ORGANOMETALLICS

Monophosphine-o-Carborane Sulfide as a Noninnocent Ligand for C, S, S,S', and B,S,S' Coordination Modes of Half-Sandwich Iridium and Rhodium Complexes

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Supporting Information

ABSTRACT: Half-sandwich iridium and rhodium complexes with three different coordination modes were successfully synthesized by using the monophosphine-*o*-carborane sulfide 1-SPPh₂-1,2-*closo*- $C_2B_{10}H_{11}$ (1) as the ligand. Treatments of the dimeric metal complexes $[Cp^*M(\mu-Cl)Cl]_2$ (M = Ir, Rh; $Cp^* = \eta^5 - C_5Me_5$) with the lithium salt of monophosphine-*o*-carborane sulfide generate the C,Scoordinated complexes $[Cp^*IrCl(Cab^{C,S})]$ (2) and $[Cp^*RhCl(Cab^{C,S})]$ (3) $(Cab^{C,S} = (1-SPPh_2-1,2-$ *closo* $- <math>C_2B_{10}H_{10})^-)$, respectively. Compound 1 can be modified to give the corresponding thiol 1-SH-2-SPPh₂-1,2-*closo*- $C_2B_{10}H_{10}$ (4). The unexpected B,S,S' coordination mode product $[Cp^*Ir(Cab^{B,S,S'})]$ (5) $(Cab^{B,S,S'} = (\eta^{-1}S')(\eta^{-1}SPPh_2)-(\eta^{-1}-1,2-$ *closo* $-<math>C_2B_{10}H_9))$ through B—H activation was obtained by the reaction of $[Cp^*Ir(\mu-Cl)Cl]_2$ with the lithium salt of 4. However,



reaction of $[Cp^*Ir(\mu-Cl)Cl]_2$ with the lithium salt of 4. However, $[Cp^*Rh(\mu-Cl)Cl]_2$ gave the product $[Cp^*RhCl(Cab^{S,S'})]$ (6) $(Cab^{S,S'} = (1-S'-2-SPPh_2-1,2-closo-C_2B_{10}H_{10})^-)$ with the S,S' mode under the same conditions. When it was heated in CH₃OH, complex 6 gradually transformed from a *closo*-carborane complex to the zwitterionic *nido*-carborane complex $[Cp^*Rh(7-S'-8-(SPPh_2)-7,8-C_2B_9H_{10})]$ (7). They represent the first examples of halfsandwich complexes incorporating a monophosphine-*o*-carborane sulfide ligand. In addition, the iridium complex 2 exhibits catalytic activity up to 1.40×10^6 g of PNB (mol of Ir)⁻¹ h⁻¹ for the polymerization of norbornene in the presence of methylaluminoxane (MAO) as cocatalyst. All complexes were fully characterized by elemental analysis and IR and NMR spectroscopy. The structures of 1, 2, and 5–7 were further confirmed by single-crystal X-ray diffraction.

INTRODUCTION

Since the discovery of 1,2-dicarba-*closo*-dodecaborane in the 1960s, research interest in carboranyl- and carbollide-based transitionmetal complexes has greatly increased due to their high thermal and chemical stabilities.¹ Their various applications in the fields of BNCT (boron-neutron capture therapy),² catalysis,³ nuclearwaste remediation,⁴ and ion-selective electrodes⁵ have also been developed. The C–H bonds in this cage are moderately acidic and can be deprotonated with strong bases; thus, the negatively charged carbon atoms can be subsequently functionalized with electrophilic reagents. Among these functionalized carboranyl derivatives, monophosphine-*o*-carborane (1-PR₂-1,2-*closo*-C₂B₁₀H₁₁) is one of the most attractive starting precursors.⁶ It has a high tendency to coordinate to metal centers with its lone pair,⁷ and it has one arylphosphine group that can satisfactorily stabilize the metal ion by bulky steric effects.

Generally, tertiary phosphines are sensitive species that are easily oxidized to produce more weakly basic oxidative products. Among these compounds, phosphine chalcogenides have attracted considerable attention because of their use for the preparation of metal chalcogenide nanoparticles,⁸ the synthesis of complexes with P-E (E = S, Se) ligands,⁹ the remediation of

nuclear waste,¹⁰ and chalcogen-exchange reactions.¹¹ Despite the well-known affinity of phosphines for chalcogens and destruction of the transition-metal catalysts through oxidation of the phosphorus-containing ligands, there are still very few studies on the reactivity of carboranyl-based phosphorus oxide^{13a-d} and chalcogenide.^{13e,f} Up to October 2010, only one crystal structure for a carboranyl phosphine sulfide was given in the Cambridge Crystallographic Database.¹² Additionally, our previous studies proved that a carboranyl-based half-sandwich complex is an important model to form a variety of useful transition-metal complexes.¹⁴ These complexes have advantages in solubility, thermal stability, and flexible fine-tuning processes of half-sandwich units,¹⁵ as well as applications in catalysis.¹⁴ Thus, the unexplored reactivity of half-sandwich transition-metal complexes with monophosphine-o-carborane chalcogenide has greatly encouraged us to conduct the present study.

Our previous systematic study exhibited the versatile coordination modes of monophosphine-*o*-carborane and their diverse reactivities.¹⁶ We herein report some pioneering examples of

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unique half-sandwich transition-metal complexes using monophosphine-*o*-carborane sulfide $(1-SPR_2-1,2-closo-C_2B_{10}H_{11})$ and its thiolate derivative $((1-S-2-SPR_2-1,2-closo-C_2B_{10}H_{10})^-)$ as noninnocent ligands. A series of Ir and Rh complexes containing versatile coordination modes (C,S, S,S', and B,S,S') have been conveniently obtained. The norbornene polymerization behavior of some of these complexes has also been investigated. All complexes were fully characterized by elemental analysis and IR and NMR spectroscopy.

RESULTS AND DISCUSSION

In comparison with ordinary phosphines, monophosphine-ocarborane shows high stability because of the bulky carborane unit. The oxidation of these stable phosphines was studied by Vinãs et al. very recently.^{13f} However, the yields of 1-SPR₂-2-R'-1,2-closo- $C_2B_{10}H_{10}$ were not very high, even when the reaction mixture was refluxed in toluene for several days. In our present study, we found that addition of a small amount of base such as NEt₃ could largely prompt the oxidation process. Under mild reaction conditions, the target product 1-SPPh2-1,2-closo- $C_2B_{10}H_{11}$ (1) was obtained with a high isolated yield of 81% after column chromatography. The detailed synthesis procedure as well as ¹H, ¹³C, ³¹P, and ¹¹B NMR spectral data are presented in the Experimental Section. The sharp signal at δ 51.33 ppm in the ³¹P NMR spectrum shows obvious evidence for the oxidation of the phosphorus atom, which falls in the range expected for compounds that contain P(S) moieties.^{13f} Single crystals suitable



Figure 1. Molecular structure of 1 with thermal ellipsoids drawn at the 30% level. Selected bond lengths (Å) and angles (deg): P(1)-C(1), 1.883(3); P(1)-S(1), 1.9397(10); C(1)-C(2), 1.643(3); C(2)-C(1)-P(1), 114.84(17); C(1)-P(1)-S(1), 109.82(8); C(3)-P(1)-C(9), 110.27(12).

for X-ray diffraction analyses were obtained by the slow diffusion of hexane into a saturated solution of 1 in dichloromethane. The molecular structure of 1 and selected bond lengths and angles are given in Figure 1.

Synthesis of C,S Coordination Mode Complexes 2 and 3. The reaction of the lithium salt of a monophosphine-*o*-carborane sulfide 1-Li-2-SPPh₂-1,2-*closo*-C₂B₁₀H₁₁ with 0.5 equiv of dimeric metal complexes $[(Cp^*MCl_2)_2]$ (M = Ir, Rh) gave, after workup, the half-sandwich C,S-chelated complexes $[Cp^*MCl(Cab^{C,S})]$ in good yields (Scheme 1) (M = Ir (2), 68%; M = Rh (3), 63%; Cab^{C,S} = 1-SPPh₂-1,2-*closo*-C₂B₁₀H₁₀). Despite the existence of a metal—carbon bond, these complexes remain very stable in the solid state in air. The reason for this can be attributed to the formation of a five-membered chelate ring. They are soluble in CH₂Cl₂ and THF and slightly soluble in hexane and diethyl ether.

Complexes 2 and 3 were characterized by various spectroscopic data and elemental analyses. For complex 2, the ¹H NMR spectrum in CDCl₃ shows a sharp peak at δ 1.49 and several groups of signals in the range of 8.33-7.47 ppm, which can be assigned to the methyl groups of Cp* and protons in aromatic rings, respectively. In the ¹³C NMR spectrum of **2**, the resonance of the Cp^{*} ring carbon atoms was found at δ 91.3 ppm and those of the methyl groups at δ 8.8 ppm. The ¹¹B NMR spectrum exhibits resonances at δ 2.18 (2B), -5.47 (4B), and -8.64 (4B), while that of **3** shows a similar pattern. In the ³¹P NMR spectrum, only one resonance at about δ 60.79 ppm was observed, which was shifted downfield in comparison to that of 1. The IR spectrum displays a typical strong and broad characteristic B-H absorption at approximately 2565 cm⁻¹, and the absorption at 625 cm^{-1} is ascribed to P=S bond vibrations. A detailed analysis of the spectroscopic data (IR and ¹H, ¹³C, ¹¹B, and ³¹P NMR spectroscopy) indicates that the structure of 3 is identical with that of **2**, which was also confirmed by elemental analysis.

Single crystals suitable for X-ray diffraction analyses were obtained by the slow diffusion of hexane into a saturated solution of 2 in dichloromethane. Complex 2 crystallized in the monoclinic space group $P2_1/c$. The crystallographic data of 2 are summarized in Table 1. Figure 2 shows the molecular structure of 2 together with selected bond lengths and angles. The molecular structure shows that the geometry at the iridium(III) center is that of a three-legged piano stool with the iridium atom coordinated by the η^{5} -Cp^{*} and the C and S atoms, as well as one chloride ligand. The metal center has a distorted-octahedral environment, assuming that the η^5 -Cp^{*} group occupies three *fac* coordination sides. The of Ir(1)-C(1) and Ir(1)-Cl(1) bond distances are approximately 2.111(3) and 2.4161(6) Å, respectively, which are both within the range of known values for these bonds in analogous complexes.¹⁴ The P(1)-S(1) bond length of 2 is greater than that of 1, probably due to the coordinative

Scheme 1. Synthesis of C,S Coordination Mode Complexes 2 and 3



	1	2	5	6	7
chem formula	C14H21B10PS	C24H35B10ClIrPS	C24H34B10IrPS2	C24H34B10ClRhPS2	C24H35B9PRhS2
fw	360.44	722.30	717.90	665.07	618.81
T/K	293(2)	173(2)	296(2)	296(2)	173(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.710 73	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	triclinic	triclinic
space group	C2/c	$P2_{1}/c$	$P\overline{1}$	P1	$P\overline{1}$
a/Å	30.126(11)	10.1268(7)	11.9243(13)	11.596(5)	11.6277(8)
b/Å	9.913(4)	11.9506(8)	12.0239(14)	12.077(5)	11.8557(15)
c/Å	14.001(5)	24.0726(16)	12.8524(14)	12.949(6)	12.0237(8)
$lpha/{ m deg}$	90	90	84.482(2)	78.644(7)	99.3110(10)
β /deg	111.102(5)	91.4750(10)	62.969(2)	87.963(7)	112.3500(10)
γ/deg	90	90	84.006(2)	77.167(6)	99.7310(10)
$V/Å^3$	3901(2)	2912.3(3)	1630.0(3)	1733.3(13)	1463.7(2)
Ζ	8	4	2	2	2
$ ho/{ m Mg}~{ m m}^{-3}$	1.227	1.647	1.463	1.274	1.404
μ/mm^{-1}	0.242	4.819	4.287	0.751	0.795
<i>F</i> (000)	1488	1416	704	676	632
heta range/deg	1.45-25.01	1.69-27.89	1.71-27.56	1.76-27.01	1.80-28.24
no. of rflns collected	5870	21 504	11 900	12 106	11 368
completeness to θ /%	95.9	99.5	98.1	98.2	98.3
no. of data/restraints/params	3299/1/249	6926/0/358	7378/2/364	9865/48/722	7117/2/355
goodness of fit on F^2	0.960	1.068	1.091	1.033	1.204
final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.0482,	R1 = 0.0194,	R1 = 0.0485,	R1 = 0.0619,	R1 = 0.0279,
	wR2 = 0.1211	wR2 = 0.0541	wR2 = 0.1505	wR2 = 0.1862	wR2 = 0.0871
largest diff peak, hole/e Å ^{-3}	0.345, -0.236	1.039, -0.670	1.739, -1.567	0.781, -1.175	0.900, -0.999

Table 1. Crystallographic Data and Structure Refinement Parameters for 1, 2, and 5–7



Figure 2. Molecular structure of 2 with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ir(1)-C(1), 2.111(3); Ir(1)-S(1), 2.3829(7); Ir(1)-Cl(1), 2.4161(6); S(1)-P(1), 1.9993(10); C(1)-C(2), 1.768(4); C(2)-C(1)-Ir(1) 119.59(16); C(1)-C(2)-P(1), 111.86(16); P(1)-S(1)-Ir(1), 105.65(3); C(2)-P(1)-S(1), 108.04(9).

interaction between the S atom and the metal center. The C(2)–C(1)–Ir(1) angle of 119.59(16)° in 2 within the five-membered ring is slightly larger than the expected 108°.

Synthesis of B,S,S' and S,S' Coordination Mode Complexes 5 and 6. In view of another untouched C–H bond in the carborane cage of 1, it is a natural extension for us to do the stepwise modification of 1 after successful preparation of the C,S-chelated complexes 2 and 3. Therefore, a thiolate-bridged model was constructed on the basis of our previous systematic studies of the 16-electron "pseudo-aromatic" $Cp^*MS_2(C_2B_{10}H_{10})$ (M = Co, Rh, Ir) complexes.¹⁷

As shown in Scheme 2, the half-sandwich complexes 5 and 6 were prepared in a one-pot reaction by the in situ formation of the S-lithium salt of 1, followed by the addition of the dimeric metal complex $[Cp^*MCl_2]_2$ (M = Ir, Rh) in THF at room temperature. Two different products, $[Cp^*IrCl(Cab^{B,S,S'})]$ (**5**) and $[Cp^*RhCl-(Cab^{S,S'})]$ (**6**) $(Cab^{B,S,S'} = (\eta^1 - S')(\eta^1 - SPPh_2)(\eta^1 - 1, 2 - close - C_2B_{10}H_9)$, $Cab^{S,S'} = [1-S'-2-SPPh_2-1,2-closo-C_2B_{10}H_{10}]^-)$, were obtained in yields of 72% and 65%, respectively. Aside from this method, the corresponding thiol 1-SH-2-SPPh₂-1,2-closo-C₂B₁₀H₁₀ (4) was isolated with a good yield of 85%. Using NaH as a base, the following reaction of 4 with $[Cp^*MCl_2]_2$ (M = Ir, Rh) occurred smoothly. For 5, the ¹H NMR spectrum shows a sharp signal at δ 1.96 ppm for the Cp* resonance and several groups of signals in the range of δ 8.32–7.38 ppm for the protons of the phenyl ring. The ¹¹B NMR spectrum shows overlapping signals at δ –0.60 (3B), -6.30 (3B), -9.39 (1B), and -12.58 (3B) ppm, whereas a 2:2:3:3 pattern is observed for 6. The ³¹P NMR spectra show signals at δ 62.80 and 49.28 ppm for 5 and 6, respectively, which further proved that the structures of these two complexes are different. To our surprise, the iridium and rhodium complexes exhibit different reactivities in this reaction. The iridium complex





Figure 3. Molecular structures of 5 and 6 with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg) are as follows. 5: Ir(1)-S(1), 2.366(2); Ir(1)-S(2), 2.431(2); S(2)-C(2), 1.785(9); Ir(1)-B(3), 2.116(10); S(1)-P(1), 1.990(3); C(1)-C(2), 1.654(12); C(2)-C(1)-P(1), 119.8(6); S(1)-Ir(1)-S(2), 91.12(9); Ir(1)-S(2)-C(2), 88.8(3); P(1)-S(1)-Ir(1), 104.02(11); C(2)-B(3)-Ir(1), 99.8(7); C(1)-P(1)-S(1), 107.9(3). 6: Rh(1)-S(1), 2.385(3); Rh(1)-S(2), 2.401(3); S(1)-C(1), 1.750(14); S(2)-P(1), 2.010(4); Rh(1)-Cl(1), 2.409(3); C(1)-C(2), 1.775(18); S(1)-Rh(1)-S(2), 92.75(10); C(1)-Rh(1), 112.1(4).

5 shows an unexpected B,S,S' coordination mode via B–H activation, whereas the rhodium complex **6** shows a normal S, S' mode. To the best of our knowledge, this carboranyl B–H bond activation of ligand **1** induced by a metal complex has been reported for the first time. A similar intramolecular oxidative addition process involving a B–H bond was originally reported by Hawthorne¹⁸ and other groups.^{19,20} The possible reason for B–H bond activation may be due to the existence of a sulfur bridge, which caused the electron-deficient metal center to be located very close to the B–H vertices.

Complexes 5 and 6 crystallized in the triclinic space group $P\overline{1}$ and the triclinic space group P1, respectively. The crystallographic data of 5 and 6 are summarized in Table 1. As shown in Figure 3, complexes 5 and 6 adopt a three-legged piano-stool geometry with a distorted-octahedral coordination environment. The distances of the M–S(C) bonds are 2.431(2) and 2.385(3) Å for **5** and **6**, respectively. These values are close to the corresponding values for M–S bonds in analogous complexes^{17e} but are much longer than those in the 16-electron complexes Cp*MS₂[C₂B₁₀H₁₀].²¹ This discrepancy may be ascribed to the fact that the p-type interaction between the metal center and sulfur atom was destroyed in the 18-electron complexes.^{22a,b} Additionally, the M–S distances of coordinatively unsaturated complexes are generally shorter than those of the electronically saturated complexes.^{22c-i} For complex **5**, the four-membered ring C(2)–B(3)–Ir(1)–S(2), the five-membered ring B(3)–C(1)–P(1)–S(1)–Ir(1), and the six-membered ring C(2)–C(1)–P(1)–S(1)–Rh(1)–S(2) were simultaneously formed due to the insertion of the sulfur bridge. The Ir–B bond length (2.116(10) Å) is similar to reported values (Figure 4),^{17e,23} but



Figure 4. Ir–B bond lengths of the analogous complexes (Å).

Scheme 3. Synthesis of the Nido S,S' Coordination Mode Zwitterionic Complex 7



this bond is longer than those of an ordinary iridium boryl complex (1.971-2.048 Å).²⁴ The possible reason for the difference can be ascribed to the carborane cage. The electron density of the boron atom was reduced because of the presence of the electron-deficient carborane cage. For complex **6**, the Rh(1)–S(1) bond (2.385(3) Å) is shorter than the Rh(1)–S(2) coordinative bond (2.401(3) Å), which indicates a stronger interaction between Rh and S(1). The dihedral angle between S(1)–Rh(1)–S(2) and S(2)–P(1)–C(2)–C(1)–S(1) is 4.7° along the S···S vector.

Synthesis of Zwitterionic Nido S,S' Coordination Mode Complex 7. Strong Lewis bases, such as alkoxides, amines, and fluoride, are known to induce the deboronation of *closo*-carboranes. Upon heating in CH₃OH, the solution of 6 clearly changed from dark red to dark green, and the clear solution turned turbid. This result indicated that the neutral complex 6 readily loses one boron atom and was gradually converted to the zwitterionic complex [Cp*Rh(7-S'-8-(SPPh₂)₂-7,8-C₂B₉H₁₀)] (7) (Scheme 3). To explore the reactivity of this process, different weak bases such as NaOAc, NaHCO₃, and Na₂CO₃ were added to the reaction solution. However, the products were all the same with more or less different yields. In addition, the strong base CH₃ONa greatly prompted this reaction and complex 7 was obtained in 83% yield at ambient temperature.

The solubility of the *nido*-carborane complex 7 is much less than that of the *closo*-carborane complex 6 because of the destruction of a symmetric structure. X-ray-quality single crystals of 7 were obtained by slow diffusion of *n*-hexane into a concentrated solution of the complex in CH₂Cl₂. The crystallographic data of 7 are summarized in Table 1. The molecular structure of 7 with selected bond lengths and angles are given in Figure 5. The coordination of the bidentate ligand 7-S'-8-(SPPh₂)₂-7,8-C₂B₉H₁₀ to the Rh atom results in a six-membered RhPS₂C₂ ring. The four atoms C(7), C(8), P(1), and S(2) nearly form a plane, with a dihedral angle of 1.51° between the planes of S(2)-P(1)-C(7) and C(8)-C(7)-S(2). The Rh(1)-S(1) (2.3248(7) Å) and Rh(1)-S(2) bond distances (2.2728(6) Å) are both shorter than the corresponding bond of complex **6**, respectively (Chart 1). On the basis of the molecular framework of 7 (Figure 5), the four atoms Rh(1), P(1), S(1), and S(2) are arranged on one side and can be regarded as constituting the handle of a spoon-shaped *nido*-carborane complex.

Norbornene Polymerization. On the basis of previous work,¹⁴ we decided to investigate the use of the iridium complex **2** in homogeneous catalysis. Fortunately, complex **2** shows a good catalytic activity in the polymerization of norbornene. When the Al/Ir molar ratio was 2000, the catalytic activity of **2** was up to 1.40×10^6 g of PNB (mol of Ir)⁻¹ h⁻¹ (Table 2, entry 2). However, when the Al/Ir ratio was further increased, the activity appeared to decrease (Table 2, entries 3 and 4).

The microstructure of the obtained polynorbornenes were characterized by ¹H NMR and ¹³C NMR spectroscopy. The polynorbornenes had similar ¹H NMR and ¹³C NMR spectra. No resonance was displayed at about δ 5.1 and 5.3 ppm in the ¹H NMR spectrum of the polynorbornene assigned to the cis and trans forms of the double bond,²⁵ which generally indicates the presence of the ring-opening metathesis polymerization (ROMP) structure. The $^{13}\mathrm{C}$ NMR spectrum shows the four main groups of resonances δ 49.5, 49.1, 48.4, 47.1, 46.3, δ 38.2, δ 37.2, 34.8, 33.8, and δ 30.2, 29.0 ppm, attributed to carbons 2 and 3, carbons 1 and 4, carbon 7, and carbons 5 and 6, respectively (Scheme 4).²⁶ The ¹³C NMR spectrum is similar to that reported by Wu et al.^{25b} and Patil et al.²⁷ These data indicate that the polynorbornene obtained with the aforementioned catalysts is a vinyl-type (2,3-linked) addition product: i.e., no ROMP was observed. Furthermore, the ¹³C NMR spectrum shows that the polymer is exo enchained. The spectrum did not exhibit resonances in the δ 20–24 ppm region. The presence of such resonances has been taken as evidence of endo enchainment on the basis of mode studies.²⁵ The multiplicity of the peaks suggested that the insertion of monomer units took place in more than one stereospecific way. Therefore, the obtained polynorbornenes were atactic.²⁸ Indeed, all polynorbornenes are soluble at room temperature in chlorobenzene and cyclohexane, which indicates low stereoregularity.²⁵

All polynorbornenes obtained show similar IR spectra. The IR spectra reveal the characteristic signals of polynorbornenes at about 943 cm⁻¹. Also, there are no absorptions at 1680–1620 cm⁻¹, especially at about 960 and 735 cm⁻¹, assigned to the trans and cis forms of double bonds, respectively, which are characteristic of the ROMP structure of polynorbornenes.²⁵ These absorption peaks at about 943 cm⁻¹ can be assigned to the ring system of bicyclo[2.2.1]heptane, as Kennedy noted.²⁹



Figure 5. (left) Molecular structure of 7 with thermal ellipsoids drawn at the 30% level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)-S(1), 2.3248(7); Rh(1)-S(2), 2.2728(6); S(2)-C(8), 1.794(2); S(2)-P(1), 2.0154(8); C(7)-C(8), 1.584(3); S(1)-Rh(1)-S(2), 100.86(2); C(8)-S(2)-Rh(1), 115.83(8); C(8)-C(7)-P(1), 116.49(16). (right) Framework of the structure.





 Table 2. Norbornene Polymerization for the Ir/MAO Catalytic System^a

entry	cat.	Al/Ir	yield/mg	$activity^b$	$M_{\rm w}^{\ \ c}$
1	2	1000	189	0.76	4.95
2	2	2000	349	1.40	5.17
3	2	3000	272	1.09	5.19
4	2	4000	210	0.84	5.13

^{*a*} Polymerization conditions: [NB] = 1.00 g; V_{total} = 10 mL; catalyst iridium complex **2**, 0.5 μ mol; reaction time 30 min, *T* = 30 °C, solvent chlorobenzene. ^{*b*} In units of 10⁶ g of PNB (mol of Ir)⁻¹ h⁻¹. ^{*c*} In units of 10⁶ g mol⁻¹, measured in chlorobenzene at 25 °C using the Mark– Houwink coefficients.

CONCLUSIONS

In summary, the monophosphine-*o*-carborane sulfide 1 was used as a noninnocent ligand to form a series of half-sandwich iridium and rhodium complexes with versatile coordination modes. The two C,S coordination mode complexes 2 and 3 were successfully synthesized by the treatment of $[Cp^*MCl_2]_2$ (M = Ir, Rh) with the lithium salt of 1. Interestingly, the reactivities of S,S' bifunctional derivative 4 with dimeric iridium and rhodium complexes were different. The unexpected B,S,S' coordination mode product 5 via B–H activation and the normal S,S' coordination mode product 6 were obtained, respectively. The formation of 5 may be due to the electron-deficient metal center located in close proximity to the B–H vertices. The deboronation reaction from the neutral

Scheme 4. Schematic Representation of the Three Different Types of Polymerization for Norbornene



closo-carborane complex **6** to the zwitterionic *nido*-carborane complex 7 was also investigated. In addition, a preliminary study showed that the novel half-sandwich Ir complex **2** exhibited good catalytic activity in the polymerization of norbornene in the presence of methylaluminoxane as the cocatalyst. Further studies on the reactivity of monophosphine-*m*-carborane and diphosphine-*m*-carborane sulfides are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Data. All manipulations were performed under an atmosphere of nitrogen using standard Schlenk techniques. CH_2Cl_2 was dried over CaH_2 , chlorobenzene was dried over $MgSO_4$ and $CaCl_2$, and THF, diethyl ether, hexane, and toluene were dried over Na and then distilled under a nitrogen atmosphere immediately prior to use. Methylaluminoxane (MAO), *n*-butyllithium (1.6 M in *n*-hexane, Acros), *o*-carborane, and other chemicals were used as commercial products without further purification. $[Cp^*MCl_2]_2$ (M = Ir, Rh)³⁰ was synthesized according to the literature. ¹H NMR (400 MHz), ¹³C NMR (100 MHz), and ³¹P NMR (162 MHz) spectra were measured with a VAVCE DMX-400 spectrometer. ¹¹B NMR (160 MHz) spectra were recorded with a Bruker DMX-500 spectrometer. Elemental analysis was performed on an Elementar vario EL III analyzer. IR (KBr) spectra were measured with a Nicolet FT-IR spectrophotometer.

Synthesis of 1-SPPh₂-1,2-closo-C₂B₁₀H₁₁ (1). Sulfur powder (32 mg, 1 mmol) was added to a solution of 1-PPh₂-1,2-*closo*-C₂B₁₀H₁₁ (328 mg, 1 mmol) in toluene (20 mL) at room temperature, and then NEt₃ (1 mL) was added to the solution after the sulfur was completely dissolved. The mixture was stirred for 12 h at 80 °C. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel. Elution with petroleum ether/ CH_2Cl_2 (8/1) gave 1 (266 mg, 81%) as a slightly yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.29-8.23 (m, 4H, Ph), 7.67-7.63 (m, 2H, Ph), 7.60-7.55 (m, 4H, Ph), 4.70 (s, 1H, HC_{cage}), 2.81–1.73 ppm (br m, 11H, BH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 133.5 (d, J(C,P) = 11 Hz, Ph), 133.1 (d, J(C,P) = 3 Hz, Ph), 128.4 (d, J(C,P) = 13 Hz, Ph), 127.4 (d, J(C,P) = 13 Hz, Ph), 127.4 (d, J(C,P) = 13 Hz, Ph), 128.4 (d, J(C,P) = 13 Hz, Ph), 128.489 Hz, Ph), 72.0 (d, J(C,P) = 34 Hz, $C_{cage} - P$), 63.8 ppm (s, HC_{cage}). ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ -0.08 (1B), -2.07 (1B), -6.80 (2B), -10.53 (2B), -12.29 (4B) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 51.33 (s, P=S) ppm. IR (KBr, disk): ν 2626, 2573 (B-H), 647 (P=S) cm⁻¹. Anal. Calcd for C₁₄H₂₁B₁₀PS: C, 46.65; H, 5.87. Found: C, 46.78; H, 5.88.

Synthesis of [Cp*lrCl(Cab^{C,S})] (2). n-BuLi (1.6 M in n-hexane, 0.25 mL, 0.4 mmol) was added to a solution of 1 (144 mg, 0.4 mmol) in THF (10 mL) at -78 °C, and the mixture was stirred at -78 °C for 1 h and at room temperature for another 1 h. Then [Cp*IrCl₂]₂ (160 mg, 0.2 mmol) was added as a solid to the above mixture and stirred for 8 h at room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel. Elution with petroleum ether/THF (1/1) gave 2 (197 mg, 68%) as a yellow solid. A suitable single crystal of 2 was obtained by slow diffusion of *n*hexane into its concentrated dichloromethane solution. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.33-8.27 (m, 2H, Ph), 7.88-7.83 (m, 2H, Ph), 7.68–7.60 (m, 4H, Ph), 7.47 (br, 2H, Ph), 1.49 ppm (s, 15H, Cp*). ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ 133.8 (d, J(C,P) = 2.8 Hz, Ph), 133.7 (d, J(C,P) = 2.3 Hz, Ph), 128.9 (d, J(C,P) = 3.6 Hz, Ph), 128.7 (d, $J(C,P) = 2.3 \text{ Hz}, Ph), 91.3 (C_5 Me_5), 8.8 \text{ ppm} (C_5 Me_5).$ ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ 2.18 (2B), -5.47 (4B), -8.64 (4B) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 60.79 (s, P=S) ppm. IR (KBr, disk): ν 2601, 2548 (B–H), 625 (P=S) cm⁻¹. Anal. Calcd for C₂₄H₃₅B₁₀PSCIIr: C, 39.91; H, 4.88. Found: C, 39.63; H, 4.91. Synthesis of [Cp*RhCl(Cab^{C,S})] (3). A procedure analogous to

Synthesis of [Cp*RhCl(Cab^{C-3})] (3). A procedure analogous to the preparation of 2 was used; $[Cp*RhCl_2]_2$ (124 mg, 0.2 mmol) was added as a solid to the mixture and stirred for 8 h at room temperature. Yield: 160 mg, 63%; orange solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.35–8.26 (m, 2H, Ph), 7.91–7.87 (m, 2H, Ph), 7.67–7.60 (m, 4H, Ph), 7.45 (br, 2H, Ph), 1.53 ppm (s, 15H, Cp*). ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ 133.3 (d, *J*(C,P) = 3.0 Hz, Ph), 132.6 (d, *J*(C,P) = 2.6 Hz, Ph), 128.3 (d, *J*(C,P) = 3.6 Hz, Ph), 127.9 (d, *J*(C,P) = 2.8 Hz, Ph), 89.9 (C₅Me₅), 9.6 ppm (C₅Me₅). ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ 2.24 (2B), -5.33 (4B), -8.69 (4B) ppm. ³¹P NMR (162 MHz, CDCl₃, 13PO₄, 25 °C): δ 60.88 (s, *P*=S) ppm. IR (KBr, disk): ν 2612, 2568 (B–H), 633 (P=S) cm⁻¹. Anal. Calcd for C₂₄H₃₅B₁₀PSCIRh: C, 45.54; H, 5.57. Found: C, 45.62; H, 5.57.

Synthesis of [1-SH-2-SPPh₂-1,2-*closo*-C₂B₁₀H₁₁] (4). *n*-BuLi in hexane (1.6 M, 0.25 mL, 0.4 mmol) was added to a solution of 1 (144 mg, 0.4 mmol) in THF (10 mL). The mixture was stirred at 0 °C for $^{1}/_{2}$ h and for another 1 h at room temperature. Sulfur powder was added to the above solution and stirred for 2 h, and then a few drops of water was added to the solution. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel. Elution with CH₂Cl₂ gave 4 (135 mg, 85%) as a yellow solid. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.41–8.36 (q, 4H, Ph), 7.66–7.56 (m, 6H, Ph), 5.54 (s, SH), 2.76–1.76 ppm (br m, 10H, BH). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 134.5 (d, *J*(C,P) = 9 Hz, Ph), 133.6 (d, *J*(C,P) = 10 Hz, Ph), 128.5 (d, *J*(C,P) = 13 Hz, Ph), 128.2 (d, *J*(C,P) = 13 Hz, Ph), 72.4 ppm (d, *J*(C,P) = 34 Hz, C_{cage}–P). ³¹P NMR (162 MHz, CDCl₃, 25 °C): δ 49.35 (s, *P*=S) ppm. IR (KBr, disk): ν 2619, 2563

(B-H), 643 (P=S) cm⁻¹. Anal. Calcd for $C_{14}H_{21}B_{10}PS_2$: C, 42.84; H, 5.39. Found: C, 42.86; H, 5.63.

Synthesis of [Cp*lr(Cab^{B,S,S'})] (5). n-BuLi in hexane (1.6 M, 0.25 mL, 0.4 mmol) was added to a solution of L_{PS} (144 mg, 0.4 mmol) in THF (10 mL). The mixture was stirred at 0 °C for 1/2 h and for another 1 h at room temperature. Sulfur powder was added to the above solution and stirred for 2 h, and then [Cp*IrCl₂]₂ (160 mg, 0.2 mmol) was added as a solid to the solution and continuously reacted for 8 h at room temperature. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel. Elution with petroleum ether/ $CH_2Cl_2(2/1)$ gave 5 (207 mg, 72%) as a light red solid. A suitable single crystal of 5 was obtained by slow diffusion of nhexane into its concentrated dichloromethane solution. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.32–8.27 (m, 2H, Ph), 8.19–8.14 (m, 2H, Ph), 7.64–7.56 (m, 4H, Ph), 7.38 (br, 2H, Ph), 1.96 ppm (s, 15H, Cp*). ¹³C NMR (400 MHz, CDCl₃, 25 °C): δ 135.5 (d, *J*(C,P) = 9.8 Hz, Ph), 134.9 (d, *J*(C,P) = 9.6 Hz, Ph), 133.0, 132.7 (dd, *J*(C,P) = 3.0 Hz, 3.1 Hz, Ph), 128.2 (d, J(C,P) = 12.4 Hz, Ph), 127.7 (d, J(C,P) = 13.2 Hz, Ph), 100.8 (s, C_{cage} -S), 88.1 (d, J(C,P) = 72.8 Hz, C_{cage} -P), 90.3 ($C_{5}Me_{5}$), 9.3 ppm (C₅ Me_5). ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ –0.60 (3B), -6.30 (3B), -9.39 (1B), -12.58 (3B) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 62.80 (s, P=S) ppm. IR (KBr, disk): ν 2562 (B-H), 630 (P=S) cm⁻¹. Anal. Calcd for $C_{24}H_{34}B_{10}PS_2Ir: C$, 40.15; H, 4.77. Found: C, 40.02; H, 4.80.

Synthesis of [Cp*RhCl(Cab^{5,5'})] (6). A procedure analogous to the preparation of 4 was used; [Cp*RhCl₂]₂ (124 mg, 0.2 mmol) was added as a solid to the mixture and stirred for 8 h at room temperature. Yield: 173 mg, 63%; dark red solid. A suitable single crystal of 6 was obtained by slow diffusion of *n*-hexane into its concentrated dichloromethane solution. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 8.66–8.61 (m, 2H), 8.10–8.06 (m, 2H), 7.60–7.51 (m, 6H), 1.59 ppm (s, 15H, Cp*). ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ 136.4 (d, *J*(C,P) = 11.1 Hz, Ph), 133.8, 133.4 (s, Ph), 128.4 (d, *J*(C,P) = 13.3 Hz, Ph), 128.1 (d, *J*(C,P) = 14.0 Hz, Ph), 97.9 (C₅Me₅), 93.0 (C_{cage} – S), 78.1 (d, *J*(C,P) = 36.2 Hz, C_{cage} – P), 9.6 ppm (C₅Me₅). ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ 2.06 (2B), -4.04 (2B), -7.42 (3B), -10.30 (3B) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 49.28 (s, *P*=S) ppm. IR (KBr, disk): ν 2571 (B–H), 629 (P=S) cm⁻¹. Anal. Calcd for C₂₄H₃₅B₁₀ClPS₂Rh: C, 43.34; H, 5.30. Found: C, 43.56; H, 5.38.

Synthesis of [Cp*Rh(7-S')-(8-SPPh₂)-7,8-C₂B₉H₁₀] (7). Complex 5 (0.2 mmol, 132 mg) was added to CH₃OH (20 mL), followed by the addition of a small amount of CH₃ONa, and then the mixture was stirred at 50 °C for 8 h. After removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel. Elution with CH₂Cl₂ gave 7 (103 mg, 83%) as a dark green solid. A suitable single crystal of 7 was obtained by slow diffusion of *n*-hexane into its concentrated dichloromethane solution. ¹H NMR (400 MHz, CDCl₃, 25 °C): δ 7.89–7.84 (m, 2H), 7.64–7.50 (m, 6H), 7.40–7.38 (m, 2H), 1.54 (s, Cp*). ¹¹B NMR (160 MHz, CDCl₃, 25 °C): δ –6.43 (2B), –10.09 (2B), –17.50 (1B), –21.60 (1B), –31.66 (3B) ppm. ³¹P NMR (162 MHz, CDCl₃, H₃PO₄, 25 °C): δ 46.28 (s, *P*=S) ppm. Anal. Calcd for C₂₄H₃₅B₉PS₂Rh: C, 46.58; H, 5.70. Found: C, 46.43; H, 5.68.

Norbornene Polymerization. A 0.5 μ mol amount of iridium complex 2 in 2.0 mL of chlorobenzene, 1.00 g of norbornene in 2 mL of chlorobenzene, and 6 mL of fresh chlorobenzene were added into a special polymerization bottle (50 mL) with a stirrer under a nitrogen atmosphere. After the mixture was kept at 30 °C for 10 min, a certain amount of MAO was charged into the polymerization system via a syringe and the reaction was started. After 15 min, acidic ethanol ($V_{ethanol}/V_{conc HCl} = 20/1$) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol, and dried at 80 °C for 36 h under vacuum. For all polymerization procedures, the total reaction volume was 10.0 mL, which can be achieved by varying the amount of chlorobenzene when necessary. The viscosity-average molar

masses (M_w) of PNB were obtained in chlorobenzene at 25 °C using Mark–Houwink coefficients:³¹ α = 0.56, K = 5.97 × 10⁻⁴ dL g⁻¹.

X-ray Crystallography. Diffraction data of 1, 2, and 5–7 were collected on a Bruker Smart APEX CCD system with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). All the data were collected at room temperature, and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL).³² SADABS³³ absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. All calculations were performed using the Bruker program Smart. A summary of the crystallographic data and selected experimental information are given in Table 1.

ASSOCIATED CONTENT

Supporting Information. CIF files giving crystallographic data for 1, 2, and 5-7. This material is available free of charge via the Internet at http://pubs.acs.org.

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DEDICATION

Dedicated to Herr Professor Dr. Gerhard Erker on the occasion of his 65th birthday.

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