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Articles

Iridium Coordination to *exo*-Dithio-7,8-dicarba-*nido*-undecaborate Derivatives

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Ligands incorporating two sulfur atoms directly connected to the carbon atoms of the unit 7,8-dicarba-*nido*-undecaborate(1−) react with $[IrCl(CO)(PPh_3)_2]$ in the presence of $AgNO_3$ in ethanol to form stable metal complexes. Each Ir(I) atom is four-coordinated to two phosphorus atoms of the PPh_3 groups and the two sulfur atoms of the 7,8-dicarba-*nido*-undecaborate(1−)-containing ligand. The influence of the S,S′ outer chain was studied by reacting these Ir(I)−dithioether complexes with O_2. The complex with a short chain ligand (six element mesocycle) decomposed, complexes with seven or eight chain atoms in the ligand did not react, and those with a noncyclic ligand reacted by oxidative addition forming a stable complex. The crystal structure of $\mathbf{[IrO_2(L_{s2n})(PPh_3)_2]{\cdot}Me_2CO}$ verified unambiguously the coordination of this peroxo complex. The compound $C_{43}H_{51}B_9IrP_2O_3S_2$, $M_r = 1031.45$, crystallizes in the monoclinic space group $P2_1/n$ (No. 14), with $a = 15.369$ (1) Å, $b = 19.481(2)$ Å, $c = 16.027(4)$ Å, $\beta = 101.92(1)°$, $V = 4695(1)$ Å^3, $Z = 4$, $R = 0.039$, and $R_w = 0.044$.

Bonding of electron-rich elements, S or P, to the cluster carbon atoms in 7,8-dicarba-*nido*-undecaborate(1−)[1] substantially modifies the chemistry of this anionic ligand. In several publications[2] we have shown that the coordinating ability of the sulfur atoms in 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) (Figure 1) derivatives depends on the length of the S,S′ outer chain. One of the major features is the capacity of these ligands to form B(3)−H⇀M agostic bonds or B(3)−M direct bonds in their complexes. For this to occur a short outer S,S′ chain and a metal ion in an oxidation state demanding hexacoordination are required. Such interactions have been demonstrated for Ru(II) and Rh(III) with the relatively small ring systems shown in Figure 1A. An interesting result of the carborane/macrocyclic interaction is the formation of a B(3)−Rh σ bond in $[N(CH_3)_4][RhCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}\{\sigma\text{-}7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_9\}]$[3] and a B(3)−H⇀Ru bond in $[RuCl\{7,8\text{-}\mu\text{-}S(CH_2CH_2)S\text{-}C_2B_9H_{10}\}(PPh_3)_2]$ (Figure 2).[4] With d^8 metal ions (Rh(I) and Ir(I)) in square-planar environments, no B(3)···M interaction is anticipated. However, other new features are not ruled out: a "built-in" negative charge is one, and the eclipsed nature of the two sulfur atoms is another. The

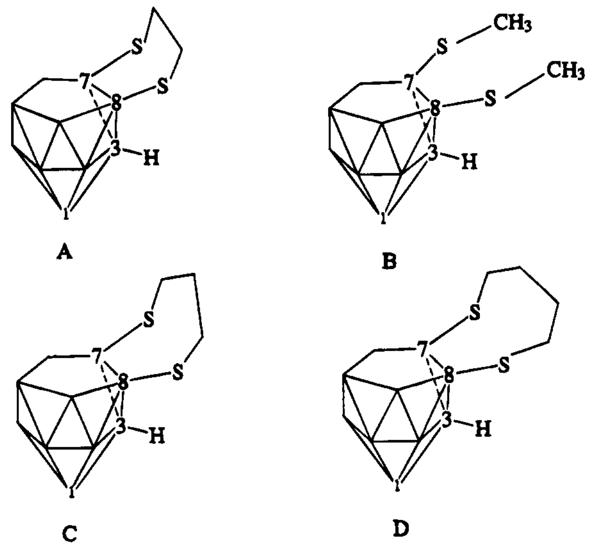

Figure 1. Schematic representation of the ligands (A) L_{s2c6}^-, (B) L_{s2n}^-, (C) L_{s2c7}^-, and (D) L_{s2c8}^-.

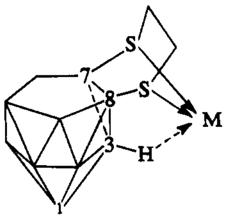

Figure 2. Motif of the B(3)−H⇀M interaction with $\mathbf{L_{s2c6}^-}$.

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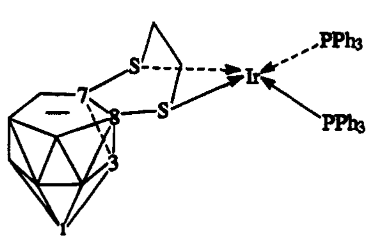

Figure 3. Schematic representation of the proposed structure of $[Ir(L_{S2c6})(PPh_3)_2]$.

Table 1. *nido*-Carbaborane Ligands with Their Abbreviations and the Complexes Obtained

L_{s2c6}^-	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
L_{s2c7}^-	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
L_{s2c8}^-	$\{7,8\text{-}\mu\text{-}(SCH_2CH_2CH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
L_{s2n}^-	$\{7,8\text{-}(SCH_3)_2\text{-}7,8\text{-}C_2B_9H_{10}\}^-$
	$[Ir(L_{s2c6})(PPh_3)_2]$
	$[Ir(L_{sc27})(PPh_3)_2]$
	$[Ir(L_{s2c8})(PPh_3)_2]$
	$[Ir(L_{s2n})(PPh_3)_2]$
	$[IrO_2(L_{s2n})(PPh_3)_2]\cdot Me_2CO$

data we are gathering show that the S atoms may be strongly coordinating when linked to the negatively charged 7,8-dicarba-*nido*-undecaborate(1−) moiety. Contrary to the common view that dithioethers are poorly coordinating groups, we have been studying the coordination chemistry of these 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1−) derivatives with Ir(I) for which, to our knowledge, stable dithioether complexes are not known. We show herein that stable Ir(I)−dithioether complexes are easily produced. In addition, we comment upon the influence of the length of the S,S′ outer chain on the reactions of the complexes with O_2.

Results and Discussion

The ligands (Figure 1) are represented as follows: **L** defines the moiety 7,8-dicarba-*nido*-undecaborate(1−), the subindex refers to the carborane external fragment, e.g. **s2** indicates two exocluster sulfur atoms, and **c** or **n** refers to the **c**yclic or **n**oncyclic nature of the exocluster unit. In the case of $\mathbf{L_{s2c}}^-$ ligands, the ring size is indicated by a number, e.g. $\mathbf{L_{s2c6}}^-$ means a 7,8-$C_2B_9H_{10}$ moiety with two sulfur atoms connected to the cage at the 7,8 positions and externally joined by a spacer producing a ring of total size 6. The ligands are listed in Table 1. The reaction of the *nido* ligands $\mathbf{L_{s2c6}}^-$, $\mathbf{L_{s2c7}}^-$, and $\mathbf{L_{s2c8}}^-$ with $[IrCl(CO)(PPh_3)_2]$ in the presence of $AgNO_3$ in ethanol, under refluxing conditions, yielded orange crystalline precipitates with stoichiometry $\mathbf{[Ir(L_{s2cx})(PPh_3)_2]}$ (x = 6−8). A similar reaction with the open chain ligand $\mathbf{L_{s2n}}^-$ (nonconnecting S,S′ string) yielded $\mathbf{[Ir(L_{s2n})(PPh_3)_2]}$. Equation 1 exemplifies the reactions for $\mathbf{L_{s2c6}}^-$.

$$[IrCl(CO)(PPh_3)_2] \xrightarrow[\text{acetonitrile}]{Ag(NO_3)} \xrightarrow[\text{ethanol}]{L_{s2c6}^-} \mathbf{[Ir(L_{s2c6})(PPh_3)_2]} + \text{other} \quad (1)$$

The stoichiometries indicated are supported by elemental analysis and a ^1H-NMR study. The $^{11}B\{H\}$-NMR spectra of the complexes resemble those of the respective $\mathbf{L_{s2c6}}^-$, $\mathbf{L_{s2c7}}^-$, and $\mathbf{L_{s2c8}}^-$ ligands, which exhibit a 2:1:2:2:1:1 pattern. The pattern found in the Ir complexes is 3:2:2:1:1, and the spectral range (δ) is between −11 and −37 ppm. These signal patterns do not suggest any boron cage-to-metal interaction, thus the structure indicated in Figure 3 is proposed for all of these $\mathbf{[Ir(L_{s2})(PPh_3)_2]}$ complexes, where Ir(I) is coordinated in a square planar arrangement to two sulfur atoms of the $\mathbf{L_{s2}}^-$, $\mathbf{L_{s2cx}}^-$, or $\mathbf{L_{s2n}}^-$ ligand and two phosphorus atoms of the triphenylphosphine moieties.

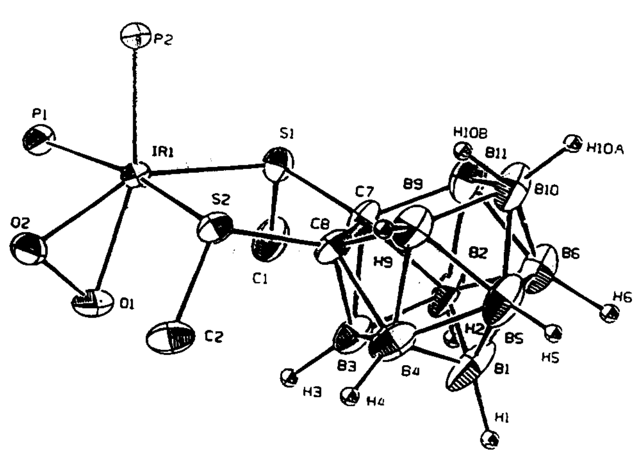

Figure 4. Simplified ORTEP view of $\mathbf{[IrO_2(L_{s2n})(PPh_3)_2]\cdot Me_2CO}$ showing 40% thermal ellipsoids.

When an acetone solution of $\mathbf{[Ir(L_{s2n})(PPh_3)_2]}$ was allowed to stand in air at 6 °C, crystals of the stoichiometry $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$ were obtained, according to eq 2.

$$\mathbf{[Ir(L_{s2n})(PPh_3)_2]} \xrightarrow[6\ ^\circ C,\ \text{acetone}]{O_2} \mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]} \quad (2)$$

The $^{11}B\{H\}$-NMR spectra of the freshly formed acetone solutions showed features different from those of the starting $\mathbf{[Ir(L_{s2n})(PPh_3)_2]}$ complex. The cage symmetry has been lost, and six resonances with the pattern 1:1:2:3:1:1 are found in the normal field range. Again the chemical shifts of the resonances did not suggest a cage to metal interaction but instead showed the resulting complex to have a symmetry perturbing unit. An IR absorption at 850 cm^{-1}, was attributed to the O−O stretching frequency[5] and suggested a peroxo (O_2^{2-}) group bonded to an Ir center in an η^2 fashion. For the other $\mathbf{[Ir(L_{s2cx})(PPh_3)_2]}$ (x = 6−8) complexes, similar reactions with oxygen under the identical conditions gave dissimilar results. Thus $\mathbf{[Ir(L_{s2c6})(PPh_3)_2]}$ decomposed to produce borates, whereas $\mathbf{[Ir(L_{s2c7})(PPh_3)_2]}$ and $\mathbf{[Ir(L_{s2c8})(PPh_3)_2]}$ appeared to be inert to O_2.

To verify the nature of the product $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$ unambiguously an X-ray analysis was undertaken. Figure 4 shows the molecular structure. Table 2 lists the positional parameters and Table 3 selected interatomic distances and angles. The molecule crystallizes with a molecule of acetone. The iridium atom is hexacoordinated to two triphenylphosphine units, two oxygen atoms of the peroxo unit in a side-on η^2 disposition, and to two sulfur atoms of the $\mathbf{L_{s2n}}^-$ ligand. In agreement with the ^{11}B-NMR results, no cage-to-metal interaction was indicated, and a noninteracting B(3)···Ir distance of 3.95(1) Å was observed. The Ir−P,[6] Ir−O, and O−O[7] distances are normal for Ir(III) complexes: Ir(1)−P(1) = 2.358(2), Ir(1)−P(2) = 2.354(2), Ir(1)−O(1) = 2.033(6), Ir(1)−O(2) = 2.032(6), and O(1)−O(2) = 1.471(8) Å. The O(1)−Ir(1)−O(2) angle is 42.4(2)°. The Ir(III)−S(thioether) distances found in $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$, viz. Ir(1)−S(1) = 2.349(2) and Ir(1)−S(2) = 2.376(2) Å, compare very well with previously reported Ir(I)−S(thiolate) distances, e.g. those in [(cod)Ir(μ-

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Table 2. Final Positional Parameters and Isotropic Thermal Parameters with Esd's in Parentheses for **$[IrO_2(L_{s2n})(PPh_3)_2]\cdot Me_2CO$**

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Ir(1)	0.75495(2)	0.13016(2)	0.81867(2)	2.37(1)
S(1)	0.8473(1)	0.0363(1)	0.8060(1)	3.1(1)
S(2)	0.8534(1)	0.1996(1)	0.7587(1)	3.2(1)
P(1)	0.6547(1)	0.0787(1)	0.8931(1)	2.9(1)
P(2)	0.6657(1)	0.1260(1)	0.6804(1)	2.69(9)
O(1)	0.8052(4)	0.1756(3)	0.9326(4)	3.9(3)
O(2)	0.7265(4)	0.2125(3)	0.8861(4)	3.8(3)
O(3)	0.2196(7)	0.1136(5)	0.3839(7)	9.9(7)
C(1)	0.8866(6)	0.0071(5)	0.9130(7)	4.5(5)
C(2)	0.8939(6)	0.2652(5)	0.8353(6)	4.6(5)
C(3)	0.101(1)	0.1582(7)	0.440(1)	8.6(9)
C(4)	0.195(1)	0.1401(7)	0.446(1)	7.3(8)
C(5)	0.258(1)	0.155(1)	0.526(1)	11(1)
C(7)	0.9482(5)	0.0700(5)	0.7770(6)	3.3(4)
C(8)	0.9493(5)	0.1468(4)	0.7529(6)	3.2(4)
C(11)	0.5388(5)	0.1043(6)	0.8528(5)	3.7(4)
C(12)	0.4702(6)	0.0547(6)	0.8445(6)	4.4(5)
C(13)	0.3821(7)	0.0745(8)	0.8149(8)	6.3(7)
C(14)	0.3624(7)	0.1420(8)	0.7945(8)	6.8(7)
C(15)	0.4301(7)	0.1905(7)	0.8038(7)	6.0(6)
C(16)	0.5192(6)	0.1720(5)	0.8333(6)	3.7(4)
C(21)	0.6572(5)	−0.0146(5)	0.8987(6)	3.4(4)
C(22)	0.6415(7)	−0.0496(5)	0.9695(6)	4.4(5)
C(23)	0.6449(8)	−0.1217(6)	0.9721(7)	6.1(6)
C(24)	0.6638(8)	−0.1573(5)	0.9051(8)	5.9(6)
C(25)	0.6796(7)	−0.1226(5)	0.8353(7)	5.1(5)
C(26)	0.6739(6)	−0.0526(5)	0.8303(6)	4.0(5)
C(31)	0.6714(6)	0.1056(5)	1.0051(6)	3.9(4)
C(32)	0.7510(6)	0.0899(5)	1.0629(6)	4.4(5)
C(33)	0.7663(7)	0.1091(6)	1.1472(7)	5.5(6)
C(34)	0.701(1)	0.1437(7)	1.1767(7)	7.2(7)
C(35)	0.624(1)	0.1599(8)	1.1209(8)	8.6(8)
C(36)	0.6096(7)	0.1408(6)	1.0375(6)	5.6(6)
C(41)	0.5840(6)	0.0566(5)	0.6476(5)	3.3(4)
C(42)	0.4964(6)	0.0622(5)	0.6527(6)	3.9(5)
C(43)	0.4361(7)	0.0093(7)	0.6297(7)	5.9(6)
C(44)	0.4661(9)	−0.0521(6)	0.6012(7)	5.8(6)
C(45)	0.5529(8)	−0.0592(5)	0.5950(7)	5.2(5)
C(46)	0.6118(7)	−0.0050(5)	0.6183(6)	4.4(5)
C(51)	0.7279(6)	0.1261(5)	0.5929(5)	3.3(4)
C(52)	0.7130(7)	0.1781(6)	0.5301(7)	4.7(5)
C(53)	0.7557(9)	0.1717(8)	0.4612(7)	6.6(7)
C(54)	0.808(1)	0.118(1)	0.4518(8)	8.1(9)
C(55)	0.8244(8)	0.0684(8)	0.5147(8)	6.7(7)
C(56)	0.7858(7)	0.0715(5)	0.5849(6)	4.5(5)
C(61)	0.5995(5)	0.2053(5)	0.6588(6)	3.1(4)
C(62)	0.6265(6)	0.2637(5)	0.7069(6)	3.5(4)
C(63)	0.5789(7)	0.3239(5)	0.6921(7)	4.7(5)
C(64)	0.5047(8)	0.3276(6)	0.6277(8)	5.4(6)
C(65)	0.4777(7)	0.2718(6)	0.5780(7)	5.4(6)
C(66)	0.5253(6)	0.2100(5)	0.5921(6)	4.4(5)
B(1)	1.1212(8)	0.110(1)	0.819(1)	7(1)
B(2)	1.0524(8)	0.0421(8)	0.825(1)	5.6(7)
B(3)	1.0164(7)	0.1232(7)	0.8479(8)	4.3(5)
B(4)	1.0544(8)	0.1823(7)	0.777(1)	5.0(6)
B(5)	1.1076(8)	0.1348(8)	0.712(1)	6.0(7)
B(6)	1.1073(9)	0.0462(9)	0.741(1)	5.9(8)
B(9)	0.9973(8)	0.1597(7)	0.6732(8)	4.3(6)
B(10)	1.0396(9)	0.0765(8)	0.646(1)	5.3(7)
B(11)	0.9959(8)	0.0200(7)	0.719(1)	4.8(6)

[a] $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}a_i \cdot a_j$.

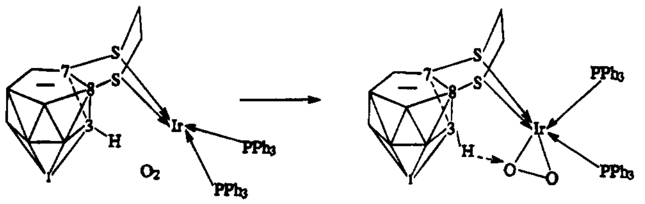

Figure 5. Proposed mechanism for O_2 attack on $[Ir(L_{S2c6})(PPh_3)_2]$.

$SPPh_2)_2PtS_2CNEt_2]$[8] where the Ir—S distances are 2.315(4) and 2.378(4) Å, respectively, and with Ir(III)-S(thioether) distances, e.g. those in the dication $[Ir(H)L_2]^{2+}$ (L = 1,4,7-trithiacyclononane) where Ir—S distances range from 2.231(5) to 2.476(5) Å. With the same ligand L in $[IrL_2]^{3+}$, the distances vary from 2.338(3) to 2.342(3) Å.[9]

In this work we have shown for the first time, that stable and discrete S_2P_2 Ir(I) environments are easily produced from *trans*-$[IrCl(CO)(PPh_3)_2]$ by replacing the Cl and CO groups. We attribute the stability of these complexes to the unique nature of the thioether groups in these $\mathbf{L_{S2}}^-$ ligands. Note that a cationic complex, presumably $[Ir(CO)(CNMe)(PPh_3)]^+$, has to be produced first in order to obtain stable $[Ir(\mathbf{L_{s2cx}})(\mathbf{PPh_3})_2]$ complexes. As shown earlier, this is not necessary for $[RhCl(PPh_3)_3]$. It is worth noting that monothioether complexes of Ir(I) with tetrahydrothiophene, $[(cod)Ir(tht)(PR_3)][ClO_4]$, have recently been claimed to be catalyst precursors.[10]

The length of the external S,S′ outer chain has an important influence on the reaction of the $[Ir(\mathbf{L_{s2cx}})(PPh_3)_2]$ complexes with molecular O_2. As indicated, the Ir complex with a six-membered ring, $\mathbf{L_{s2c6}}^-$, which tends to produce a B(3)···M interaction most readily, decomposed in the presence of O_2. However, the next two iridium species in the series, with $\mathbf{L_{s2c7}}^-$, and $\mathbf{L_{s2c8}}^-$ ligands, did not react, while an iridium complex with the less crowded $\mathbf{L_{s2n}}^-$ group afforded a stable $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$ complex. The molecular structure of this complex and that of $[Rh(\mathbf{L_{S2c6}})(PPh_3)_2]$[11] are very similar to the structure we propose for $[Ir(\mathbf{L_{S2c6}})(PPh_3)_2]$ (see Figure 3) and provide information about the oxygen ligating these Ir complexes. One of the main structural characteristics of $[Rh(\mathbf{L_{S2c6}})(PPh_3)_2]$ is the anti disposition of the Rh ion with respect to the open face of the *nido* cage. In the crystal structure of $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$, also, the O_2^{2-} group is located anti with respect to the open face. By analogy, one would expect the O_2 molecule to bond to the complex $[Ir(\mathbf{L_{S2c6}})(PPh_3)_2]$ in an anti manner with respect to the C_2B_3 open face moiety, and to be vulnerable to interaction with the B(3)—H unit, hence the complex $[Ir(O_2)(L_{s2c6})(PPh_3)_2]$ decomposes. Figure 5 shows this pathway for $\mathbf{[Ir(O_2)(L_{s2n})(PPh_3)_2]}$. By contrast, the open ligand $\mathbf{L_{S2n}}^-$ in $\mathbf{[Ir(L_{S2n})(PPh_3)_2]}$ does not force the Ir toward the B(3)—H group, and a more relaxed O_2 complex with no B(3)—H···O_2 interaction is produced. The reasons why the $\mathbf{L_{S2c7}}^-$ and $\mathbf{L_{S2c8}}^-$ complexes do not bind O_2 are not at present well understood. Possibly a steric effect is involved, as was claimed when *o*-tolylphosphine complexes of $[IrCl(CO)(PR_3)]$ did not yield O_2 adducts while PPh_3 and *m*- and *p*-tolylphosphine analogs did. The failure to react was attributed to the steric effect of the *o*-methyl group, which blocks the apical sites, preventing reaction.[12] Studies under different O_2 pressures will be carried out to ascertain exactly the influence of the outer S,S′ chain in this type of reaction.

Experimental Section

Instrumentation. Elemental analyses were performed using a Perkin-Elmer 240-B microanalyser. IR spectra were recorded with KBr

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) with Esd's in Parentheses for $[IrO_2(L_{s2n})(PPh_3)_2]\cdot Me_2CO$

Ir(1)—S(1)	2.349(2)	P(1)—C(31)	1.84(1)
Ir(1)—S(2)	2.376(2)	P(2)—C(41)	1.847(9)
Ir(1)—P(1)	2.358(2)	P(2)—C(51)	1.852(9)
Ir(1)—P(2)	2.354(2)	P(2)—C(61)	1.843(9)
Ir(1)—O(1)	2.033(6)	O(1)—O(2)	1.471(8)
Ir(1)—O(2)	2.032(6)	C(7)—C(8)	1.55(1)
S(1)—C(1)	1.79(1)	C(7)—B(3)	1.72(2)
S(1)—C(7)	1.830(8)	C(7)—B(11)	1.62(2)
S(2)—C(2)	1.79(1)	C(8)—B(3)	1.72(1)
S(2)—C(8)	1.815(8)	C(8)—B(9)	1.62(1)
P(1)—C(11)	1.835(9)	B(9)—B(10)	1.83(2)
P(1)—S(21)	1.819(9)	B(10)—B(11)	1.83(2)
S(1)—Ir(1)—S(2)	87.81(8)	Ir(1)—S(1)—C(1)	104.8(3)
S(1)—Ir(1)—P(1)	100.50(8)	Ir(1)—S(1)—C(7)	107.5(3)
S(1)—Ir(1)—P(2)	97.87(8)	C(1)—S(1)—C(7)	102.8(4)
S(1)—Ir(1)—O(1)	107.0(2)	Ir(1)—S(2)—C(2)	106.8(3)
S(2)—Ir(1)—P(1)	169.73(8)	Ir(1)—S(2)—C(8)	106.8(3)
S(2)—Ir(1)—P(2)	86.23(8)	C(2)—S(2)—C(8)	105.6(4)
S(2)—Ir(1)—O(2)	89.4(2)	S(2)—C(8)—C(7)	119.0(6)
P(1)—Ir(1)—P(2)	98.48(8)	S(2)—C(8)—B(3)	116.9(7)
O(1)—Ir(1)—O(2)	42.4(2)	C(7)—C(8)—B(9)	112.1(8)
S(1)—C(7)—C(8)	117.6(6)	C(8)—B(9)—B(10)	106.9(8)
S(1)—C(7)—B(3)	118.7(6)	B(9)—B(10)—B(11)	100.7(9)
C(8)—C(7)—B(11)	114.2(8)	C(7)—B(11)—B(10)	105.8(9)

pellets on a Nicolet 710-FT spectrophotometer. The ^{1}H-NMR and ^{11}B-NMR spectra were recorded with a Bruker AM 400WB instrument.

Materials. Before use, *o*-carborane (Dexsil Chemical Corp.) was sublimed under high vacuum ; the ligands $\mathbf{L_{s2c6}}^-$, $\mathbf{L_{s2c7}}^-$, $\mathbf{L_{s2c8}}^-$, and $\mathbf{L_{s2n}}^-$ were prepared from *o*-carborane as previously reported.[1,13] A 1.6 M solution of *n*-butyllithium in hexane from Fluka was used as received. Ethanol was reagent grade.

Synthesis of $[Ir(L_{s2c6})(PPh_3)_2]$. To 20 cm^3 of deoxygenated NCMe were added $[IrCl(CO)(PPh_3)_2]$ (100 mg, 0.128 mmol) and $AgNO_3$ (21.7 mg, 0.128 mml). The mixture was stirred for 30 min and the precipitated AgCl was filtered out. The solution was evaporated to dryness on the vacuum line, and the solid residue was treated with ethanol (40 cm^3). The reactant $[NMe_4](\mathbf{L_{s2c6}})$ (37.8 mg, 0.127 mmol) was then added. The mixture was refluxed for 4 h, and an orange crystalline solid was obtained. After filtration, the solid was washed with cold methanol and then hexane. An analytically pure solid was obtained. Yield: 65 mg (54%). IR (KBr): ν[cm^{-1}] = 2551, 2543, and 2531 (B—H). ^{1}H-NMR ($CDCl_3$, 25 °C, TMS): $\delta = -2.6$ (b, 1, —B—*H*—B), 2.65 (b, 2, —CH_2—), 2.85 (b, 2, —CH_2—), 7.50—7.10 (m, 30, P(C_6H_5)$_3$). ^{11}B-NMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -10.5$ (3B), −16.6 (2B), −18.6 (2B), −30.9 (1B), −36.2 (141 Hz, 1B). Anal. Calcd for $C_{40}H_{44}B_9IrP_2S_2$: C, 51.09; H, 4.72; S, 6.82. Found: C, 50.71; H, 4.62; S, 6.70.

Synthesis of $[Ir(L_{s2c7})(PPh_3)_2]$. The procedure was as for $[Ir(L_{s2c6})(PPh_3)_2]$ using the salt $[NMe_4](\mathbf{L_{s2c7}})$ (39.7 mg, 0.127 mmol). Yield of product: 90 mg (74%). IR (KBr): ν [cm^{-1}] = 2550 (B—H). ^{1}H-NMR ($CDCl_3$, 25 °C, TMS): $\delta = -2.8$ (b, 1, —B—*H*—B), 1.26 (b, 1, —CH_2—), 2.10 (b, 2, —CH_2—), 2.35 (b, 1, —CH_2—), 2.97 (b, 2, —CH_2—), 7.40—7.10 (m, 30, P(C_6H_5)$_3$). ^{11}B-NMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -11.7$ (3B), −17.6 (2B), −19.5 (2B), −32.4 (1B), −36.3 (130 Hz, 1B). Anal. Calcd for $C_{41}H_{46}B_9IrP_2S_2$: C, 51.60; H, 4.86; S, 6.72. Found: C, 51.63; H, 5.05; S, 6.62.

Synthesis of $[Ir(L_{s2c8})(PPh_3)_2]$. The procedure was as for $[Ir(L_{s2c6})(PPh_3)_2]$ the reagent $[NMe_4](L_{s2c8})$ (41.5 mg, 0.127 mmol) being used. Yield: 70 mg (58%). IR (KBr): ν [cm^{-1}] = 2550 (B—H). ^{1}H-NMR ($CDCl_3$, 25 °C, TMS): $\delta = -2.8$ (b, 1, —B—*H*—B), 1.23 (b, 2, —CH_2—), 1.46 (b, 2, —CH_2—), 2.24 (b, 2, —CH_2—), 2.83 (b, 2, —CH_2—), 7.40—7.10 (m, 30, P(C_6H_5)$_3$). ^{11}B-NMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -12.7$ (3B), −18.0 (4B), −31.8 (1B), −36.6 (130 Hz, 1B). Anal. Calcd for $C_{42}H_{48}B_9IrP_2S_2$: C, 52.09; H, 5.00; S, 6.62. Found: C, 51.79; H, 5.15; S, 6.73.

Table 4. Crystallographic Data for $[Ir(L_{s2n})(O_2)(PPh_3)_2]\cdot Me_2CO$

chem formula: $C_{43}H_{51}B_9IrP_2O_3S_2$	space group: monoclinic $P2_1/n$ (No. 14)
fw = 1031.45	$T = 23$ °C
$a = 15.369(1)$ Å	$\lambda = 0.710\,69$ Å
$b = 19.481(2)$ Å	$\varrho_{calcd} = 1.459$ g cm^{-3}
$c = 16.027(4)$ Å	$\mu = 30.22$ cm^{-1}
$\beta = 101.92(1)°$	transm coeff = 0.81—1.000
$V = 4695(1)$ Å^3	$R(F_o) = 0.039$
$Z = 4$	$R_w(F_o) = 0.044$

Synthesis of $[Ir(L_{s2n})(PPh_3)_2]$. The procedure was as for $[Ir(L_{s2c6})(PPh_3)_2]$ with the salt $[NMe_4](L_{s2n})$ (60.0 mg, 0.200 mmol) being used. Yield: 130 mg (72%). IR (KBr): ν [cm^{-1}] = 2541 (B—H). ^{1}H-NMR ($CDCl_3$, 25 °C, TMS): $\delta = -2.7$ (b, 1, —B—*H*—B), 1.90 (s, 6, —CH_3), 7.40—7.10 (m, 30, P(C_6H_5)$_3$). ^{11}B-NMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -11.4$ (3B), −17.4 (4B), −30.8 (1B), −35.9 (136 Hz, 1B). Anal. Calcd for $C_{40}H_{46}B_9IrP_2S_2$: C, 50.98; H, 4.92; S, 6.80. Found: C, 50.17; H, 4.78; S, 6.50.

Synthesis of $[IrO_2(L_{s2n})(PPh_3)_2]\cdot CH_3COCH_3$. In air, $[Ir(L_{s2n})(PPh_3)_2]$ (50 mg) was dissolved in 5 cm^3 of acetone, yielding after 24 h at 6 °C an orange crystalline solid. This was filtered and washed with acetone. Yield: 35 mg (64%). IR (KBr): ν [cm^{-1}] = 2586, 2563, 2550 and 2532 (B—H). ^{11}B-NMR (128 MHz, CH_2Cl_2, 25 °C, $BF_3\cdot Et_2O$): $\delta = -7.6$ (1B), −9.6 (1B), −16.3 (133 Hz, 2B), −21.8 (3B), −28.8 (1B), −33.7 (136 Hz, 1B). Anal. Calcd C, 50.02; H, 5.08; S, 6.21. Found: C, 49.78; H, 5.06; S, 6.01.

X-ray Structure Determination of $[IrO_2(L_{s2n})(PPh_3)_2]\cdot Me_2CO$. The unit cell parameters were determined by least-squares refinements of 25 carefully centred reflections ($25° < 2\theta < 31°$). The data obtained were corrected for Lorentz and polarization effects and for dispersion. A correction for empirical absorption (ψ scan) was also applied. A total of 8824 reflections were collected by $\omega/2\theta$ scan mode ($2\theta_{max} = 50°$), giving 8489 unique reflections ($R_{int} = 0.034$). Of these, 5089 were considered as observed according to the criterion $I > 3\sigma(I)$. The three check reflections monitored after every 150 reflections showed a decay of 9% during the course of the data collection, and this was also taken into account in the final calculations. The crystal data are shown in Table 4.

The structure was solved by direct methods using MITRIL.[14] Least-squares refinements and all subsequent calculations were performed using the TEXSAN[15] crystallographic software package, which minimized the function $\Sigma w(\Delta F)^2$ where $w = 1/\sigma^2(F_o)$. Refinement of all non-hydrogen atoms with anisotropic and BH hydrogen atoms with fixed isotropic temperature parameters (the rest of the hydrogen atoms were included in calculated positions with fixed isotropic temperature factors) reduced the R value to 0.039 ($R_w = 0.044$) for 572 parameters. Neutral atomic scattering factors were those included in the program. The structure was plotted with ORTEP-II.[16]

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Supplementary Material Available: Tables including experimental details, *U* values, positional parameters and thermal parameters, geometric parameters, and distances and angles involving the hydrogen atoms (10 pages), for $\mathbf{[IrO_2(L_{s2n})(PPh_3)_2].Me_2CO}$. Ordering information is given on any current masthead page.

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