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Steric Influence on the Reactivity of the (*o*-Carboranedithiolato)iridium(III) Complex [Ir(η^5-C_5Me_5)(η^2-$S_2C_2B_{10}H_{10}$)]: New Types of Addition Reactions Involving Cyclometalation or Isomerization[†]

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The reactivity of the mononuclear 16-electron iridadithiolene ring complex Cp*Ir($S_2C_2B_{10}H_{10}$) (**1**) toward alkynes, a diazoalkane, and quadricyclane has been investigated. Reaction of **1** with an excess of alkyne resulted in the incorporation of one alkyne molecule, giving Cp*Ir[*o*-$BC_2B_9H_9SS\{\eta^2$-($R^1HC{=}CR^2$)$\}$-*S*] (**2**: $R^1 = H$, $R^2 = Ph$, **2a**; $R^1 = COOCH_3$, $R^2 = COOCH_3$, **2b**), containing a cyclometalated four-membered metallacycle ring of Ir−B−C−S and a coordinating alkenethiol group. Reaction of **1** with (trimethylsilyl)diazomethane resulted in the formation of the bicyclic iridium metal complex Cp*Ir[*o*-$BC_2B_9H_9SS(CH_2SiMe_3)$-*S,S′*] (**3**), in which cyclometalation of a coordinated dithiolato ligand at the iridium(III) metal center has occurred, accompanied by transfer of the methylene group to one end of the sulfur atom of the dithiolato ligand. The X-ray structures of **2a** and **3** are reported. In both complexes, the central iridium atom is coordinated to the boron atom in a three-legged piano-stool structure. On the other hand, the reaction of **1** with quadricyclane afforded the addition product Cp*Ir[$C_2B_{10}H_{10}SS\{\eta^1$-($CH{=}CH$)$C_5H_6\}$-*S*] (**4**), formed through the isomerization of a quadricyclane unit. The six-membered metallacyclic compound **4** was proven by the X-ray structure determination of the complex. Interestingly, the reaction of LiCab^{N,S} (LiCab^{N,S} = $C_2B_{10}H_{10}(LiS)(CH_2NMe_2)$-*N*,$S^-$) with $[Cp^*IrCl_2]_2$ yielded the cyclometalated compound Cp*Ir[*o*-$BC_2B_9H_9S(CH_2NMe_2)$-*N*,*S*] (**5**). The structure of **5** was determined by X-ray diffraction analysis, exhibiting a three-legged piano-stool structure consisting of a four-membered metallacyclic ring of Ir−B−C−S and a five-membered metallacyclic ring due to intramolecular coordination of a B,N-chelating ligand system.

Introduction

The synthesis and study of organometallic complexes possessing an ancillary *o*-carboranedithiolato ligand have continued to receive attention.[1] Our interest in the synthesis and reactivity of coordinatively unsaturated low-valent metal complexes[2] now leads us to explore the use of an *o*-carboranedithiolato ligand in the formation of metalladithiolene ring complexes. An attractive feature of such reactive metalladithiolene ring complexes is the unsaturation at the metal and sulfur atoms.[3] It has been observed that addition reactions between the metal and sulfur atoms are reactions characteristic of the metalladithiolene ring complex CpCo($S_2C_2B_{10}H_{10}$) (**A**). Consequently, **A** has reacted with alkynes and a diazoalkane, generating the new class of 1:1 addition products **B** and **C** incorporating alkene and alkylidene units, respectively (Scheme 1).[4]

In this respect, we have started investigating the reactivity of Cp*Ir($S_2C_2B_{10}H_{10}$) (**1**),[5] bearing a bulky Cp* ligand that might confer some additional reactivity on the metal−sulfur bond. A rationale with respect to cyclometalation and isomerization for the addition reactions, based on the steric bulkiness of the ancillary Cp* ligand, has been established. Using two suitable metal

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[†] This contribution is dedicated to Professor Dietmar Seyferth on the occasion of his 70th birthday.

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(1) (a) Base, K.; Grinstaff, M. W. *Inorg. Chem.* **1998**, *37*, 1432. (b) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *J. Chem. Soc., Dalton Trans.* **1997**, 1099. (c) Crespo, O.; Gimeno, M. C.; Jones, P. G.; Laguna, A. *J. Chem. Soc., Chem. Commun.* **1993**, 1696. (d) Contreras, J. G.; Silva-trivino, L. M.; Solis, M. E. *J. Coord. Chem.* **1986**, *14*, 309. (e) Smith, H. D., Jr.; Robinson, M. A.; Papetti, S. *Inorg. Chem.* **1967**, *6*, 1014. (f) Smith, H. D., Jr.; Obenland, C. O.; Papetti, S. *Inorg. Chem.* **1966**, *5* 1013. (g) Smith, H. D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 1817.

(2) (a) Mashima, K.; Kaneyoshi, H.; Kaneko, S.; Mikami, A.; Tani, K.; Nakamura, A. *Organometallics* **1997**, *16*, 1016. (b) Michelman, R. I.; Ball, G. E.; Bergman, R. G.; Anderson, R. A. *Organometallics* **1994**, *13*, 869. (c) Garcia, J. J.; Torrens, H.; Adams, H.; Bailey, N. A.; Scacklady, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1993**, 1529. (d) Michelman, R. I.; Anderson, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 5100. (e) Garcia, J. J.; Torrens, H.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1991**, 74. (f) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

(3) Sellmann, D.; Geck, M.; Knoch, F.; Ritter, G.; Dengler, J. *J. Am. Chem. Soc.* **1991**, *113*, 3819.

(4) Kim, D.-H.; Ko, J.; Park, K.; Cho, S.; Kang, S. O. *Organometallics* **1999**, *18*, 2738.

(5) Bae, J.-Y.; Park, Y.-I.; Ko, J.; Park, K.-I.; Cho, S.-I.; Kang, S. O. *Inorg. Chim. Acta* **1999**, *289*, 141.

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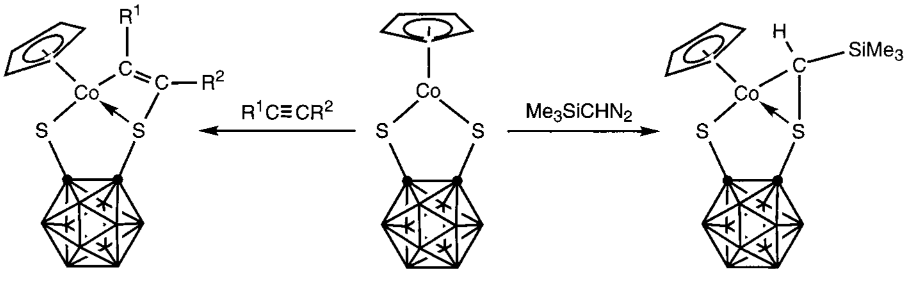
Scheme 1

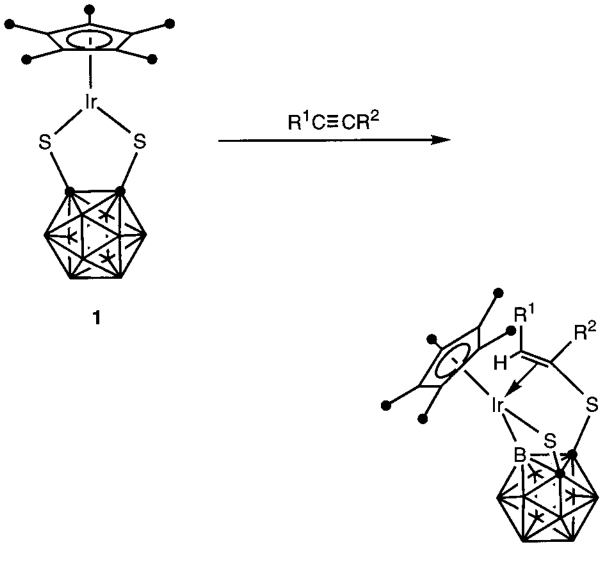


complexes of different nature of the ancillary ligand (Cp vs Cp*), it has been possible for us to show that bulkiness of the ancillary Cp* ligand in the metal complexes plays an important role in the cyclometalation and the isomerization processes. Whereas the metalladithiolene complex **A** undergoes addition reactions at the metal and the sulfur, the complex **1** undergoes addition reactions mainly at sulfur atoms, forming an S-alkylated product, accompanied by cyclometalation of a coordinated dithiolato ligand at the iridium(III) metal center. In the reaction between **1** and quadricyclane, a new type of addition reaction was observed, and the bridging of the isomerized C_7H_8 unit occurred between the metal and sulfur atoms. Thus, an iridadithiolene ring complex with a bulky ancillary Cp* ligand has been further exploited in chemical transformations such as cyclometalation and isomerization.

Results and Discussion

Reaction of 1 with Alkynes. The new complexes **2a**,**b** were prepared from reactions between **1** and a slight excess of the corresponding acetylenes (Scheme 2). After workup, the product was found to be an intramolecular B-coordinated complex rather than an insertion product of the type **A**. Thus, when a mixture of acetylenes (1.0 mmol) and **1** (0.51 mmol) in toluene (15 mL) was reacted at room temperature for 8 h, the color of the solution changed from purple to yellow. Isolation of the pure products was achieved by recrystallization. Typically, the yields of **2a**,**b** were on the order of 90−94%.

Scheme 2



R¹ = H, R² = Ph **2a**;
R¹, R² = COOCH₃ **2b**

All these complexes were characterized by a combination of elemental analysis and IR and NMR (^{1}H, ^{11}B, and ^{13}C) spectroscopy. The IR spectra of **2a**,**b** exhibit one $\nu_{C=C}$ stretching band, and the ^{1}H NMR spectra of **2a**,**b** display the characteristic resonances of a coordinated olefin. Thus, for **2a**, the terminal protons give rise to two doublets centered at 3.19 and 2.69 ppm with a $^2J_{HH}$ value of 2.7 Hz. The ^{1}H NMR spectrum of **2b** shows a singlet (3.83 ppm) of the terminal proton and two nonequivalent ^{1}H signals (3.81 and 3.77 ppm) of the O*Me* groups of the ester. For the ^{13}C{^{1}H} NMR spectra of **2a**,**b**, it is sufficient to point out that the resonances due to the π-bound olefin carbons are characteristically upfield-shifted. The ^{11}B NMR spectrum consists of an unresolved set of broad, overlapping resonances between −2.13 and −13.16 ppm. All the resonances are split into a B−H-coupled doublet, except for the resonance at around −24 ppm, which appears as a singlet in the proton-coupled spectrum. The singlet clearly represents the boron atom to which the iridium is bonded.[6] The NMR spectra of the iridium complexes are in complete agreement with the crystal structure of a representative example, **2a** (vide infra). Figure 1 and Table 2 show the ORTEP drawing and selected bond distances and bond angles, respectively. The structural analysis of **2a** indeed authenticated the cyclometalation of the coordinated dithiolato ligand at the iridium(III) metal center. In addition, **2a**·CH_2Cl_2 shows a puckering of the five-membered iridadithiolene ring in **1**, resulting in the olefinic carbon atoms being brought closer to the metal center, possibly in an effort to relieve its steric repulsion. It is also possible that a better overlap of the alkenyl moiety to the iridium metal center is responsible for such a puckering of the iridadithiolene ring. In **2a**·CH_2Cl_2, coordination of a vinyl group to the iridium atom causes the cleavage of the Ir−S bond of the iridadithiolene ring to give the alkenethiol structure. Thus, **2a**·CH_2Cl_2 adopts a three-legged piano-stool conformation with B(3), S(2), and the olefin C(13)−C(14) moiety as the legs. The olefin moiety of the thiol ligand is bonded unsymmetrically to the metal center, with the Ir−C bonds to the internal and terminal carbon atoms C(13) and C(14) being 2.103(7) and 2.147(8) Å, respectively. The five-membered ring (Ir(1), C(14), S(1), C(1), B(3)) is nearly planar, with the largest deviation of the ring

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[6] Hoel, E. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1974**, *96*, 6770.

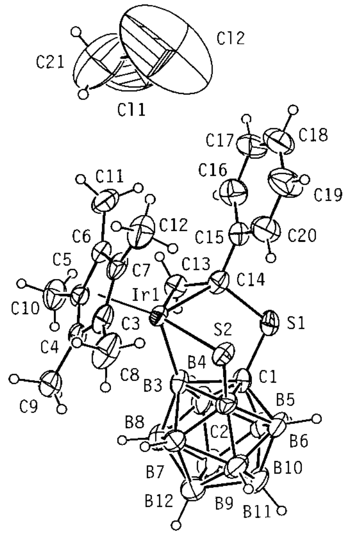


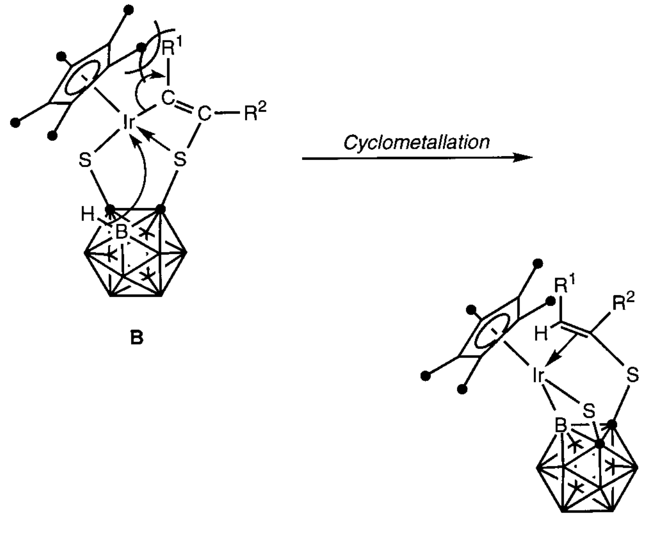
Figure 1. ORTEP drawing of **2a**·CH_2Cl_2 with the numbering scheme.

atoms from the mean plane at C(14) (0.234(4) Å). The dihedral angle between the plane defined by Ir(1), C(14), S(1), C(1), and B(3) atoms and that by Ir(1), S(2), C(2), and B(3) atoms is 75.5(2)°. The Ir(1)−B(3) bond length was found to be 2.097(8) Å. The bond length of C(13)−C(14) (1.40(1) Å) is slightly longer than the typical value for the carbon−carbon double bond and agrees with the normal metal−olefin C═C bond length. The bond length of Ir(1)−S(2) (2.406(2) Å) is longer than the corresponding value of the original complex **1** (2.257 Å (average)) and the normal Ir(III)−SR_2 bond (2.35 Å).[7]

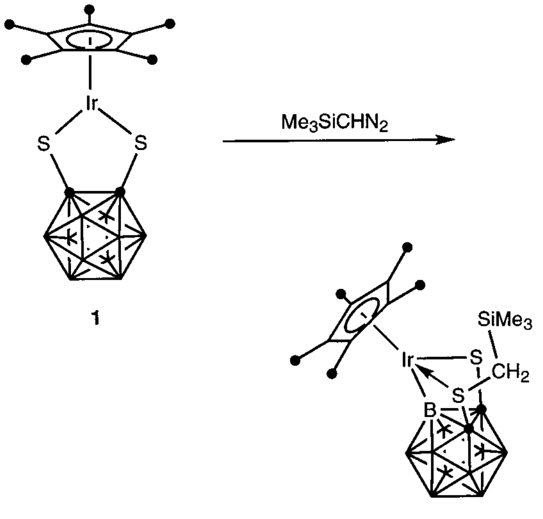
Although the process outlined in Scheme 2 proved quite general, there were, however, structural limitations observed for the metallatricyclic complexes **2**. For example, several attempts to synthesize the complexes **2** with electron-rich acetylenes such as dialkylated and silylated acetylenes were unsuccessful, yielding only decomposition under prolonged reflux conditions. Conversion of **1** to the corresponding metallatricyclic compounds **2** is generally favored by electron-deficient alkynes; therefore, we decided to investigate the reactivity of alkyne complexes as electron-deficient triple-bond systems toward complex **1**. Indeed, compounds **2a**,**b** were produced in high yields from the direct two-carbon insertion reaction of alkynes with complex **1**. The reactions of **1** with alkynes cause the Ir−S bond cleavage of the initial five-membered metallacyclic ring to yield new adducts **2a**,**b** in which alkenyl groups coordinate to the iridium atom.

We propose here a possible reaction sequence for the formation of complex **2** by cyclometalation, as shown in Scheme 3. Reaction of **1** with alkynes results first in the formation of the alkyne adducts **B**, which undergo an cyclometalation process, in which activation of the B−H bond of the coordinated dithiolato ligand has occurred, accompanied by cleavage of the Ir−C bond at one end of the alkene linkage. A similar intramolecular oxidative addition involving an *ortho* B−H bond has been originally reported by Hawthorne et al.[8] and further studied by Kalinin et al.[9]

Scheme 3



Reaction of 1 with (Trimethylsilyl)diazomethane. The reactions of **1** with $SiMe_3CHN_2$ occur rapidly at 0 °C, accompanied by vigorous evolution of N_2 to yield the S-alkylated product **3** as shown in eq 1. Treatment of **1** with the diazo complex $SiMe_3CHN_2$ afforded the soluble product Cp*Ir[*o*-$BC_2B_9H_9SS(CH_2SiMe_3)$-*S*,*S′*] (**3**) in excellent yields (96%), after recrystallization. The composition of the new complex **3** is unequivocally established by elemental analysis.



(1)

Complex **3** was isolated as an air-stable microcrystalline solid and was spectroscopically characterized. Complex **3** shows the expected ^1H, ^{11}B, and ^{13}C NMR signals. ^1H NMR data for **3** conform to the structure determined by the X-ray structural study. Thus, the ^1H NMR spectrum of compound **3** exhibits resonances for

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(7) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Tylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 61.

(8) Hoel, E. L.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1973**, *95*, 2712.

(9) (a) Kalnin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Proc. Indian Natl. Sci. Acad.* **1989**, *55*, 293. (b) Kalnin, V. N.; Usatov, A. V.; Zakharkin, L. I. *J. Organomet. Chem.* **1983**, *254*, 127. (c) Kalinin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Zh. Obshch. Org. Khim.* **1983**, *53*, 945. (d) Kalinin, V. N.; Usatov, A. V.; Popello, I. A.; Zakharkin, L. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1982**, 1433. (e) Kalinin, V. N.; Usatov, A. V.; Zakharkin, L. I. *Zh. Obshch. Org. Khim.* **1981**, *51*, 2151.

Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds 2a and 3−5

	2a·CH_2Cl_2	**3**	**4**	**5**
formula	$B_{10}C_{21}H_{33}Cl_2IrS_2$	$B_{10}C_{16}H_{35}IrS_2Si$	$B_{10}C_{19}H_{33}IrS_2$	$B_{10}C_{15}H_{32}IrNS$
fw	720.79	619.95	625.87	558.78
cryst class	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)	$P2_1/n$ (No. 14)
Z	4	4	2	4
cell constants				
a, Å	14.9000(8)	10.199(1)	11.1446(5)	10.1031(8)
b, Å	10.1128(7)	14.834(5)	10.996(1)	16.4241(7)
c, Å	19.4403(9)	17.139(7)	11.39550(5)	14.159(2)
V, Å^3	2917.8(3)	2591(1)	1237.0(1)	2241.1(4)
α, deg				
β, deg	95.083(4)	92.24(2)	117.642	107.46(1)
γ, deg				
μ, cm^{-1}	4.914	5.364	5.573	6.052
cryst size, mm	0.25 × 0.30 × 0.50	0.20 × 0.30 × 0.30	0.30 × 0.10 × 0.30	0.20 × 0.25 × 0.30
D_{calcd}, g/cm^3	1.641	1.589	1.680	1.656
F(000)	1408	1216	612	1088
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
λ, Å	0.7170	0.7170	0.7170	0.7170
θ range, deg	1.65−25.97	1.82−25.98	2.02−25.97	1.95−25.97
h, k, l collected	+18, +12, ±23	+12, +18, ±21	+13, +13, ±12	+12, +20, ±16
no. of rflns measd	5966	5409	2562	4687
no. of unique rflns	5705	5080	2400	4395
no. of rflns used in refinement ($I > 2\sigma(I)$)	5705	5080	2400	4395
no. of params	344	288	307	269
data/param ratio	16.58	17.64	7.82	16.34
R1[a]	0.0388	0.0535	0.0532	0.0376
wR2[b]	0.1074	0.1299	0.1538	0.0976
GOF	0.889	0.872	1.500	0.844

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

Table 2. Selected Interatomic Distances and Angles in 2a and 3−5

		Bond Distances (Å)			
		Compound **2a**			
Ir(1)−B(3)	2.097(8)	Ir(1)−C(13)	2.103(7)	Ir(1)−C(14)	2.147(8)
Ir(1)−S(2)	2.4057(16)	S(1)−C(1)	1.753(8)	S(1)−C(14)	1.829(7)
S(2)−C(2)	1.772(7)	C(1)−C(2)	1.731(9)	C(1)−B(3)	1.762(10)
C(2)−B(3)	1.746(10)	C(13)−C(14)	1.403(10)		
		Compound **3**			
Ir(1)−B(6)	2.082(12)	Ir(1)−S(1)	2.387(3)	Ir(1)−S(2)	2.391(3)
S(1)−C(1)	1.784(11)	S(1)−C(13)	1.818(13)	S(2)−C(2)	1.784(11)
Si(1)−C(13)	1.892(11)	C(1)−C(2)	1.713(16)	C(1)−B(6)	1.732(17)
C(2)−B(6)	1.734(16)				
		Compound **4**			
Ir(1)−C(13)	2.15(3)	Ir(1)−S(1)	2.277(5)	Ir(1)−S(2)	2.473(5)
S(2)−C(2)	1.91(4)	S(1)−C(1)	1.788(18)	S(1)−C(19)	1.79(3)
C(2)−C(1)	1.79(4)	C(13)−C(14)	1.28(4)	C(14)−C(15)	1.54(3)
C(15)−C(19)	1.47(3)	C(15)−C(16)	1.80(3)	C(16)−C(17)	1.50(4)
C(17)−C(18)	1.51(4)	C(18)−C(19)	1.53(3)		
		Compound **5**			
Ir(1)−B(6)	2.085(8)	Ir(1)−N(1)	2.185(6)	Ir(1)−S(1)	2.397(2)
S(1)−C(1)	1.782(8)	N(1)−C(3)	1.506(10)	C(1)−C(2)	1.664(10)
C(2)−C(3)	1.484(10)				
		Bond Angles (deg)			
		Compound **2a**			
B(3)−Ir(1)−C(13)	84.3(3)	C(13)−Ir(1)−C(14)	38.5(3)	B(3)−Ir(1)−S(2)	72.1(2)
C(14)−Ir(1)−S(2)	87.0(2)	C(1)−S(1)−C(14)	102.7(4)	C(2)−S(2)−Ir(1)	89.0(2)
		Compound **3**			
B(6)−Ir(1)−S(1)	71.7(4)	B(6)−Ir(1)−S(2)	73.5(4)	S(1)−Ir(1)−S(2)	80.86(10)
C(1)−S(1)−C(13)	103.2(5)	C(1)−S(1)−Ir(1)	87.6(4)	C(13)−S(1)−Ir(1)	119.4(4)
C(2)−S(2)−Ir(1)	86.4(4)				
		Compound **4**			
C(13)−Ir(1)−S(1)	90.1(6)	S(1)−Ir(1)−S(2)	71.15(18)	C(2)−S(2)−Ir(1)	101.8(7)
C(1)−S(1)−C(19)	106.3(12)	C(1)−S(1)−Ir(1)	109.5(6)	C(19)−S(1)−Ir(1)	111.7(8)
		Compound **5**			
B(6)−Ir(1)−N(1)	82.0(3)	N(1)−Ir(1)−S(1)	84.30(18)	C(1)−S(1)−Ir(1)	87.4(2)
C(5)−N(1)−C(3)	107.6(7)	C(4)−N(1)−C(3)	109.2(7)	C(3)−N(1)−Ir(1)	111.7(4)

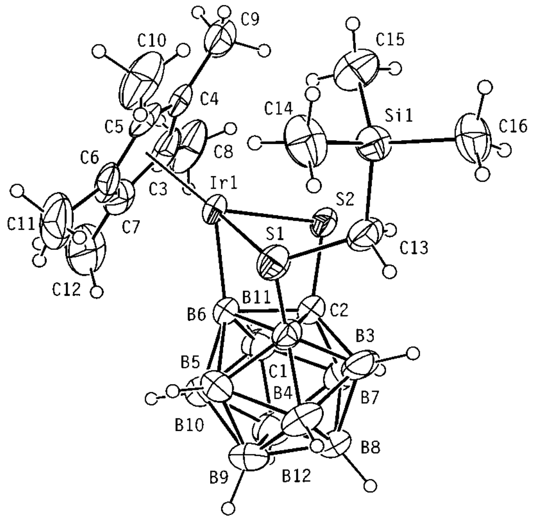
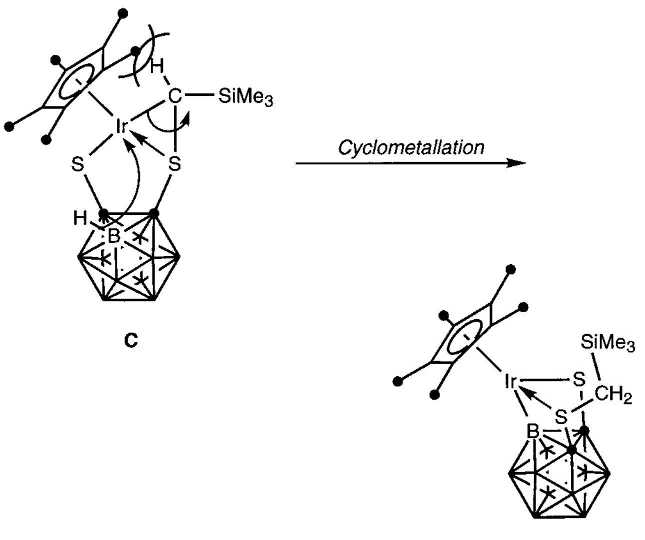


Figure 2. ORTEP drawing of **3** with the numbering scheme.

Scheme 4



a Cp* ligand at 1.94 ppm, a trimethylsilyl group at 0.17 ppm, and an AB pattern for the NCH_2 protons (3.28 and 1.62 ppm ($^2J_{HH} = 12.4$ Hz)). The initial indication of cyclometalation for **3** stemmed from the observation of a singlet resonance in the $^{11}B-^{1}H$ NMR spectrum at −21.91 ppm. The ^{13}C NMR spectrum also corresponds to the S-alkylated structure: two types of carbon atoms of the Cp* ring and carbon atoms of the S-substituted (trimethylsilyl)methylene unit.

The product from this unusual reaction was finally confirmed on the basis of the X-ray structure determination. The molecular structure of **3** is shown in Figure 2. Selected bond lengths and bond angles are given in Table 2. The X-ray structure of **3** shows that the iridium takes a three-legged piano-stool configuration with two four-membered metallacyclic rings. This is due to the cyclometalation of the coordinated dithiolato ligand at the iridium(III) metal center. The four Ir, S, C, and B atoms comprising the central skeleton of the molecule are all nearly coplanar, with a dihedral angle of 80.4(3)° between the two planes defined by [Ir(1), S(1), C(1), B(6)] and [Ir(1), S(2), C(2), B(6)]. The iridadithiolene ring in **1** is puckered at Ir(1); the remaining four atoms [S(1), C(1), C(2), S(2)] form an almost perfect plane. The Ir(1)−B(6) bond length of 2.08(1) Å is shorter than the iridium−boron distance in **2a**. The Ir−S distances (Ir(1)−S(1) = 2.387(3) Å, Ir(1)−S(2) = 2.391(3) Å) of compound **3** at the formally 18-electron iridium center are significantly longer than that (2.257 Å (average)) of complex **1**. This difference in bond length may be attributed to π-orbital donation of the lone pairs from the sulfur atoms to the electron-deficient iridium center of complex **1**.[10] The Ir−S bond lengths and the S(1)−Ir(1)−S(2) bond angle (80.9(1)°) in **3** can be compared with the corresponding parameters in Cp*Ir(PMe_3)(S_6) (2.375 Å (average) and 101.1(1)°),[11] Cp*Ir(PMe_3)$(SH)_2$ (2.375 Å (average) and 88.74(7)°),[10a] and [Cp*Ir($CNBu^t$)(μ-S)]$_2$ (2.372 Å (average) and 79.32(9)°)[10c] as well as in [Cp*Ir(μ_3-S)]$_4$ (2.372 Å and 81.2° (average)).[10c]

One reasonable description of the formation of **3** is shown in Scheme 4. The formation of a methylene bridge between the metal and a chalcogen in the reaction with diazo compounds is a typical reaction due to unsaturation.[12] It has been observed that a diazo compound reacts with metalladitholene complex **A** to yield alkylidene-bridged complex **C** containing an M−C−S three-membered ring.[4] Upon formation of a methylene bridge between the metal and a sulfur, the iridium atom comes in close proximity to the *ortho* B−H of the pendant *o*-carboranyl group of the dithiolato ligand for cyclometalation. Cyclometalation followed by cleavage of the alkylidene ligand are the two most plausible steps in this reaction.

Reaction of 1 with Quadricyclane. The formation of a 1:1 adduct of (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) and quadricyclane is well-established.[13] Thus, we carried out an analogous reaction of **1** with quadricyclane. The reaction between **1** and 4 equiv of quadricyclane in refluxing toluene for 8 h produced a product **4** of yellow crystals in 88% yield (eq 2).

The compound **4** has been characterized by NMR, IR, and elemental analysis. Seven resonances in the ^1H NMR spectrum and seven singlets in the ^{13}C NMR spectrum of **4** assigned to the quadricyclane group on the iridium atom demonstrate that the seven carbon atoms are not equivalent. In addition, the IR spectrum of **4** shows a new signal for an internal C=C bond. The

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(10) (a) Dobbs, D. A.; Bergmann, R. G. *Inorg. Chem.* **1994**, *33*, 5329. (b) Dobbs, D. A.; Bergmann, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 6908. (c) Klein, D. P.; Kloster, G. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 2022.

(11) Herberhold, M.; Jin, G.-X.; Rheingold, A. L. *Chem. Ber.* **1991**, *124*, 2245.

(12) (a) Takayama, C.; Takeuchi, K.; Kajitani, M.; Sugiyama, T.; Sugimori, A. *Chem. Lett.* **1998**, 241. (b) Sakurada, M.; Kajitani, M.; Dohki, K.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *423*, 141. (c) Sakurada, M.; Okubo, J.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Phosphorous, Sulfur, Silicon Relat. Elem.* **1992**, *67*, 145. (d) Kajitani, M.; Sakurada, M.; Dohki, K.; Suetsugu, T.; Akiyama, T.; Sugimori, A. *J. Chem. Soc., Chem. Commun.* **1990**, 19. (e) Sakurada, M.; Okubo, J.; Kajitani, M.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1990**, 1837.

(13) (a) Kajitani, M.; Hatano, H.; Fujita, T.; Okumachi, T.; Nagao, H.; Akiyama, T.; Sugimori, A. *J. Organomet. Chem.* **1992**, *430*, C64. (b) Kajitani, M.; Fujita, T.; Okumachi, T.; Yokoyama, M.; Hatano, H.; Ushijima, H.; Akiyama, T.; Sugimori, A. *J. Mol. Catal.* **1992**, *77*, L1. (c) Kajitani, M.; Eguchi, Y.; Abe, R.; Akiyama, T.; Sugimori, A. *Chem. Lett.* **1990**, 359.

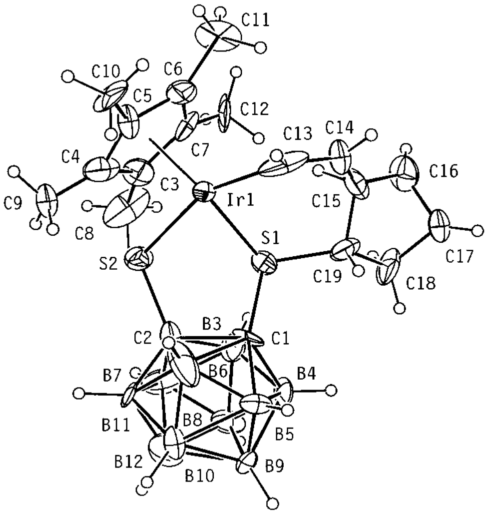
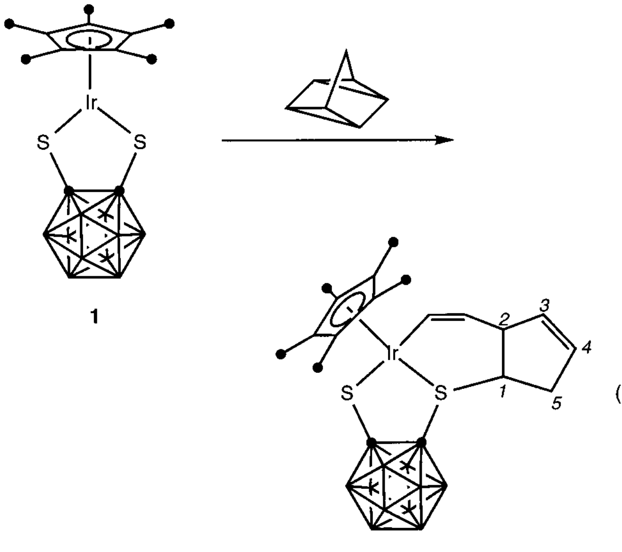


Figure 3. ORTEP drawing of **4** with the numbering scheme.

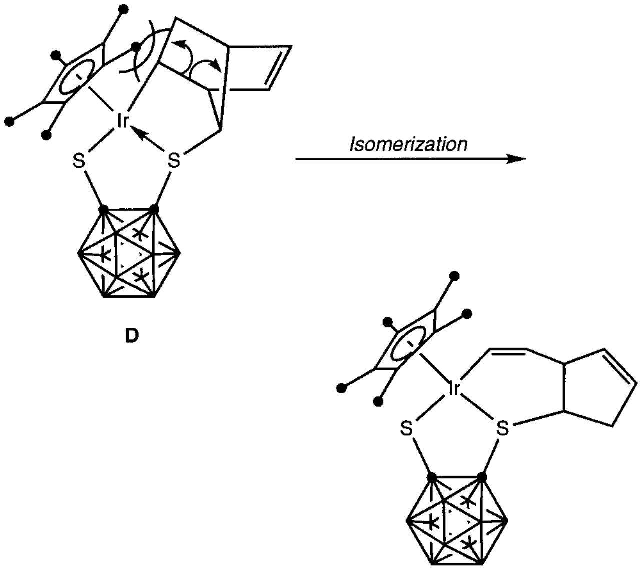
ambiguous spectroscopic data led us to carry out a single-crystal X-ray diffraction study in order to elucidate the structure of **4**.



(2)

The molecular structure of **4** is shown in Figure 3. Selected bond lengths and angles are given in Table 2. To our surprise, an X-ray study revealed **4** to be an isomerized product which contains a cyclopent-3-enyl-2-vinylen-1-yl moiety, which is connected between the iridium and sulfur atoms. The five-membered iridadithiolene ring [Ir(1), S(1), C(1), C(2), S(2)] displays an envelope conformation with S(2) 0.63(1) Å out of the mean plane of the other atoms, probably to relieve the steric interaction with the cyclopent-3-enyl-2-vinylen-1-yl moiety. The core structure consists of a six-membered metallacyclic ring with the Ir(1), C(13), C(14), C(15), C(19), and S(1) atoms adopting a distorted boat conformation. This structure results from the addition of quadricyclane to the Ir−S bond of **1**. In adduct **4**, the cyclopent-3-enyl-2-vinylen-1-yl moiety thus formed bridges between Ir(1) and S(1) of the iridadithiolene ring without breaking the Ir−S bond (Ir(1)−S(1) = 2.277(5) Å, Ir(1)−S(2) = 2.473(5) Å). This adduct has a piano-stool structure consisting of a five-membered and a six-membered ring. The central metal is coordinatively saturated, in contrast to the pentacoordinate structure of complex **1**. Such a transformation of quadricyclane to cyclopent-3-enyl-2-vinylen-1-yl has not been observed in other metalladithiolene complexes. For example, in the reaction between bis(1,2-ethylenedithiolato)metal complexes (metal: Ni, Pd, and Pt) and quadricyclane, the addition reaction was observed, but the bridging occurred between two sulfur atoms.[14] In the reaction of (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) with quadricyclane, the 5-norbornene-2,3-diyl unit adds between Co and S of the dithiolato complex.[13] The manner of the addition reaction of **1** to quadricyclane is quite different from that to other metalladithiolene complexes, resulting in isomerization of quadricyclane to a cyclopent-3-enyl-2-vinylen-1-yl structure.

Scheme 5



A reasonable explanation for the formation of **4** (Scheme 5) involves the initial insertion of the quadricyclane group into one of the iridium−sulfur bonds, leading to the five-membered intermediate **D**, followed by the isomerization to the cyclopent-3-enyl-2-vinylen-1-yl complex **4**. It was well established that, in the (η^5-cyclopentadienyl)(1,2-benzenedithiolato)cobalt(III) reaction, quadricyclane was converted into the 5-norbornene-2,3-diyl of type **D**.[13] Subsequent isomerization of quadricyclane in intermediate **D** is interpreted by a steric effect; to alleviate the steric congestion around the iridium atom, the C−C bond cleavage on the coordinated 5-norbornene-2,3-diyl unit occurs to give a six-membered metallacyclic ring.

Synthesis of the Cyclometalated Compound Cp*Ir[*o*-$BC_2B_9H_9S(CH_2NMe_2)$-*N*,*S*] (5). In an attempt to understand the cyclometalation process, we carried out the reaction of LiCab^{N,S} with [Cp*$IrCl_2$]$_2$. We found the N,S-bidentate coligand LiCab^{N,S} most promising for the further study of cyclometalation, because the aminothiolato coligand LiCab^{N,S} is sterically more demand-

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[14] (a) Kajitani, M.; Kohara, M.; Kitayama, T.; Akiyama, T.; Sugimori, A. *J. Phys. Org. Chem.* **1989**, *2*, 131. (b) Kajitani, M.; Kohara, M.; Kitayama, T.; Asano, Y.; Sugimori, A. *Chem. Lett.* **1986**, 2106.

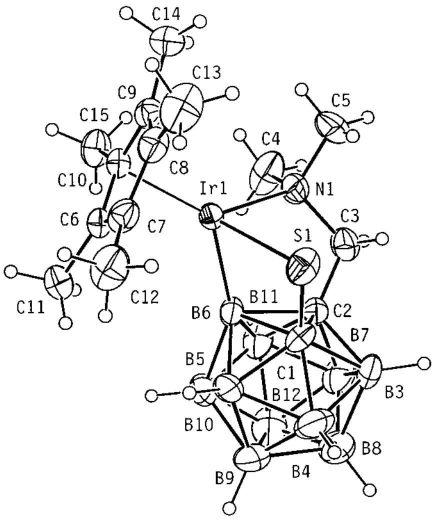
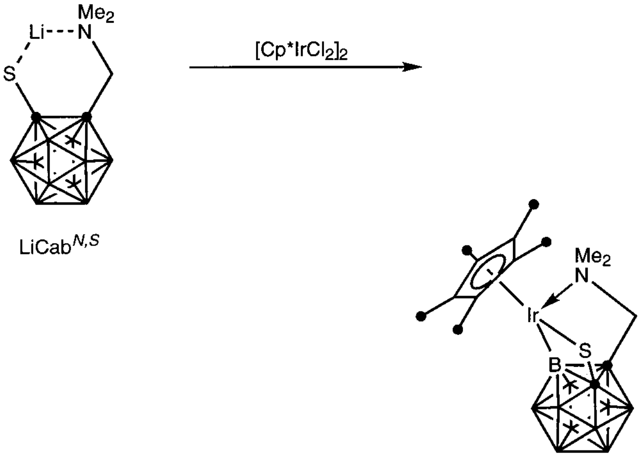


Figure 4. ORTEP drawing of **5** with the numbering scheme.

ing than the corresponding dithiolato ligand.[15] This effect may be attributed to the pronounced sterical demand of the NMe_2 moiety. Indeed, the reaction of LiCab^{N,S} with $[Cp^*IrCl_2]_2$ in THF at room temperature afforded the cyclometalated compound **5** with the intramolecular coordination of the aminomethyl fragment (eq 3).



LiCab^{N,S}

5

The resulting yellow compound was isolated as an air-stable solid in 38% yield, which is soluble in benzene, toluene, and THF. The compound **5** was confirmed by NMR and elemental analysis. The formation of **5** was most easily observed by noting the $^{11}B-^{1}H$ NMR resonance of the cyclometalated boron at −23.80 ppm. The presence of the cyclometalated iridium complex is indicated by the presence of an AB pattern and a pair of methyl singlets in the ^1H NMR spectrum assignable to the $Ir-CH_2NMe_2$ protons. Thus, intramolecular oxidative addition of the *ortho* B−H bond readily proceeds to give a four-membered-ring compound with a thiolato group. The structure of **5** was unambiguously established by single-crystal X-ray analysis. The structure of **5** is shown in Figure 4. Selected bond lengths and angles are given in Table 2. The structure of **5** reveals a three-legged piano-stool geometry with the iridium(III) center coordinated by the η^5-Cp* and an η^3-$[o\text{-}BC_2B_9H_9S(CH_2NMe_2)\text{-}N,S]^-$ cyclometalated ligand. The four Ir, S, C, and B atoms comprising the central skeleton of the molecule are all nearly coplanar with a dihedral angle of 75.3(2)° between the two planes defined by [Ir(1), S(1), C(1), B(6)] and [Ir(1), N(1), C(3), C(2), B(6)]. The chelate bite angle B(6)−Ir(1)−N(1) is decreased to 82.0(3)° due to the formation of an intramolecularly coordinated complex with a bulky *o*-carboranyl ligand.[16] The Ir(1)−B(6) bond length of 2.085(8) Å is similar to that of complex **3**. The Ir(1)−N(1) bond length (2.185(6) Å) is within known values of Ir−N bond lengths in analogous complexes.[15] Thus, the utility of the *o*-carboranylaminothiolato coligand, LiCab^{N,S}, has allowed for new examples of cyclometalated M−B−C−S compounds to be prepared.

Conclusions

The present work reports a series of novel addition reactions via cyclometalation or isomerization. The above results have clearly demonstrated that either a cyclometalation or an isomerization reaction is favored in the case of a bulky Cp* ancillary ligand. Because of the presence of a bulky Cp* unit, the complex **1** exhibits unusual reactivities which have not been observed in the related complex **A**. For example, the reaction of **1** with alkynes and a diazoalkane affords the cyclometalated products of a coordinated dithiolato ligand. The reaction of **1** with quadricyclane also affords an unusual isomerization product which contains a six-membered metallacyclic ring.

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of argon using Schlenk techniques. Tetrahydrofuran, toluene, and hexane were distilled under an atmosphere of nitrogen from sodium/benzophenone. Methylene chloride and chloroform-*d* were distilled under nitrogen from P_2O_5 and stored in a Schlenk storage flask until needed. All ^1H (200.13 MHz, measured in $CDCl_3$), ^{11}B (64.2 MHz, measured in C_6D_6), and ^{13}C (50.3 MHz, measured in $CDCl_3$) NMR spectra were recorded on a Varian Gemini 2000 spectrometer unless otherwise stated. ^1H and ^{13}C NMR chemical shifts are reported relative to Me_4Si and were determined by reference to the residual ^1H or ^{13}C solvent peaks. ^{11}B NMR chemical shifts are reported relative to $BF_3{\cdot}O(C_2H_5)_2$ used as an external reference, with a negative sign indicating an upfield shift. Coupling constants, *J*, are given in hertz. IR spectra were recorded on a Biorad FTS-165 spectrophotometer spectrometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. Complex **1**,[5] LiCab^{N,S},[15] and $[Cp^*IrCl_2]_2$[17] were prepared according to the literature methods.

General Synthesis of Cp*Ir[*o*-$BC_2B_9H_9SS\{\eta^2\text{-}(R^1HC{=}CR^2)\}$-*S*] (2: R^1 = H, R^2 = Ph, 2a; R^1 = $COOCH_3$, R^2 = $COOCH_3$, 2b). In a typical run **1** (0.27 g, 0.51 mmol) and alkynes were dissolved in toluene (15 mL) under N_2 and the solution was stirred for 8 h at room temperature. The purple color of the solution slowly faded to give a yellow solution, suggesting the formation of an adduct. The completion of the

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[15] Chung, S.-W.; Ko, J.; Park, P.; Cho, S.; Kang, S. O. *Collect. Czech. Chem. Commun.* **1999**, *64*, 883.

[16] Lee, J.-D.; Baek, C.-K.; Ko, J.; Park, K.; Cho, S.; Min, S.-K.; Kang, S. O. *Organometallics* **1999**, *18*, 2189.

[17] Kong, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.

reaction was monitored by ^{11}B NMR spectroscopy. The solution was reduced in vacuo to about half its original volume, and some insoluble material was removed by filtration. Addition of hexane to the resulting solution afforded **2** as a dark yellow precipitate.

Analytical Data for 2a. 2a was prepared from 1.0 mmol (0.11 mL) of phenylacetylene. After recrystallization from toluene, **2a** (0.29 g, 0.46 mmol, 90% yield) was isolated as a yellow solid. Mp: 177 °C dec. Anal. Calcd for $C_{20}H_{31}B_{10}S_2Ir$: C, 37.78; H, 4.91. Found: C, 37.73; H, 4.95. IR (KBr, cm^{-1}): ν(CH) 3062, 2911; ν(BH), 2586; ν(C=C), 1443. ^{11}B NMR (J_{BH}): δ −2.13 (d, 1B, 150), −6.01 (d, 4B, 140), −9.37 (d, 1B, 140), −13.16 (d, 3B, 180), −24.88 (s, 1B). ^{1}H NMR: δ 7.71 (m, 2H, C_6H_5), 7.47 (m, 2H, C_6H_5), 7.20 (m, 3H, C_6H_5), 3.19 (d, 1H, C=CH, $^2J_{HH}$ = 2.70), 2.69 (d, 1H, C=CH, $^2J_{HH}$ = 2.70), 1.56 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR: δ 128.33 (m, C_6H_5), 101.06 (s, C_5Me_5), 73.98 (s, $H_2C{=}CC_6H_5$), 71.77 (s, $H_2C{=}CC_6H_5$), 8.31 (s, C_5Me_5).

Analytical Data for 2b. 2b was obtained by essentially the same procedure from 1.0 mmol (0.12 mL) of dimethyl acetylenedicarboxylate. After recrystallization from toluene, **2b** (0.32 g, 0.47 mmol, 94% yield) was isolated as a yellow solid. Mp: 178 °C dec. Anal. Calcd for $C_{18}H_{31}B_{10}O_4S_2Ir$: C, 31.99; H, 4.62. Found: C, 31.92; H, 4.52. IR (KBr, cm^{-1}): ν(CH) 3050, 2900; ν(BH) 2575; ν(C=O), 1715; ν(C=C), 1494; ν(C−O), 1260. ^{11}B NMR (J_{BH}): δ −6.18 (d, 4B, 170), −8.66 (d, 2B, 140), −11.80 (d, 3B, 140), −24.31 (s, 1B). ^{1}H NMR: δ 3.83 (s, 1H, C=CH), 3.81 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 1.79 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR: δ 178.13 (s, MeOCO), 155.25 (s, MeOCO), 94.26 (s, C_5Me_5), 60.84 (HC=C), 58.40 (HC=C), 52.85 (s, OMe), 51.77 (s, OMe), 8.86 (s, C_5Me_5).

Synthesis of Cp*Ir[*o*-BC$_2$B$_9$H$_9$SS(CH$_2$SiMe$_3$)-*S,S′*] (3). A solution of complex **1** (0.27 g, 0.51 mmol) in toluene (20 mL) was treated with a 2.0 M hexane solution of (trimethylsilyl)diazomethane (0.60 mL, 1.2 mmol) at room temperature for 5 min. The purple 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 **3** as yellow-orange crystals. Yield: 0.30 g (0.48 mmol, 96%). Mp: 170 °C dec. Anal. Calcd for $C_{16}H_{35}B_{10}S_2SiIr$: C, 31.00; H, 5.69. Found: C, 31.07; H, 5.74. IR (KBr, cm^{-1}): ν(CH) 2980, 2910; ν(BH) 2608, 2579; ν(C=C) 1450. ^{11}B NMR (J_{BH}): δ −5.13 (d, 1B, 150), −7.42 (d, 4B, 140), −10.43 (d, 4B, 150), −21.91 (s, 1B). ^{1}H NMR: δ 3.28 (d, 1H, Me_3SiCH_2, $^2J_{HH}$ = 12.4), 1.94 (s, 15H, C_5Me_5), 1.62 (d, 1H, Me_3SiCH_2, $^2J_{HH}$ = 12.4), 0.17 (s, 9H, SiMe_3). ^{13}C{^{1}H} NMR: δ 90.66 (s, C_5Me_5), 17.40 (s, Me_3SiCH_2), 10.07 (s, C_5Me_5), −1.48 (s, SiMe_3).

Synthesis of Cp*Ir[C$_2$B$_{10}$H$_{10}$SS{η^1-(CH=CH)C$_5$H$_6$}-*S*] (4). To a solution of **1** (0.27 g, 0.51 mmol) in toluene (10 mL) was added dropwise quadricyclane (0.11 mL, 1.2 mmol), and the resulting purple solution was stirred for 30 min at room temperature. The solution was then heated for several hours at 60 °C, until TLC indicated complete conversion. After the mixture was cooled to room temperature, the solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel and recrystallization from methylene chloride and hexane. Yield: 0.28 g (0.45 mmol, 88%). Mp: 140 °C dec. Anal. Calcd for $C_{19}H_{33}B_{10}S_2Ir$: C, 36.46; H, 5.31. Found: C, 36.51; H, 5.40. IR (KBr, cm^{-1}): ν(CH) 3035, 2958; ν(BH), 2596; ν(C=C), 1436. ^{11}B NMR (J_{BH}): δ −5.49 (d, 5B, 170), −8.98 (d, 3B, 140), −10.52 (d, 2B, 150). ^{1}H NMR: δ 7.40 (d, 1H, J_{HH} = 8.4), 6.26 (dd, 1H, J_{HH} = 9.2), 6.03 (s, 1H), 3.59 (t, 1H, J_{HH} = 7.0), 2.46 (dd, 1H, J_{HH} = 6.0), 2.36 (d, 1H, J_{HH} = 6.4), 2.26 (d, 1H, J_{HH} = 3.8), 1.70 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR: δ 134.68 (s, C=C of C_7H_8), 126.43 (s, C=C of C_7H_8), 94.95 (s, C_5Me_5), 78.36, 60.33, 45.46, 42.01, 28.47 (s × 5, C of C_7H_8), 8.59 (s, C_5Me_5).

Synthesis of Cp*Ir[*o*-BC$_2$B$_9$H$_9$S(CH$_2$NMe$_2$)-*N,S*] (5). A 3.5 mmol solution of the complex LiCab^{N,S} in THF (20 mL) was added to a stirred solution of [Cp*IrCl$_2$]$_2$ (2.39 g, 3.0 mmol) in THF (30 mL) cooled to −78 °C. 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 an *o*-carboranedithiolato 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: 0.64 g (1.15 mmol, 38%). Mp: 161−162 °C dec. Anal. Calcd for $C_{15}H_{32}B_{10}SNIr$: C, 32.24; H, 5.77; N, 2.51. Found: C, 32.27; H, 5.82; N, 2.57. IR (KBr, cm^{-1}): ν(CH) 2963, 2920; ν(BH), 2597, 2560. ^{11}B NMR (J_{BH}): δ −6.38 (d, 5B, 120), −12.55 (d, 4B, 125), −23.80 (s, 1B). ^{1}H NMR: δ 4.06 (d, 1H, NCH_2, $^2J_{HH}$ = 14.0), 3.28 (s, 3H, NMe_2), 3.18 (s, 3H, NMe_2), 2.78 (d, 1H, NCH_2, $^2J_{HH}$ = 14.0), 1.76 (s, 15H, C_5Me_5). ^{13}C{^{1}H} NMR: δ 86.89 (s, C_5Me_5), 68.27 (s, NCH$_2$), 58.04 (s, NMe_2), 55.91 (s, NMe_2), 8.21 (s, C_5Me_5).

X-ray Crystallography. Suitable crystals of **2a**·CH_2Cl_2 and **3**−**5** 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. Crystal data and experimental details are given in Table 1. Diffraction measurements were made on an Enraf CAD4 automated diffractometer with graphite-monochromated Mo Kα 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 ψ scans were also applied. Each structure was solved by the application of Patterson methods using the SHELXL-86 program[18a] and least-squares refinement using SHELXL-93.[18b] The absolute configuration of **4** was confirmed by the refinement of the Flack parameter. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and were refined riding with the aroms to which they were bonded.

Acknowledgment. Financial support by the BK-21 program from the Korean Ministry of Education is gratefully appreciated.

Supporting Information Available: Tables describing the X-ray analysis (data collection and analysis), crystal data, atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and least-squares planes for **2a** and **3**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. SHELXL, Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.