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Iridium Coordination Compounds of Stanna-*closo*-dodecaborate

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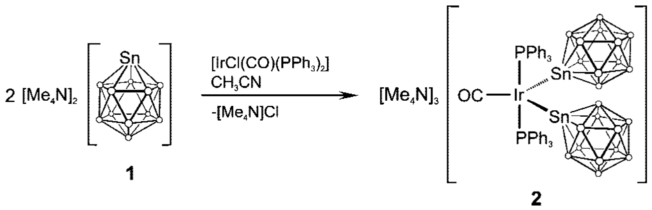
The reaction of Vaska's complex $[IrCl(CO)(PPh_3)_2]$ with stanna-*closo*-dodecaborate $[SnB_{11}H_{11}]^{2-}$ (**1**) resulted in the formation of the trigonal bipyramidal iridium(I) compound $[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]^{3-}$ (**2**). In this compound, one stannaborate moiety can be readily substituted with CO or ethylene at RT and atmospheric pressure to give the trigonal bipyramidal compounds $[Et_4N][Ir(SnB_{11}H_{11})(CO)_2(PPh_3)_2]$ (**3**) and $[Me_4N][Ir(SnB_{11}H_{11})(CO)(C_2H_4)(PPh_3)_2]$ (**4**). Oxidative addition of H_2 was accomplished by the reaction of **2** with H_2, yielding the iridium(III) compound $[Et_3NMe][IrH_2(SnB_{11}H_{11})(CO)(PPh_3)_2]$ (**5**), whereas the protonation of **2** resulted in the formation of $[Et_3NMe]_2[IrH(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ (**6**). All compounds have been characterized by single-crystal X-ray diffraction analysis, multinuclear NMR spectroscopy, IR spectroscopy, and elemental analysis.

Introduction

Iridium−tin coordination compounds are well established for a variety of tin ligands, such as $[SnX_3]^-$ ($X = Cl, Br$), $[SnR_3]^-$ ($R = Me, Ph$), and $[Sn(SiMe_2N(3,5\text{-xyl}))_3SiMe]^-$.[1–9] In particular, trichlorostannate-substituted iridium complexes $[Ir(SnCl_3)L_n]$ have been proven to catalyze hydrogenations as well as Friedel−Crafts alkylations (FCA) in high yield.[10–14] In polynuclear metal carbonyl complexes of iridium and rhodium, tin ligands act as effective ligands.[15–17]

Vaska's iridium(I) complex $[IrCl(CO)(PPh_3)_2]$ is characterized by its ability to add a fifth ligand such as CO or ethylene.[18–21] Furthermore, this compound is known for oxidative addition reactions of a large variety of subtrates such as H_2 and HCl to yield hexacoordinated octahedral iridium(III) compounds.[21,22] Recently, the halide in $[IrCl(CO)(PPh_3)_2]$ was abstracted with $[Et_3Si]^+$ to activate Vaska's compound toward oxidative addition of chlorobenzene.[23] It has been well documented that stanna-*closo*-dodecaborate can act as a versatile ligand with nucleophilic properties in the coordination chemistry of various transition metals.[24] In fact, one iridium coordination compound of the group 14 heteroborate has been established with $[Ir(Cp^*)(SnB_{11}H_{11})(bipy')]$ (bipy′ = 4,4′-di-*tert*-butyl-2,2′-bipyridine, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl).[25]

Scheme 1. Synthesis of $[Me_4N]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ ($[Me_4N]_3[2]$)



Herein, the product of the reaction between Vaska's iridium complex $[IrCl(CO)(PPh_3)_2]$ and stanna-*closo*-dodecaborate is presented, and the reactivity of this reaction product was studied with respect to substitution reactions, oxidative addition, and protonation.

Results and Discussion

Syntheses. The pentacoordinated complex $[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]^{3-}$ (**2**) was isolated from the reaction of Vaska's complex $[IrCl(CO)(PPh_3)_2]$ with the stanna-*closo*-dodecaborate nucleophile in acetonitrile (Scheme 1). The ^{31}P NMR spectrum of the reaction mixture clearly shows that the pentacoordinated complex **2** is the only reaction product of this nucleophilic substitution reaction. Thus, in reaction with 2 equiv. of tinborate

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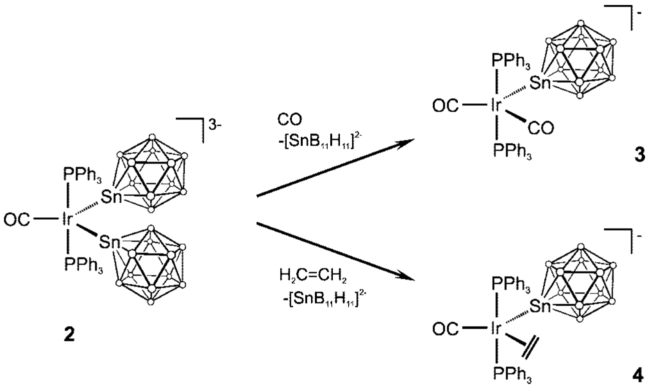
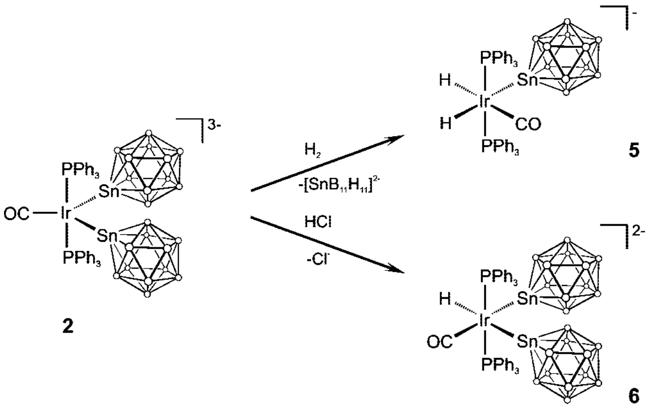
Scheme 2. Synthesis of $[Et_4N][Ir(SnB_{11}H_{11})(CO)_2(PPh_3)_2]$ (3) and $[Me_4N][Ir(SnB_{11}H_{11})(CO)(C_2H_4)(PPh_3)_2]$ (4)



Scheme 3. Synthesis of $[Et_3NMe][IrH_2(SnB_{11}H_{11})(CO)(PPh_3)_2]$ (5) and $[Et_3NMe]_2[IrH(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ (6)



1 the isolated yield of **2** was almost quantitative. Single crystals of this novel iridium tin coordination compound were obtained in the case of the $[Me_4N]^+$ salt by slow diffusion of Et_2O into an acetonitrile solution. In order to influence the crystallization behavior, compound **2** was synthesized with different tetraalkylammonium salts (viz., $[Me_4N]^+$, $[Bu_3NMe]^+$, $[Et_3NMe]^+$, $[Et_4N]^+$) by the reaction of $[IrCl(CO)(PPh_3)_2]$ with the appropriate tetraalkylammonium salts of stanna-*closo*-dodecaborate.

The reactivity study of complex **2** with the ligands CO and C_2H_4 shows that one of the stanna-*closo*-dodecaborate ligands in complex **2** coordinates in a labile manner and is easily substituted. The substitution reaction was conducted by addition of gaseous CO or C_2H_4 into a freeze-pumped acetonitrile solution of the iridium complex **2**. After warming the respective reaction mixtures to RT, the color of the solutions turned from yellow to light yellow. The formation of the substitution products $[Et_4N][Ir(SnB_{11}H_{11})(CO)_2(PPh_3)_2]$ (**3**) and $[Me_4N][Ir(SnB_{11}H_{11})(CO)(C_2H_4)(PPh_3)_2]$ (**4**) was proven by NMR spectroscopy and single-crystal structure analysis (Scheme 2).

Oxidative addition with complex **2** was studied in reaction with H_2. Hydrogen adds to iridium of the pentacoordinated complex **2** at room temperature and atmospheric pressure and replaces a stannaborate ligand (Scheme 3). Single crystals of the dihydride **5** were prepared with the $[Et_3NMe]^+$ countercation.

The Brønstedt basicity of the trianion **2** was investigated in reaction with HBF_4, HCl, $[Bu_3NH]^+$, $[Et_3NH]^+$, or water. Only in reaction with water is the basicity of the trianion not high enough to be protonated. In the other cases the hydride complex **6** was straightforwardly synthesized. From the reaction with HCl and in the case of the $[Et_3NMe]^+$ cation we were able to isolate crystals suitable for X-ray structure analysis (Scheme 3).

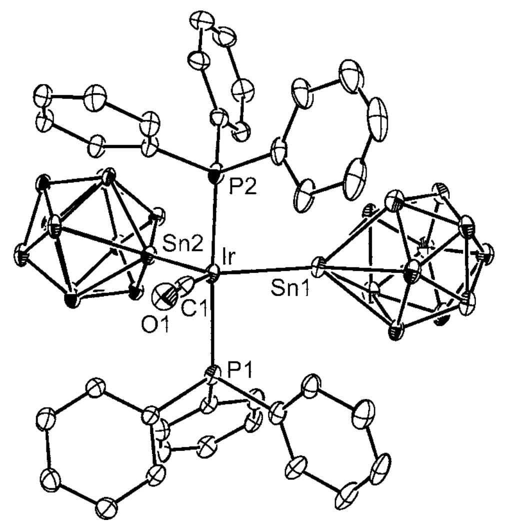


Figure 1. ORTEP plot of the anion of $[Me_4N]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ ($[Me_4N]_3[\mathbf{2}]$). H atoms and the cation have been omitted for clarity; ellipsoids are at 30% probability. Selected interatomic distances [Å] and angles [deg]: Ir−C1: 1.852(7), Ir−P2: 2.3221(18), Ir−P1: 2.3240(18), Ir−Sn2: 2.6462(5), Ir−Sn1: 2.6620(5), Ir−Sn1: 2.6620(5), Ir−Sn2: 2.6462(5), Ir−P1: 2.3240(18), Ir−P2: 2.3221(18), Ir−C1: 1.852(7), C1−O1: 1.163(9), P1−Ir−Sn1: 90.64(4), P1−Ir−Sn2: 94.38(4), P2−Ir−Sn1: 90.33(4), P2−Ir−Sn2: 94.33(4), P1−Ir−P2: 170.82(6), P1−Ir−C1: 86.8(2), P2−Ir−C1: 85.8(2), Sn1−Ir−C1: 132.1(2), Sn2−Ir−C1: 125.4(2).

Solid-State Structures. The solid-state structures of compounds **2**−**6** have been determined by single-crystal structure analysis. The structure refinement of the iridium complex **2** in space group $P\bar{1}$ reveals a trigonal bipyramidal coordination of the iridium(I) center with *trans* PPh_3 groups in apical positions and two stannaborate moieties as well as CO in the equatorial plane. In this compound, the Ir−Sn distances of 2.6462(5) and 2.6620(5) Å are slightly elongated but in good agreement with the reported Ir−Sn distances.[1−9,11,25] The molecular structure of the anion together with selected interatomic distances and angles is depicted in Figure 1.

In the solid-state structures of the reaction products **3** and **4**, the substitution of one stannaborate moiety by CO and ethylene becomes evident and the Ir center employs a trigonal bipyramidal coordination mode as in **2**. The Ir−Sn separations of 2.6520(9) Å (**3**) and 2.6447(14) Å (**4**) are in accordance with compound **2** and the reported Ir−Sn distances.[1−9,11,25] The molecular structures of dicarbonyl **3** and the ethylene adduct **4** are shown in Figures 2 and 3 together with selected interatomic distances and angles. In compound **4**, the ethylene lies in the equatorial plane of the trigonal bipyramid. For the ethylene molecule of **4** the C−C bond length [1.44(3) Å] is longer than in free ethylene (1.339 Å)[26] but compares well with corresponding bond lengths in $[Ir(C_2H_4)_2(PMe_2Ph)_3]BF_4$ (1.40, 1.43 Å),[27] $[Ir(C_2H_4)_2(PPh_2C_6H_4PPh_3)]$, and $[Ir(C_2H_4)_2(P^iPr_2C_3H_6P^iPr_3)]$ (av 1.45 and 1.43 Å, respectively).[28] The structure refinements of the hydrides **5** and **6** reveal a slightly distorted octahedral coordination geometry of the iridium(III) centers in both compounds. The Ir−Sn distances of 2.6601(13) Å (**5**) as well as 2.6524(7) and 2.6740(7) Å (**6**) are in the range of compounds **2**−**4** and the reported distances.[1−9,11,25] Interestingly, the Ir−Sn distance

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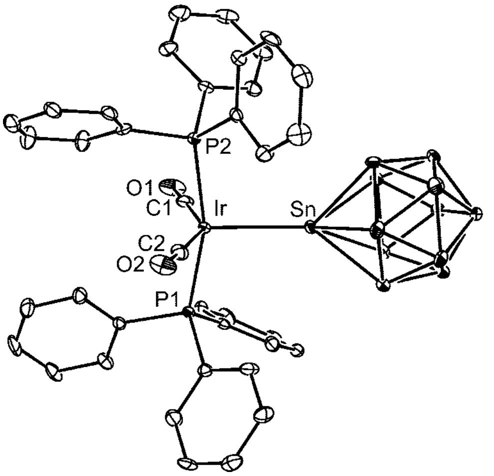

Figure 2. ORTEP plot of the anion of $[Et_4N][Ir(SnB_{11}H_{11})(CO)_2(PPh_3)_2]$ (**3**). H atoms and the cation have been omitted for clarity; ellipsoids are at 30% probability. Selected interatomic distances [Å] and angles [deg]: Ir−Sn: 2.6520(9), Ir−P1: 2.3399(16), Ir−P2: 2.3470(16), Ir−C1: 1.902(6), Ir−C2: 1.904(6), C1−O1: 1.133(7), C2−O2: 1.123(7), P1−Ir−P2: 163.69(5), C1−Ir−C2: 147.1(3), P1−Ir−Sn: 99.87(4), P2−Ir−Sn: 96.41(4), C1−Ir−Sn: 104.02(19), C2−Ir−Sn: 108.82(18).

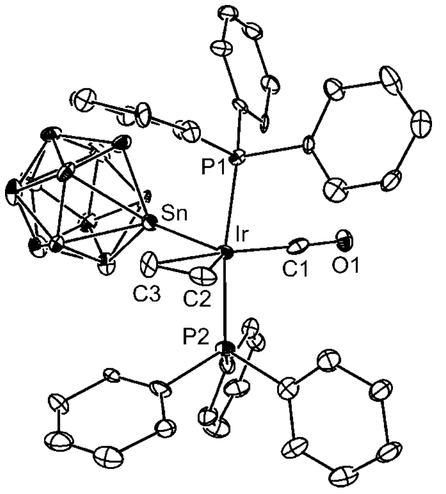

Figure 3. ORTEP plot of the anion of $[Me_4N][Ir(SnB_{11}H_{11})(CO)(C_2H_4)(PPh_3)_2]$ (**4**). H atoms and the cation have been omitted for clarity; ellipsoids are at 30% probability. Selected interatomic distances [Å] and angles [deg]: Ir−Sn: 2.6447(14), Ir−P1: 2.347(4), Ir−P2: 2.352(5), Ir−C1: 1.87(2), Ir−C2: 2.20(2), Ir−C3: 2.247(19), C1−O1: 1.15(2), C2−C3: 1.44(3), P1−Ir−Sn: 92.36(12), P2−Ir−Sn: 96.83(14), P1−Ir−P2: 170.72(18), C1−Ir−Sn: 113.0(6), C1−Ir−C2: 123.4(8), C1−Ir−C3: 160.9(8), C1−Ir−P1: 85.0(5), C1−Ir−P2: 90.2(5), C2−Ir−P1: 88.4(5), C2−Ir−P2: 87.6(5), C2−Ir−Sn: 123.3(6), C3−Ir−P1: 90.9(5), C3−Ir−P2: 91.0(5), C3−Ir−Sn: 85.7(5).

in *trans* position to the hydride is slightly longer than the Ir−Sn distance in *trans* position to the CO ligand. Unfortunately, the hydrogen atoms Ir−H of both structures could not be found in the difference Fourier maps. The molecular structures of **5** and **6** are pictured in Figures 4 and 5 together with selected distances and angles.

NMR Spectroscopy in Solution. In order to gain more information about the solution behavior of the synthesized compounds, a multinuclear NMR study has been carried out. In general, the tin coordination of stannaborate in **2**−**6** is

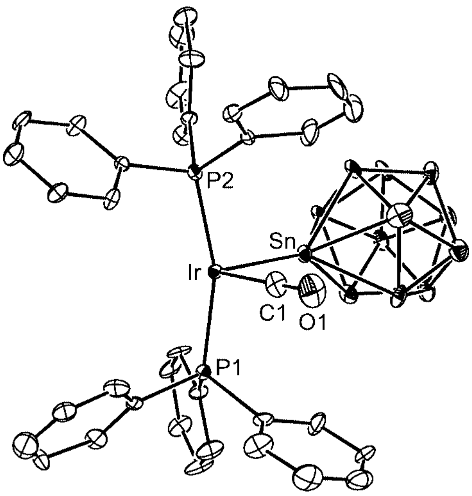

Figure 4. ORTEP plot of the anion of $[Et_3NMe][IrH_2(SnB_{11}H_{11})(CO)(PPh_3)_2]$ (**5**). H atoms and the cation have been omitted for clarity; ellipsoids are at 30% probability. Selected interatomic distances [Å] and angles [deg]: Ir−Sn: 2.6601(13), Ir−P2: 2.322(4), Ir−P1: 2.329(4), Ir−C1: 1.93(2), C1−O1: 1.12(2), P2−Ir−P1: 162.20(13), C1−Ir−Sn: 87.1(5), P1−Ir−Sn: 95.38(10), P2−Ir−Sn: 98.73(10), C1−Ir−P2: 96.4(6), C1−Ir−P1: 95.1(6).

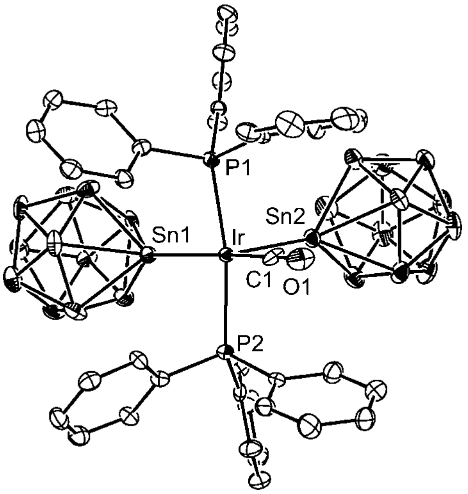

Figure 5. ORTEP plot of the anion of $[Et_3NMe]_2[IrH(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ (**6**). H atoms and the cation have been omitted for clarity; ellipsoids are at 30% probability. Selected interatomic distances [Å] and angles [deg]: Ir−Sn1: 2.6524(7), Ir−Sn2: 2.6740(7), Ir−P1: 2.374(2), Ir−P2: 2.368(2), Ir−C1: 1.895(10), C1−O1: 1.131(10), Sn1−Ir−Sn2: 98.19(2), C1−Ir−P1: 89.0(3), C1−Ir−P2: 87.8(3), C1−Ir−Sn1: 170.6(3), C1−Ir−Sn2: 91.2(3), P1−Ir−Sn1: 90.28(6), P1−Ir−Sn2: 94.30(6), P2−Ir−P1: 165.48(8), P2−Ir−Sn1: 90.63(6), P2−Ir−Sn2: 99.90(6).

indicated by broad signals at −15 ppm in the $^{11}B\{^1H\}$ NMR spectra.[24] The $^{31}P\{^1H\}$ NMR spectrum of **2** features one singlet at 8.6 ppm, flanked by tin satellites with $^2J(^{119/117}Sn-^{31}P) = 97$ Hz. The integration of these satellites confirms the presence of two coordinated heteroborate units.

After the addition of CO or C_2H_4, in the $^{11}B\{^1H\}$ NMR spectra of these reaction mixtures signals of uncoordinated (−6, −11, −12 ppm) and coordinated stannaborate can be detected.[24] In addition, the $^{31}P\{^1H\}$ NMR spectra of the dicarbonyl **3** and the ethylene adduct **4** exhibit singlets with tin satellites at 3.7 ppm [$^2J(^{119/117}Sn-^{31}P) = 160$ Hz] and 7.4 ppm [$^2J(^{119/117}Sn-^{31}P) = 180$ Hz], respectively. In contrast to compound **2**, the integration of these

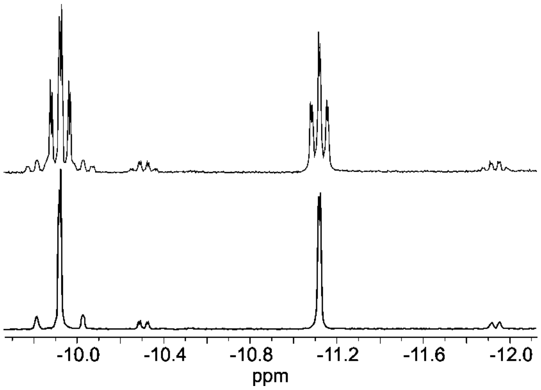

Figure 6. ^{1}H NMR (top) and ^{1}H{^{31}P} NMR (bottom) of $[Et_3NMe][IrH_2(SnB_{11}H_{11})(CO)(PPh_3)_2]$ (**5**).

satellites indicates the presence of one coordinated heteroborate. The ^{1}H NMR spectrum of **4** consists of two broad resonances at 1.74 and 0.35 ppm for the ethylene protons. These signals couple with each other (^{1}H−^{1}H COSY) and can be assigned to resonances in the ^{13}C{^{1}H} spectrum at 21.2 ppm (1.74 ppm) and 27.6 ppm (0.35 ppm) through recording a ^{1}H−^{13}C HSQC spectrum.

After addition of H_2 to complex **2**, the ^{11}B{^{1}H} NMR spectrum of the reaction mixture exhibits signals for coordinated and uncoordinated tin nucleophiles.

In the ^{31}P{^{1}H} NMR spectrum of the dihydride **5** the integration of the tin satellites corresponds with coordination of one stannaborate ligand. In the case of the formation of complex **6**, in the ^{11}B{^{1}H} NMR spectrum of the reaction mixture only coordinated heteroborate can be detected. Due to different substituents in *trans* position to the stannaborate ligands, two signals can be observed in the ^{11}B{^{1}H} spectrum at −14.8 and −15.6 ppm. In the ^{31}P{^{1}H} spectrum of **6**, this different *trans* environment of the tin ligands leads to one resonance at −5.8 ppm with two tin coupling constants: $^2J(^{119/117}\mathrm{Sn}-^{31}\mathrm{P}) = 130$ Hz and $^2J(^{119/117}\mathrm{Sn}-^{31}\mathrm{P}) = 234$ Hz.

In the hydride region of the ^{1}H NMR spectrum of the dihydride **5**, two triplets of doublets at −9.9 and −11.1 ppm can be observed (Figure 6). The doublet structure of both signals with $^2J(^1\mathrm{H}-^1\mathrm{H}) = 4$ Hz arises from the *cis* coupling of the hydrides with each other. Upon ^{31}P decoupling of the ^{1}H spectrum, the triplet structure of both signals with $^2J(^{31}\mathrm{P}-^1\mathrm{H}) = 17$ Hz vanishes and the corresponding tin satellites can be observed more clearly. These tin satellites allow the specific assignment of the resonance at −9.9 ppm [$^2J(^{119/117}\mathrm{Sn}-^1\mathrm{H}) = 87$ Hz] to the hydride in *cis* position to the tin heteroborate. Therefore, the resonance at −11.1 ppm [$^2J(^{119}\mathrm{Sn}-^1\mathrm{H}) = 668$ Hz] can be ascribed to the resonance in *trans* position to the stannaborate moiety.

In the hydride spectra of protonation product **6**, one triplet can be observed at −9.7 ppm with $^2J(^{31}\mathrm{P}-^1\mathrm{H}) = 13$ Hz. The examination of the ^{1}H{^{31}P} NMR spectrum reveals tin satellites with a small *cis* coupling of 94 Hz and a large *trans* coupling of 632 Hz.

The ^{119}Sn{^{1}H} NMR spectra of the synthesized iridium complexes contain very broad signals at −497 ppm (**2**), −500 ppm (**3**), −530 ppm (**4**), −531 ppm (**5**), and −502 ppm (**6**). Since uncoordinated stannaborate exhibits one resonance at −550 ppm, these signals indicate the coordination of the heteroborate. Remarkably, the resonances are significantly shifted toward lower frequencies compared to hitherto know η^1(Sn)-coordinated stannaborate complexes.[24] Since the NMR spectra of **2**−**6** are consistent with the solid-state structures, it can be summarized that the solid-state structures of all compounds remain intact in solution.

IR Spectroscopy. The IR spectra of all compounds contain the B−H stretching vibrations at about 2470 cm^{-1}. In addition, the CO stretching mode of the trianion **2** gives rise to a signal at 1972 cm^{-1}. This is in good agreement with the CO stretching mode of Vaska's complex.[22] The CO stretching frequencies of dicarbonyl **3** and the ethylene adduct **4** can be detected at 1955 and 1942 cm^{-1}, respectively, which are slightly shifted to lower wavenumbers in comparison with **2**. In the IR spectrum of the dihydride **5**, two Ir−H stretching modes at 2166 and 2100 cm^{-1} as well as one CO vibration at 1980 cm^{-1} can be found and compare well with the stretching modes in $[IrClH_2(PPh_3)_2(CO)]$.[22] Finally, the IR spectrum of the protonation product **6** shows one Ir−H stretching mode at 2250 cm^{-1} and one CO stretching vibration at 2053 cm^{-1}, which is in good agreement with the corresponding stretching modes of $[IrCl_2H(PPh_3)_2(CO)]$.[20]

Conclusion

Stanna-*closo*-dodecaborate reacts readily with Vaska's complex under formation of the trigonal bipyramidal compound $[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]^{3-}$ (**2**). In this compound, one stannaborate moiety is coordinated in a labile manner and can be easily substituted by CO or ethylene. In addition, oxidative *cis* addition of H_2 can be accomplished under extrusion of one heteroborate unit. It was further found that the iridium center in **2** shows basicity and can be protonated by the addition of HCl, HBF_4, and protic cations such as $[Et_3NH]^+$ and $[Bu_3NH]^+$.

Experimental Section

General Comments. All manipulations were carried out under an argon atmosphere in Schlenk glassware. Solvents were dried and purified by standard methods and were stored under argon. NMR spectra were recorded on a Bruker DRX-250 NMR spectrometer equipped with a 5 mm ATM probe head and operating at 250.13 MHz (^{1}H), 80.25 MHz (^{11}B), 101.25 MHz (^{31}P) and 92.25 MHz (^{119}Sn). Chemical shifts are reported in δ values in ppm relative to external TMS (^{1}H, $BF_3 \cdot Et_2O$ (^{11}B), 85% aqueous H_3PO_4 (^{31}P), or $SnMe_4$ (^{119}Sn)) using the chemical shift of the solvent ^{2}H resonance frequency. Elemental analyses were performed by the Institut für Anorganische Chemie Universität Tübingen using a Vario EL analyzer.

The starting material $[IrCl(CO)(PPh_3)_2]$ was synthesized according to the literature procedure.[29] $[Me_4N]_2[SnB_{11}H_{11}]$, $[Bu_3NMe]_2[SnB_{11}H_{11}]$, $[Et_3NMe]_2[SnB_{11}H_{11}]$, and $[Et_4N]_2[SnB_{11}H_{11}]$ were synthesized using a modified protocol of the original work of the group of Todd.[30]

Crystallography. X-ray data for compounds **2**−**6** were collected on a Stoe IPDS 2T diffractometer and were corrected for Lorentz and polarization effects and absorption by air. The programs used in this work are Stoe's X-Area[31] and the WinGX suite of programs[32] including SHELXS[33] and SHELXL[34] for structure solution and refinement. Numerical absorption correction based on crystal-shape optimization was applied for **2**, **5**, and **6** with Stoe's X-Red and X-Shape.[35,36]

Synthesis of $[Me_4N]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ (2). To a solution of 39 mg (0.05 mmol) of $[IrCl(CO)(PPh_3)_2]$ in 10 mL of

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Table 1. Crystal Data and Structure Refinement Parameters for 2−6

	2·Et$_2$O·3CH$_3$CN	**3**	**4·2CH$_3$CN**	**5**	**6·2CH$_3$CN**
empirical formula	$C_{59}H_{107}B_{22}IrN_6O_2P_2Sn_2$	$C_{46}H_{61}B_{11}IrNO_2P_2Sn$	$C_{47}H_{59}B_{11}IrN_3OP_2Sn$	$C_{44}H_{59}B_{11}IrNOP_2Sn$	$C_{55}H_{94}B_{22}IrN_4OP_2Sn_2$
fw [g/mol]	1661.85	1151.70	1173.71	1109.66	1556.68
wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
temperature [K]	173	173	173	173	173
θ range [deg]	5.67−26.37	5.68−25.68	5.68−25.35	5.68−25.35	5.68−25.35
cryst syst	triclinic	monoclinic	triclinic	monoclinic	orthorhombic
space group	$P\bar{1}$	$P2_1$	$P1$	$P2_1/c$	$Pbca$
Z	2	2	4	4	8
a [Å]	13.2855(11)	12.381(5)	14.1852(11)	20.380(5)	18.7819(11)
b [Å]	14.8771(11)	14.880(3)	17.6952(12)	18.465(7)	21.2139(11)
c [Å]	22.0379(16)	13.831(4)	23.3093(17)	13.154(3)	35.3915(16)
α [deg]	84.917(6)	90.00	108.571(5)	90.00	90.00
β [deg]	79.096(6)	98.11(3)	96.613(6)	97.689(19)	90.00
γ [deg]	68.619(6)	90.00	101.763(6)	90.00	90.00
volume [Å^3]	3981.9(5)	2522.8(14)	5326.5(7)	4906(2)	14101.3(13)
ρ_{calc} [g/cm^3]	1.386	1.516	1.464	1.502	1.466
μ [mm^{-1}]	2.371	3.231	3.062	3.318	2.671
no. of reflns collected	32 006	30 351	30 075	38 893	66 749
no. of indep reflns	16 027 ($R_{int} = 0.0596$)	9441 ($R_{int} = 0.0590$)	26 414 ($R_{int} = 0.0784$)	8856 ($R_{int} = 0.1850$)	12 335 ($R_{int} = 0.1188$)
no. of params/restraints	850/0	577/1	2249/1813	525/490	786/0
absorb corr	none	numerical	none	numerical	numerical
min. and max. transmn		0.3800 and 0.6565		0.6079 and 0.7241	0.5582 and 0.8068
final R indices [$I > 2\sigma$]	$R_1 = 0.0542$, $wR_2 = 0.1232$	$R_1 = 0.0296$, $wR_2 = 0.0570$	$R_1 = 0.0610$, $wR_2 = 0.1122$	$R_1 = 0.1046$, $wR_2 = 0.1645$	$R_1 = 0.0677$, $wR_2 = 0.0987$
R indices all data	$R_1 = 0.0739$, $wR_2 = 0.1330$	$R_1 = 0.0338$, $wR_2 = 0.0559$	$R_1 = 0.0812$, $wR_2 = 0.1251$	$R_1 = 0.1531$, $wR_2 = 0.1796$	$R_1 = 0.1144$, $wR_2 = 0.1107$
GooF on F^2 (all/obsd data)	1.078/1.078	1.083/1.083	1.117/1.082	1.237/1.204	1.135/1.135
largest diff peak and hole	2.486 and −1.737	0.841 and −1.044	1.314 and −1.049	2.040 and −2.363	0.836 and −1.381

acetonitrile was added 40 mg (0.1 mmol) of $[Me_4N]_2[SnB_{11}H_{11}]$. Slow diffusion of Et_2O into the yellow solution resulted in the formation of 67 mg (92% yield) of large yellow crystals of **2**. IR (ATR): 2472 (BH), 1972 cm^{-1} (CO). ^{1}H NMR (CD_3CN): 7.49−6.96 (30H, P*Ph*$_3$), 2.93 (36H, *Me*$_4$N). ^{11}B{^{1}H} NMR (CD_3CN): −15.2. ^{13}C{^{1}H} NMR (CD_3CN): 185.1 (CO), 134.6, 128.6, 126.9 (P*Ph*$_3$), 54.9 (*Me*$_4$N). ^{31}P{^{1}H} NMR (CD_3CN): 8.6 [$^2J(^{119/117}Sn-^{31}P)$ = 97 Hz]. ^{119}Sn{^{1}H} NMR (CD_3CN): −492. Anal. Calcd (%) for $C_{49}H_{88}B_{22}IrN_3OP_2Sn_2$: C, 40.18; H, 6.06; N, 2.87. Found: C, 39.92; H, 6.19; N, 3.24.

Alternative Synthesis of ([Bu$_3$NMe]$_3$[2]). $[IrCl(CO)(PPh_3)_2]$ (150 mg, 0.19 mmol) dissolved in 30 mL of CH_2Cl_2 was treated with 250 mg (0.38 mmol) of $[Bu_3NMe]_2[SnB_{11}H_{11}]$ at RT. After stirring for 30 min the dichloromethane phase was washed several times with 30 mL of water. Evaporation of all volatiles under vacuum gave $[Bu_3NMe]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ in almost quantitative yield.

Synthesis of [Et$_4$N][Ir(SnB$_{11}$H$_{11}$)(CO)$_2$(PPh$_3$)$_2$] (3). To a solution of 39 mg (0.05 mmol) of $[IrCl(CO)(PPh_3)_2]$ in 10 mL of acetonitrile was added 51 mg (0.1 mmol) of $[Et_4N]_2[SnB_{11}H_{11}]$. The resulting solution of $[Et_4N]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ was freeze-pumped and gaseous CO was added. After coming to RT and stirring for 10 min, the solution was layered with Et_2O to yield 43 mg (76% yield) of **3** as light yellow needles. IR (ATR): 2467 (BH), 1955 cm^{-1} (CO). ^{1}H NMR (CD_3CN): 7.73−7.23 (30H, P*Ph*$_3$), 2.96 (8H, *Et*$_4$N), 0.96 (12H, *Et*$_4$N). ^{11}B{^{1}H} NMR (CD_3CN): −14.7. ^{13}C{^{1}H} NMR (CD_3CN): 184.2 (CO, $^2J(^{31}P-^{13}C)$ = 13.6 Hz), 133.6, 130.9, 128.2 (P*Ph*$_3$), 51.8 (*Et*$_4$N), 6.5 (*Et*$_4$N). ^{31}P{^{1}H} NMR (CD_3CN): 3.7 [$^2J(^{119/117}Sn-^{31}P)$ = 160 Hz]. ^{119}Sn{^{1}H} NMR (CD_3CN): −500. Anal. Calcd (%) for $C_{46}H_{61}B_{11}IrNO_2P_2Sn$: C, 47.97; H, 5.34; N, 1.22. Found: C, 47.77; H, 5.73; N, 1.30.

Synthesis of [Me$_4$N][Ir(SnB$_{11}$H$_{11}$)(CO)(C$_2$H$_4$)(PPh$_3$)$_2$] (4). To a solution of 39 mg (0.05 mmol) of $[IrCl(CO)(PPh_3)_2]$ in 10 mL of acetonitrile was added 40 mg (0.1 mmol) of $[Me_4N]_2[SnB_{11}H_{11}]$. The resulting solution of $[Me_4N]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ was freeze-pumped and gaseous ethylene was added. After coming to RT and stirring for 10 min, the solution was layered with Et_2O to yield 40 mg (70% yield) of **4** as light yellow needles. IR (ATR): 2480 (BH), 1942 cm^{-1} (CO). ^{1}H NMR (CD_3CN): 0.35, 1.74 (C_2H_4). ^{13}C{^{1}H} NMR (CD_3CN): 21.2, 27.6 (C_2H_4). ^{11}B{^{1}H} NMR (CD_3CN): −14.9. ^{31}P{^{1}H} NMR (CD_3CN): 7.4 [$^2J(^{119/117}Sn-^{31}P)$ = 180 Hz]. ^{119}Sn{^{1}H} NMR (CD_3CN): −530. Anal. Calcd (%) for $C_{43}H_{57}B_{11}IrNOP_2Sn$: C, 47.14; H, 5.24; N, 1.28. Found: C, 47.49; H, 5.21; N, 1.21.

Synthesis of [Et$_3$NMe][IrH$_2$(SnB$_{11}$H$_{11}$)(CO)(PPh$_3$)$_2$] (5). To a solution of 39 mg (0.05 mmol) of $[IrCl(CO)(PPh_3)_2]$ in 10 mL of acetonitrile was added 48 mg (0.1 mmol) of $[Et_3NMe]_2[SnB_{11}H_{11}]$. The solution of $[Et_3NMe]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$ was freeze-pumped and gaseous hydrogen was added. After coming to RT and stirring for 10 min, the solution was layered with Et_2O to yield 36 mg (65% yield) of **5** as colorless crystals. IR (ATR): 2475 (BH), 2166 (IrH), 2100 (IrH), 1980 cm^{-1} (CO). ^{1}H NMR (CD_3CN): −9.9 ($^2J(^1H-^1H)$ = 4 Hz, $^2J(^{31}P-^1H)$ = 17 Hz, *cis*-$^2J(^{119/117}Sn-^1H)$ = 87 Hz), −11.1 [$^2J(^1H-^1H)$ = 4 Hz, $^2J(^{31}P-^1H)$ = 17 Hz, *trans*-$^2J(^{119/117}Sn-^1H)$ = 668 Hz]. ^{11}B{^{1}H} NMR (CD_3CN): −15.1. ^{31}P{^{1}H} NMR (CD_3CN): 7.8 [$^2J(^{119/117}Sn-^{31}P)$ = 154 Hz]. ^{119}Sn{^{1}H} NMR (CD_3CN): −531. Anal. Calcd (%) for $C_{44}H_{61}B_{11}IrNOP_2Sn$: C, 47.54; H, 5.53; N, 1.26. Found: C, 46.98; H, 5.90; N, 1.23.

Synthesis of [Et$_3$NMe]$_2$[IrH(SnB$_{11}$H$_{11}$)$_2$(CO)(PPh$_3$)$_2$] (6). To a solution of 39 mg (0.05 mmol) of $[IrCl(CO)(PPh_3)_2]$ in 10 mL of acetonitrile was added 48 mg (0.1 mmol) of $[Et_3NMe]_2[SnB_{11}H_{11}]$. Etheric HCl was added to the resulting solution of $[Et_3NMe]_3[Ir(SnB_{11}H_{11})_2(CO)(PPh_3)_2]$. After stirring for 10 min, the solution was layered with Et_2O to yield 50 mg (68% yield) of **6** as light yellow crystals. IR (ATR): 2470 (BH), 2250 (IrH), 2053

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cm^{-1} (CO). ^{1}H NMR (CD$_3$CN): −9.7 [$^2J(^{31}P-^1H) = 13$ Hz, *cis*-$^2J(^{119/117}Sn-^1H) = 94$ Hz, *trans*-$^2J(^{119/117}Sn-^1H) = 632$ Hz]. ^{11}B{^{1}H} NMR (CD$_3$CN): −14.8 (11B), −15.6 (11B). ^{31}P{^{1}H} NMR (CD$_3$CN): −5.8 [$^2J(^{119/117}Sn-^{31}P) = 130$ Hz, $^2J(^{119/117}Sn-^{31}P) = 234$ Hz]. ^{119}Sn{^{1}H} NMR (CD$_3$CN): −502. Anal. Calcd (%) for $C_{51}H_{89}B_{22}IrN_2OP_2Sn_2$: C, 41.51; H, 6.08; N, 1.90. Found: C, 41.54; H, 6.53; N, 1.92.

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