbca* (No.61)	*Pbca* (No.61)
Z	8	8
Cell constants		
a, Å	14.7968(9)	14.0179(9)
b, Å	20.5270(8)	23.4178(11)
c, Å	13.4554(8)	10.3508(1)
V, Å^3	4 086.9(4)	3 397.8(3)
μ, cm^{-1}	4.67	11.22
Crystal size, mm	0.10 × 0.35 × 0.60	0.20 × 0.35 × 0.40
D_{calc}, g cm^{-3}	1.441	1.530
$F(000)$	1 808	1 552
Radiation	MoKα (λ = 0.7170 Å)	MoKα (λ = 0.7170 Å)
Θ range, deg	1.98–25.97	1.74–25.97
h,k,l	+18, +25, +16	+17, +28, +12
No. of reflections measured	4 050	3 365
No. of reflections used in refinement	4 013	3 329
[$I > 2\sigma(I)$]		
No. of parameters	4 013	3 329
Data/parameter ratio	247	211
$R1^a$	0.0368	0.0375
$wR2^b$	0.0988	0.1131
GOF	0.813	0.918

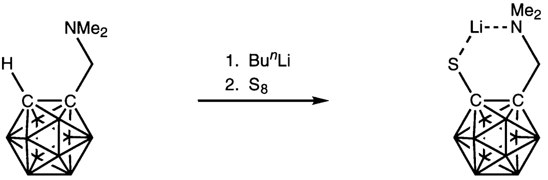
[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ (based on reflections with $F_o^2 > 2\sigma F_o^2$).
[b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.095P)^2]$; $P = [\max(F_o^2, 0) + 2F_c^2]/3$ (also with $F_o^2 > 2\sigma F_o^2$).

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-119696 (**3a**) and CCDC-118985 (**4a**). Copies of the data can be obtained free of charge on application to CCDC, e-mail: deposit@ccdc.cam.ac.uk.

RESULTS AND DISCUSSION

*Synthesis of Lithium ortho-Carboranethiolate **2***

Reaction of the known *ortho*-carborane reagent HCab^{N} **1** (ref.[2]) [HCab^{N} = *closo*-1-(dimethylaminomethyl)-*ortho*-carborane] with 1.1 equivalent of BuLi, followed by the addition of 1 equivalent of sulfur in THF at low temperature (Scheme 1), results in virtually quantitative formation of the corresponding lithium *ortho*-carboranethiolate LiCab^{N,S} **2** [LiCab^{N,S} = *closo*-2-(dimethylaminomethyl)-1-(lithiumthiolato)-*ortho*-carborane].



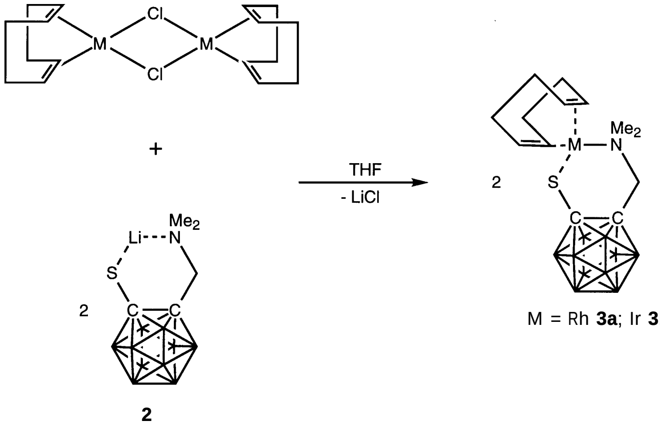
1 **2**

SCHEME 1

The pure THF-free lithium *ortho*-carboranethiolate **2** is a yellowish, off-white powder which, although slightly hygroscopic, can be handled safely in air for several minutes. Its solutions slowly decompose upon exposure to air. Complex **2** is readily soluble in Et_2O and THF and is somewhat less soluble in benzene and toluene.

*Reactions of LiCab^{N,S} (**2**) with [M(μ-Cl)(cod)]$_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene)*

N,S-Chelated amino-*ortho*-carboranethiolate metal complexes **3a**, **3b** were prepared by reactions between the dimeric metal complexes [M(μ-Cl)(cod)]$_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) and a slight excess of the corresponding lithium *ortho*-carboranethiolate **2** (Scheme 2). Isolation of pure products, which ranged in color from yellow to orange, was achieved by recrystallization. Typically, the yields of **3a**, **3b** were of the order of 62–69%.



SCHEME 2

Elemental analysis and mass spectrometry results show that the air-stable complexes **3a**, **3b** have compositions corresponding to a 1 : 1 metal complex of the M(cod) fragment and amino-*ortho*-carboranethiolate. Compounds **3a**, **3b** were characterized by IR and NMR (^{1}H, ^{11}B, and ^{13}C) spectra. The ^{1}H NMR spectrum of **3a**, **3b** shows signals for the cyclooctadiene ligand at 1.5–3.0 (methylene) and 4.0–4.4 ppm (olefinic protons). The amine moiety exhibits a singlet at 2.3–2.6 ppm assigned to the methyl group and a signal at 3.0–3.4 ppm due to the methylene protons. The IR spectrum of **3a**, **3b** exhibits one ν(C=C) stretching band at about 2 180 (s) cm^{-1} and an intense B–H stretch at about 2 600 (s) cm^{-1}. A detailed analysis of ^{1}H, ^{11}B and ^{13}C NMR, and IR spectra showed that the *ortho*-carboranyl ligand is coordinated to the metal(I) ion through sulfur and nitrogen atoms. The above spectral data suggest that the *N,S*-chelates **3a**, **3b** have the structure shown in Scheme 2. Confirmation of this structure came from a single-crystal X-ray structure determination.

X-Ray Diffraction Structure of the N,S-Chelate ***3a***

Molecular structure of **3a** is shown in Fig. 1, and a listing of selected bond lengths and angles for **3a** can be found in Table II. The crystal structure shows that coordination around the rhodium atom is approximately square-planar. The carborane cage is coordinated bidentately through N and S atoms to the Rh(I) ion, while cod is η^4-coordinated to the metal. In Table II the Rh–C(cod) distance *trans* to C–S is 2.1595(5) Å (average), which is a normal value for Rh(I) complexes containing cod ligands *trans* to S donor atoms[6]. On the contrary, the Rh–C(cod) distance *trans* to C–NMe_2 is

2.119(5) Å (average), which is comparable to that in Rh(I) complexes with a *trans* N donor ligand[7]. Thus, the Rh–C(cod) distance *trans* to C–S is longer than that *trans* to C–NMe$_2$. Higher contribution by back-donation is found in the alkene fragment of cod *trans* to C–NMe$_2$. The Rh–S bond length 2.359(1) Å is in the range of bond lengths found for binuclear thiolate-bridged complexes; the longest related bond was reported for [Rh(μ-SC$_6$H$_5$)(cod)]$_2$ [2.41 Å (average)][8], and the shortest was reported for [Rh(μ-S(CH$_2$)$_3$NMe$_2$)(cod)]$_2$ [2.34 Å (average)][9]. The Rh–N bond distance is 2.272(4) Å, which is a normal value for Rh(I) complexes containing a cod ligand[10]. The six-membered Rh–S–C–C–C–N ring is non-planar, with the dihedral angles between the planes defined by [Rh(1), S(1), C(3), N(1)] and [S(1), C(1), C(2), C(3)] being 61.46(15)°. The sum of the angles [360.9(4)°] around Rh formed by the coordinated N and S atoms and the midpoints of the double-bond carbon atoms of cod indicates the planarity of the (*N*,*S*)Rh(diene) moiety. The bond lengths and angles associated with cod and the coordinated *ortho*-carboranethiolate ligand in **2** are unexceptional with respect to other *ortho*-carborane-substituted compounds[11].

*Synthesis and Spectroscopic Characterization of Compounds Cab^{N,S}M(CO)$_2$ **4** (M = Rh **4a**, Ir **4b**)*

The reactions of **3a**, **3b** with excess carbon monoxide occur rapidly at room temperature to yield CO-coordinated products Cab^{N,S}M(CO)$_2$ **4a**, **4b** [M =

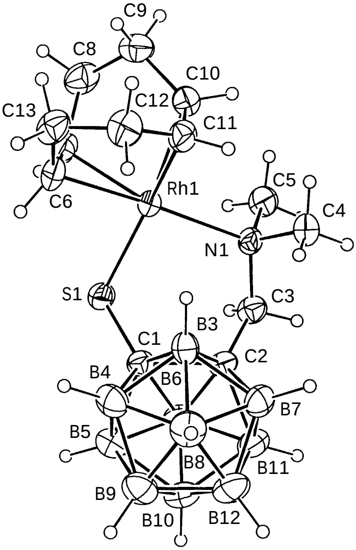
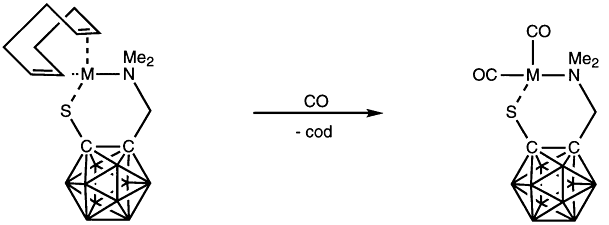


FIG. 1
Molecular structure of Cab^{N,S}Rh(cod) (**3a**). The thermal ellipsoids are drawn at the 30% probability level

Rh (**4a**), Ir (**4b**)] as shown in Scheme 3. Thus carbon monoxide easily replaces the cod in complexes **3a**, **3b** to give the orange-yellow colored complexes **4a**, **4b** in excellent yields. Complexes **4a**, **4b** were isolated as air-stable microcrystalline solids and were spectroscopically characterized. The composition of the new complexes **4a**, **4b** is unequivocally established by elemental analysis and mass spectrometry.



3

M = Rh **4a**; Ir **4b**

SCHEME 3

Furthermore, the spectroscopic data (^{1}H, ^{11}B, and ^{13}C NMR) associated with **4a**, **4b** are also consistent with their assigned structure. Indeed, the ^{1}H NMR spectrum consists of two singlets from the NMe_2 resonances (at 3.02 and 2.99 ppm) in **4a** and an AB pattern for the NCH_2 protons [3.38 ppm (J_{gem} = 13 Hz)] in **4b**. This result demonstrates that, under these conditions, the NMe_2 and NCH_2 hydrogen atoms are diastereotopic and are in agreement with the coordination of at least one NMe_2 ligand to the metal atom. This points to coordination of the N atoms to M (Rh, Ir) resulting in blocking of the inversion at the nitrogen on the NMR time scale because only in this situation is the N atom in a stable square-pyramidal array, producing diastereotopic Me groups. This observation is consistent with similar findings for the general intramolecularly coordinated metal complexes of the $HCab^N$ ligand system[12]. The ^{13}C NMR spectra have signals for compounds **4a**, **4b**, one for the unique $N(CH_3)_2$ carbons, one for the NCH_2 group, and one set of signals attributable to the carbonyl ligand. The pattern and relative intensity of the ν(CO) bands of **4a**, **4b** resemble closely those of the compounds having the *cis*-dicarbonylrhodium environments[13].

X-Ray Diffraction Analyses of $Cab^{N,S}Rh(CO)_2$ ***4a***

The molecular structure of **4a** is shown in Fig. 2, and the selected bond lengths and angles are listed in Table II. The complex contains the expected

TABLE II
Selected interatomic distances (Å) and angles (°) in **3a** and **4a**

Bond distances in **3a**			
Rh–S1	2.359(1)	Rh–N1	2.272(4)
Rh–C6	2.128(5)	Rh1–C7	2.110(5)
Rh1–C10	2.171(5)	Rh1–C11	2.148(5)
S1–C1	1.771(5)	N1–C3	1.493(6)
C1–C2	1.670(7)	C2–C3	1.514(7)
C6–C7	1.405(7)	C7–C8	1.497(8)
C8–C9	1.519(8)	C9–C10	1.517(7)
C10–C11	1.379(7)	C11–C12	1.515(8)
C12–C13	1.516(8)	C6–C12	1.521(7)
Bond angles in **3a**			
N1–Rh1–S1	89.89(11)	C1–S1–Rh1	101.80(17)
C3–N1–Rh1	115.7(3)	C2–C1–S1	116.9(3)
N1–C3–C2	118.1(4)	C3–C2–C1	114.7(4)
Interatomic angles in **3a**			
C6–Rh1–C7	38.7(2)	C6–Rh1–C11	81.0(2)
C10–Rh1–C11	37.2(2)	C7–Rh1–C10	81.5(2)
Bond distances in **4a**			
Rh1–S1	2.368(2)	Rh1–N1	2.190(4)
Rh1–C6	1.868(8)	Rh1–C7	1.834(7)
C6–O1	1.131(8)	C7–O2	1.127(7)
N1–C3	1.490(6)	C2–C3	1.510(7)
S1–C1	1.773(5)	C1–C2	1.677(7)
Bond angles in **4a**			
N1–Rh1–S1	92.72(11)	N1–Rh1–C6	91.2(2)
C6–Rh1–C7	88.8(3)	S1–Rh1–C7	87.1(2)
C1–S1–Rh1	101.81(17)	C2–C3–N1	118.5(4)
C2–C1–S1	116.7(3)	C1–C2–C3	115.5(4)

square-planar environment of rhodium atom, coordinated to two carbonyl ligands and to the anionic amino-*ortho*-carboranethiolate ligand, *via* the nitrogen and the sulfur atom. The Rh–C(6) bond distance *trans* to the sulfur atom [1.868(8) Å] is longer than that *trans* to the nitrogen atom [1.834(7) Å]. This lengthening agrees well with the *trans* influences expected for the various ligands. The Rh–S and Rh–N distances in **4a** are comparable with those involving the aminoethanethiolato ligands found in [{Rh_2(2-aminoethanethiolato)$_4$(cystamine)}$^{2+}$] (ref.[14]) [2.3099(6) and 2.135(2) Å], even if the Rh atoms are in different oxidation states and environments. The six-membered Rh–S–C–C–C–N ring is non-planar, with the dihedral angles between the planes defined by [Rh(1), S(1), C(3), N(1)] and [S(1), C(1), C(2), C(3)] being 59.50(15)°. The sum of the angles [359.8 (2)°] around Rh formed by the coordinated *ortho*-carboranethiolate N and S atoms and two carbonyl carbon atoms clearly indicates the planarity of the (*N*,*S*)$Rh(CO)_2$ moiety.

CONCLUSIONS

The results presented on complexes **3a**, **3b** and **4a**, **4b** are the first detailed structural studies of an *N*,*S*-chelating *ortho*-carboranethiolate with intramolecular coordination, and they nicely demonstrate a variety of coordinations possible with an *N*,*S*-chelating *ortho*-carboranethiolate

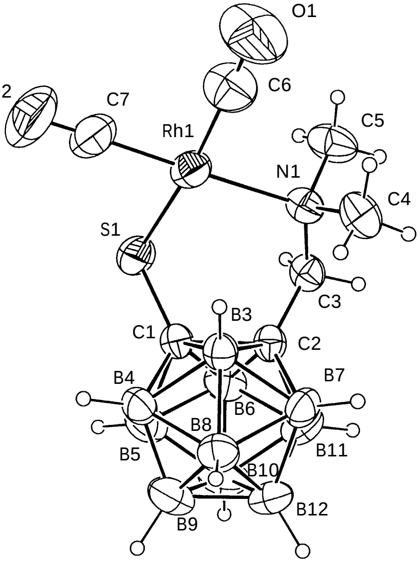


FIG. 2
Molecular structure of $Cab^{N,S}Rh(CO)_2$ (**4a**). The thermal ellipsoids are drawn at the 30% probability level

ligand. In summary, we have synthesized and fully characterized the 16-electron rhodium and iridium complex **3a**, **3b** containing a bulky *N*,*S*-chelating *ortho*-carboranethiolate ligand. When the metal amino-*ortho*-carboranethiolate complexes Cab^{N,S}M(cod) **3** are treated with carbon monoxide, conversion to the carbonyl *ortho*-carboranethiolate complexes, **4**, takes place. Thus, the first organometallic *ortho*-carboranethiolate complexes possessing two carbonyl ligands are included. Further study on the utilization of complexes **3a**, **3b** and **4a**, **4b** for the synthesis of new types of organometallic complexes is under extensive investigation.

Financial support by the Korea Research Foundation (1997–1999) is gratefully appreciated.

REFERENCES

1. a) Bader A., Linder E.: *Coord. Chem. Rev.* **1991**, *91*, 27; b) Murray S. G., Hartley F. R.: *Chem. Rev.* **1981**, *81*, 365.
2. Heying T. L., Ager J. W., Jr., Clark S. L., Mangold D. J., Goldstein H. L., Hilman M., Polak R. J., Szymanski J. W.: *Inorg. Chem.* **1963**, *2*, 1089.
3. Giordano G., Crabtree R. H.: *Inorg. Synth.* **1979**, *19*, 218.
4. Crabtree R. H., Morris G. E.: *J. Organomet. Chem.* **1977**, 135.
5. a) Sheldrick G. M. in: *Crystallographic Computing 3* (G. M. Sheldrick, C. Kruger and R. Goddard, Eds), p. 175. Oxford University Press, London 1985; b) Sheldrick G. M. in: *Crystallographic Computing 6* (H. D. Flack, L. Parkanyi and K. Simon, Eds), p. 111. Oxford University Press, London 1993.
6. a) Claver C., Ruiz A., Masdeu A., Viñas J., Saballs T., Lahoz F., Plau F. J.: *Organomet. Chem.* **1989**, *373*, 269; b) Pinillos M. T., Jarauta M. P., Oro L. A., Tripicchio A., Tripicchio-Camellini M.: *J. Organomet. Chem.* **1988**, *339*, 181.
7. Tejel C., Villoro J. M., Ciriano M. A., López J. A., Eguizábal E., Lahoz F. J., Bakhmutov V. I., Oro L. A.: *Organometallics* **1996**, *15*, 2967.
8. Cruz-Garritz C., Rodríguez B., Torrens H., Leal J.: *Transition Met. Chem.* **1984**, *9*, 284.
9. Polo A., Claver C., Castillón S., Ruiz A.: *Organometallics* **1992**, *11*, 3525.
10. Akita M., Ohta K., Takahashi Y., Hikichi S., Moro-oka Y.: *Organometallics* **1997**, *16*, 4121.
11. a) Teixidor F., Benakki R., Viñas C., Kivekäs R., Sillanpää R.: *Organometallics* **1998**, *17*, 4630; b) Mastryukov V. S., Dorofeeva O. V., Vilkov L. V.: *Russ. Chem. Rev.* **1980**, *49*, 1181; c) Mastryukov V. S., Dorofeeva O. V., Vilkov L. V.: *Usp. Khim.* **1980**, *49*, 2377.
12. Lee J.-D., Baek C.-K., Ko J., Park K., Cho S., Min S.-K., Kang S. O.: *Organometallics*, in press.
13. Ciriano M. A., Viguri F., Perez-Torrente J. J., Lahoz F. J., Oro L. A., Tiripicchio A., Tripicchio-Camellini M.: *J. Chem. Soc., Dalton Trans.* **1989**, 25.
14. Miyashita Y., Sakagami N., Yamada Y., Konno T., Okamoto K.: *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2153.