Cationic Iridium Phosphines Partnered with [*closo*-$CB_{11}H_6Br_6$]$^-$: $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$) and [$(PPh_3)_2Ir(\eta^2$-$C_2H_4)_3$][*closo*-$CB_{11}H_6Br_6$]. Relevance to Counterion Effects in Olefin Hydrogenation

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Treatment of [$(PPh_3)_2Ir(COD)$][*closo*-$CB_{11}H_6Br_6$] with H_2 in CH_2Cl_2 solution affords crystallographically characterized $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$), in which the weakly coordinating carborane anion is bound to the metal center. In solution the anion rapidly dissociates/recombines with the metal center, and this process can be frozen out at −50 °C. At lower temperatures (−80 °C) a solvent-stabilized complex [$(PPh_3)_2Ir(H)_2(CH_2Cl_2)$][*closo*-$CB_{11}H_6Br_6$] is suggested to also be present. $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$) reacts with ethene to give the tris-ethene complex [$(PPh_3)_2Ir(\eta^2$-$C_2H_4)_3$][*closo*-$CB_{11}H_6Br_6$]. Subsequent addition of hydrogen returns $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$). This cycle can be repeated a number of times without apparent decomposition, with the anion acting in a "catch and release" manner, stabilizing the metal center when needed. This stabilization is also apparent for the hydrogenation of cyclohexene with $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$) as a catalyst. The complex may be reused up to five times, without decomposition to di- and trimeric iridium hydride species. This is in contrast to other reported iridium hydrogenation systems with other weakly coordinating anions that, on consumption of olefin, decompose to inactive complexes. The new complexes reported here represent intermediates in the catalytic cycle of olefin hydrogenation by cationic group 9 catalysts.

Introduction

The iridium complexes [$L_2Ir(COD)$][anion] (L = phosphine or nitrogen donor, COD = cyclooctadiene) are an important class of organometallic compound. When L_2 = pyridine/PCy_3 an effective catalyst for the hydrogenation of hindered olefins results (anion = $[PF_6]^-$, Crabtree's catalyst),[1] which can be further modified by introducing a chiral ligand (L_2 = phosphine oxazolines, PHOX) to afford catalysts that display impressive enantioselectivities in the hydrogenation of tetrasubstituted olefins. In this latter case a distinct counterion effect is observed, with the $[BAr_F]^-$ anion significantly out performing $[PF_6]^-$ [BAr_F = $B\{C_6H_3(CF_3)_2\}_4$].[2] We have also recently reported a substantial counterion effect in cationic rhodium Shrock−Osborn hydrogenation systems [$(PPh_3)_2Rh(NBD)$][anion] (NBD = norbornadiene).[3] Here, use of the "weakly coordinating" carborane anion [*closo*-$CB_{11}H_6Br_6$]$^-$, developed by Reed,[4] results in a catalyst that significantly out performs $[BF_4]^-$ in the room temperature and pressure hydrogenation of internal alkenes (cyclohexenes) and will also hydrogenate tetrasubstituted alkenes, which is unusual for a Rh catalyst. Enhanced hydrogenation activity for the reduction of 1-octene with cationic rhodium complexes partnered with highly fluorous weakly coordinating tetraphenylborate anions has also recently been reported.[5] The precise factors that control the enhanced activity observed with certain counterions in iridium and rhodium hydrogenation systems currently remain unresolved, but no doubt they involve a combination of the low coordinating character of the anion (vacant site availability) coupled with catalyst longevity (anion stability verses anion-promoted catalyst decomposition). Very recent work by Pfaltz and Pregosin on cationic iridium PHOX precatalyst and trinuclear bridging hydride decomposition product ion pairs, using NMR diffusion techniques, has afforded valuable data on their structures in solution.[6,7] However, spectroscopic and structural data on model systems for the catalytically active species containing a weakly coordinating anion are scarce.[8] We report here a cationic iridium complex

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partnered with [*closo*-$CB_{11}H_6Br_6$]$^-$ that represents such a model along with some preliminary reactivity studies with olefins and comment on the role of this anion in stabilizing the catalyst.

Experimental Section

General. All manipulations were carried out under an atmosphere of argon, using standard Schlenk-line and glovebox techniques, unless otherwise stated.[9] Glassware was predried in an oven at 130 °C and flamed with a blowtorch under vacuum prior to use. CH_2Cl_2, CH_3CN, and pentane were distilled from CaH_2. Toluene, diethyl ether, THF, and hexane were distilled from sodium-benzophenone-ketyl. Fluorobenzene was stirred over P_2O_5 for 24 h and then vacuum distilled. C_6D_6 and d_8-toluene were dried over a potassium mirror; CD_2Cl_2 was distilled under vacuum from CaH_2. $[(COD)IrCl]_2$,[10] Ag[*closo*-$CB_{11}H_6Br_6$],[11] and K[BAr_F][12] were prepared by the published literature routes. All other chemicals were used as received from Aldrich or Strem. Microanalyses were performed by Mr. Alan Carver (University of Bath Microanalytical Service).

NMR Spectroscopy. ^{1}H, ^{1}H{^{11}B}, ^{11}B{^{1}H}, ^{11}B, and ^{31}P{^{1}H} NMR spectra were recorded on Brüker Avance 300-MHz or Varian Mercury 400-MHz spectrometers. Residual protio solvent was used as reference for ^{1}H and ^{1}H{^{11}B} NMR spectra (CD_2Cl_2, δ 5.30; C_7D_8, δ 2.10; $CDCl_3$, δ 7.20). ^{11}B, ^{11}B{^{1}H}, and ^{31}P{^{1}H} spectra were referenced against BF_3·OEt_2 (external) and 85% H_3PO_4 (external), respectively. Values are quoted in ppm. Coupling constants are quoted in Hz.

[(Ph_3P)$_2$Ir(COD)][*closo*-$CB_{11}H_6Br_6$]·CH_2Cl_2. $[(COD)IrCl]_2$ (200 mg, 0.297 mmol) was placed in a glass vial and suspended in 1 cm^3 of ethanol. To this suspension was added PPh_3 (312 mg, 1.19 mmol) dissolved in 3 cm^3 of ethanol dropwise with stirring. After 10 min a homogeneous red solution was obtained. Upon addition of Ag[*closo*-$CB_{11}H_6Br_6$] (431 mg, 0.595 mmol) in 3 cm^3 of ethanol a precipitate was observed. The solvent was removed under reduced pressure and the residue redissolved in 4 cm^3 of CH_2Cl_2. AgCl was removed via filtration and the product crystallized by addition of 1 cm^3 of ethanol followed by cooling at −30 °C overnight to afford 670 mg (0.43 mmol, 74%) of [(Ph_3P)$_2$Ir(COD)][*closo*-$CB_{11}H_6Br_6$] as fine red needles.

^{1}H (δ/ppm, $CDCl_3$): 7.30 (m, 30H, C_6H_5), 4.16 (s, 4H, C_8H_{12}), 2.50 (s, 1H, C*H*$_{cage}$), 2.22 (m, 4H, C_8H_{12}), 1.95 (m, 4H, C_8H_{12}). ^{31}P (δ/ppm, $CDCl_3$): 18.8 (s). ^{11}B{^{1}H} (δ/ppm, $CDCl_3$): −1.9 (s, 1B), −10.1 (s, 5B), −20.4 (s, 5B). ^{11}B (δ/ppm, CD_2Cl_2): −1.9 (br s, 1B), −10.1 (br s, 5B), −20.4 [d, J(BH) = 166 Hz]. Calcd for $C_{46}H_{50}B_{11}Br_6Cl_2IrP_2$: C, 36.2; H, 3.30. Found: C, 35.8, H, 3.21.

(Ph_3P)$_2$Ir(H_2)(*closo*-$CB_{11}H_6Br_6$)·2C_6H_5F (2). [(Ph_3P)$_2$Ir(C_8H_{12})][*closo*-$CB_{11}H_6Br_6$] (50 mg, 0.032 mmol) was placed in a 50-cm^3 Schlenk tube and dissolved in 5 cm^3 of CH_2Cl_2. The red solution was thoroughly freeze−pump−thawed and allowed to warm to room temperature under 1 atm of H_2 and with stirring. The resulting colorless solution takes on a pale yellow/green color over 10 min. Removal of the solvent in vacuo afforded a cream solid. A sample was crystallized via dissolution in 5 cm^3 of C_6H_5F and layered with 5 cm^3 of pentane to give 35 mg (0.024 mmol, 75%) of (Ph_3P)$_2$Ir(H_2)(*closo*-$CB_{11}H_6Br_6$) as cream blocks. Two molecules of C_6H_5F are found in the unit cell by X-ray diffraction.

^{1}H (δ/ppm, 22 °C, $CDCl_3$): 7.30 (m, 30H, C_6H_5), 2.55 (br s, 1H, CH), 2.01 (v br, 5H, BH), −25.7 [t, 2H, Ir−H, J(PH) = 18 Hz]. ^{1}H{^{11}B} (δ/ppm, 22 °C, $CDCl_3$): 7.30 (m, 30H, C_6H_5), 2.55 (br s, 1H, CH), 2.01 (s, 5H, BH), −25.7 [t, 2H, Ir−H, J(PH) = 18 Hz]. ^{11}B{^{1}H} (δ/ppm, 22 °C, $CDCl_3$): −0.7 (s, 1B), −9.8 (s, 5B), −21.9 (br s, 5B). ^{11}B (δ/ppm, 22 °C, $CDCl_3$): −0.8 (s, 1B), −9.8 (s, 5B), −21.9 (br s, 5B). ^{31}P{^{1}H} (δ/ppm, 22 °C, $CDCl_3$): 16.4 (br s). ^{31}P (δ/ppm, −80 °C, CD_2Cl_2): 26.0 (s)*, 21.1 [second-order d, 1P part of an AB system, J(PP) = 338 Hz], 17.1 [second-order d, 1P part of an AB system, J(PP) = 338 Hz]. Selected δ ^{1}H (δ/ppm, −80 °C, CD_2Cl_2): −23.2 [t, 2H, J(PH) = 14 Hz]*, −25.5 [t, 2H, J(PH) = 18 Hz]. Selected δ ^{1}H (δ/ppm, −80 °C, d_8-toluene): −25.1 [t, J(PH) = 18 Hz]. ^{31}P (δ/ppm, −80 °C, d_8-toluene): 21.1 [second-order d, 1P part of an AB system, J(PP) = 341 Hz], 17.8 [second-order d, 1P part of an AB system, J(PP) = 341 Hz]. Calcd for $C_{49}H_{48}B_{11}Br_6F_2IrP_2$: C, 38.54; H, 3.14. Found: C, 38.7; H 3.27. (Values with an asterisk next to them indicate peaks assigned to [(PPh_3)$_2$(H)$_2$Ir(CH_2Cl_2)][*closo*-$CB_{11}H_6Br_6$] **3** in 20% abundance at this temperature.)

[(Ph_3P)$_2$Ir(η^2-C_2H_4)$_3$][*closo*-$CB_{11}H_6Br_6$] (5). (Ph_3P)$_2$Ir(H_2)(*closo*-$CB_{11}H_6Br_6$) (25 mg, 0.019 mmol) was dissolved in 5 cm^3 of CH_2Cl_2 in a 50-cm^3 Schlenk tube. The solution was freeze−pump−thawed three times. The solution was then allowed to warm to room temperature under C_2H_4 with stirring. After 0.5 h the solvent was removed in vacuo to leave a sticky residue that was not pumped down for a prolonged period of time. Dissolution of this residue in $CDCl_3$ results in a pale yellow solution of [(Ph_3P)$_2$Ir(η^2-C_2H_4)$_3$][*closo*-$CB_{11}H_6Br_6$]. Large colorless prisms (24 mg, 0.017 mmol, 90%) of [(Ph_3P)$_2$Ir(η^2-C_2H_4)$_3$][*closo*-$CB_{11}H_6Br_6$] resulted upon standing of a $CDCl_3$ solution.

^{1}H (δ/ppm, 22 °C, CD_2Cl_2, under a partial atmosphere of ethene): 7.30 (m, 30H, C_6H_5), 5.00 (br s, free C_2H_4), 3.21 (br s, metal-bound C_2H_4), 2.55 (br s, 1H, CH), 2.01 (br q, 6H, BH). ^{31}P{^{1}H} (δ/ppm, 22 °C, CD_2Cl_2): 0.0 (br s). ^{11}B (δ/ppm, 22 °C, CD_2Cl_2): −1.9 (br s, 1B), −10.1 (br s, 5B), −20.4 [d, J(BH) = 166 Hz]. Selected ^{1}H (δ/ppm, −25 °C, CD_2Cl_2): 3.09 (s, 8H, C_2H_4), 2.55 (br s, 1H, CH). ^{31}P{^{1}H} (δ/ppm, −25 °C, CD_2Cl_2): −0.7 (s). Calcd for $C_{43}H_{48}B_{11}Br_6IrP_2$: C, 36.44; H, 3.41. Found: 35.9; H, 3.23.

[(Ph_3P)$_2$Ir(η^2-C_2H_4)$_2$][*closo*-$CB_{11}H_6Br_6$] (6). [(Ph_3P)$_2$Ir(η^2-C_2H_4)$_3$][*closo*-$CB_{11}H_6Br_6$] dissolved in CH_2Cl_2 was reduced to dryness in vacuo, during which time a color change from pale yellow to red was observed. Despite repeated attempts, efforts to isolate **6** in pure form in the solid state were unsuccessful, although spectroscopic data fit that previously reported for the [BF_4] salt.[8]

^{1}H{^{11}B} (δ/ppm, $CDCl_3$): 7.30 (m, 30H C_6H_5), 3.20 (s, 8H, C_2H_4), 2.55 (s, C*H*), 2.52 (br, 6H). ^{31}P{^{1}H} (δ/ppm, CD_2Cl_2): 16.1 (br s). ^{11}B (δ/ppm, CD_2Cl_2): −1.9 (br s, 1B), −10.1 (br s, 5B), −20.4 [d, J(BH) = 166 Hz].

[(Ph_3P)$_2$Ir(COD)][B{C_6H_3(CF_3)$_2$}$_4$] (7). A Schlenk tube equipped with a reflux jacket was loaded with $[(COD)IrCl]_2$ (0.100 g, 0.15 mmol), PPh_3 (0.156 g, 0.6 mmol), and 10 cm^3 of CH_2Cl_2 and heated to reflux for 1 h to give an orange solution. $KBAr_F$ (0.400 g, 0.45 mmol) was added in one portion resulting in an immediate color change to red. The solution was stirred for a further 15 min and then washed three times with 10-cm^3 portions of H_2O. The combined H_2O portions were further extracted with 3 × 10 cm^3 aliquots of CH_2Cl_2. The combined CH_2Cl_2 solution were dried in vacuo and the remaining red crystalline solid washed three times with cold ethanol, before drying in vacuo. Isolated yield: 0.328 g (65%, 2.00 mmol) of [(Ph_3P)$_2$Ir(COD)][BAr_F].

^{1}H (δ/ppm, CD_2Cl_2): 7.78−7.14 (30H Ph m), 4.08 (4H, s, COD), 2.16 (4H br m, COD), 1.89 (4H br m COD). ^{31}P{^{1}H} (δ/ppm, CD_2Cl_2): 18.8. Calcd for $H_{54}C_{76}BF_{24}IrP_2$: C, 54.1; H, 3.22. Found 54.3; H, 3.40.

X-ray Crystallography. The crystal structure data for compounds **2** and **5** were collected on a Nonius KappaCCD

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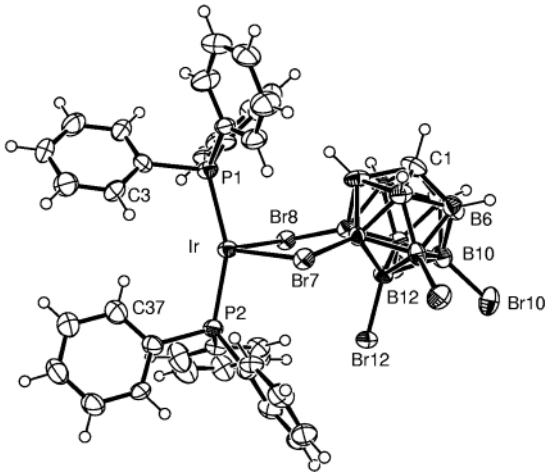

Figure 1. ORTEP plot of complex **2**. Thermal ellipsoids are shown at the 50% probability level. The two hydride ligands on the Ir center were not located. Selected bond lengths (Å) and angles (deg): Ir−P1 2.322(2), Ir−P2 2.335(2), Ir−Br7 2.680(1), Ir−Br8 2.655(1), P1−Ir−P2 155.33, Br7−Ir−Br8 87.20. The single solvent molecule (C_6H_5F) in the asymmetric unit is not shown.

diffractometer (Bath and Kings College). Structure solution, followed by full-matrix least-squares refinement was performed, using the SHELX suite of programs throughout.[13] Crystallographic data files have been deposited with the Cambridge Crystallographic Data Service.

Cyclohexene Hydrogenations. $(Ph_3P)_2Ir(H_2)$(*closo*-$CB_{11}H_6Br_6$) [0.015 g, 0.011 mmol] was weighed out in a glovebox into a 20-cm^3 vial fitted with a new septum and a stirrer bar and dissolved in CH_2Cl_2 (5 cm^3). Cyclohexene [0.100 cm^3, 1.10 mmol] was added to give a catalyst-to-substrate ratio of 1:100 and the vial pressuerized with H_2 (pressure 10 psi above room), via a needle. The H_2 needle was then removed and the reaction stirred for 30 min. GC analysis showed that all the cyclohexene had been converted to cyclohexane (i.e. no cyclohexene was observed in the GC trace). An additional aliquot of cyclohexene [0.100 cm^3] was added and the vial repressurized with H_2. GC analysis after 30 min showed only cyclohexane was present. This was repeated an additional three times (a total of 5 cycles) with complete conversion observed after 30 min each time.

Results and Discussion

Treatment of $[(PPh_3)_2Ir(COD)]$[*closo*-$CB_{11}H_6Br_6$] (**1**) with H_2 (1 atm) in CH_2Cl_2 solution cleanly affords the new complex $(PPh_3)_2Ir(H)_2$(*closo*-$CB_{11}H_6Br_6$) (**2**) in essentially quantitative yield (by NMR spectroscopy). In the solid state (Figure 1, Table 1) complex **2** exists as a closely associated ion pair, with the anion coordinated with the $\{P_2IrH_2\}^+$ fragment through two lower pentagonal belt bromine atoms. This results in the favored octahedral, 18-electron, configuration for an Ir(III) center. The structure of **2** is similar to the di-iodobenzene complex $[(PPh_3)_2Ir(H)_2(I_2C_6H_4)][PF_6]$,[14] while the coordination mode of carborane anion mimics recently reported Et_2Al(*closo*-$CB_{11}H_6Br_6$).[15] The phosphine ligands in **2** are not rigorously trans orientated, being pushed together slightly to accommodate the bulky carborane anion. While the hydride ligands were not located in the difference map they clearly must lie cis to one another and mutually trans to the bromine atoms.

The orientation of the anion results in the two phosphine ligands being inequivalent in the solid state. However, in CH_2Cl_2 solution at room temperature, only one phosphine environment is observed in the $^{31}P\{^1H\}$ NMR spectrum (singlet δ 16.4). This indicates that a fluxional process must be occurring to equivalence the PPh_3 ligands on the NMR time scale (Scheme 1). That the hydride ligands are clearly observed in the ^1H NMR spectrum as a triplet at δ −25.7 [J(PH) = 18 Hz] shows that this process cannot involve phosphine dissociation, and more probably involves loss of the anion. This is arrested at −50 °C as shown by a $^{31}P\{^1H\}$ NMR spectrum that now displays two phosphine environments as a tightly coupled set of AB doublets with a large J(PP) coupling constant [δ 21.1, 17.1, J(PP) = 338 Hz], as expected for inequivalent trans phosphine ligands. $\Delta G^{\ddagger}$ for this process has been calculated as 30.8 kJ mol^{-1}. Anion dissociation at room temperature could proceed via a solvent-separated ion pair such as $[(PPh_3)_2Ir(H)_2(CH_2Cl_2)]$[*closo*-$CB_{11}H_6Br_6$]. Consistent with this, rapid anion exchange occurs on addition of $[NBu_4]$[*closo*-$CB_{11}H_6Br_6$] to **2**, as shown by only one cage C−H resonance in the ^1H NMR spectrum being observed. In addition, further cooling of **2** to −80 °C results in the appearance of a new singlet at δ 26.0 in the $^{31}P\{^1H\}$ NMR spectrum and a new triplet hydride resonance in the ^1H NMR spectrum at δ −23.2, both in approximately 20% total intensity. These peaks are absent when the solvent is changed to d_8-toluene and the sample cooled to −80 °C, suggesting assignment as a dichloromethane complex, $[(PPh_3)_2Ir(H)_2(CH_2Cl_2)]$[*closo*-$CB_{11}H_6Br_6$] (**3**) (Scheme 1). Dichloromethane complexes are not without precedent, and structurally characterized examples are known.[16]

In the ^{11}B NMR spectrum, coordination of the anion has the effect of reducing the magnitude of the J(BH) coupling so that BH(2−6) is now observed as a broad singlet rather than a well-defined doublet [e.g. J(HB) = 166 Hz in **1**] (see Supporting Information). The carborane anion in **2** is rapidly displaced by MeCN, resulting in the solvent-separated ion-pair $[(PPh_3)_2Ir(H)_2(MeCN)_2]$[*closo*-$CB_{11}H_6Br_6$] (**4**), which has been previously characterized as the $[BF_4]^-$ salt.[8] Confirmation that the anion is no longer bound with the metal comes from the observation of a doublet [J(HB) = 166 Hz] for the carborane BH(2−6) vertexes in the ^{11}B NMR spectrum. The carborane anion in **2** is also displaced by ethene (excess, 1 atm), although subsequent rapid elimination of ethane presumably occurs, and the resulting 12-electron complex rapidly takes up three extra molecules of olefin to afford pale yellow $[(PPh_3)_2Ir(\eta^2\text{-}C_2H_4)_3]$[*closo*-$CB_{11}H_6Br_6$] (**5**) as the only organometallic product. Characterization was initially by ^1H, $^{31}P\{^1H\}$, and ^{11}B NMR spectroscopy and confirmed by a single-crystal X-ray diffraction study (Figure 2, Table 1).

The solid-state structure of **5** shows that it is an 18-electron, $[IrP_2L_3]^+$ complex, with three ethene and two

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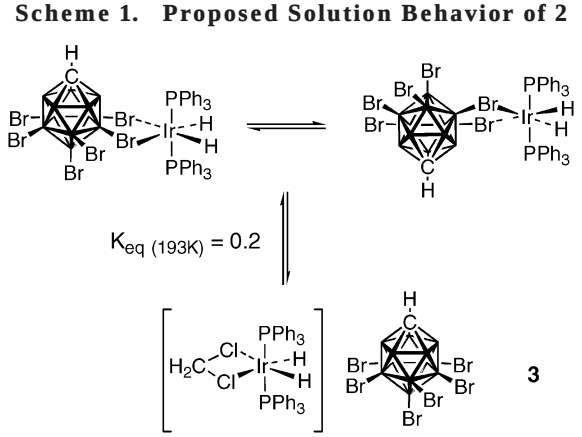
Table 1. Crystal Data and Structure Refinement for Compounds 2 and 5

compd	**2**	**5**
empirical formula	$C_{37}H_{38}B_{11}Br_6IrP_2 \cdot C_6H_5F$	$C_{44}H_{49}B_{11}Br_6IrP_2 \cdot 3CHCl_3$
formula wt	1431.28	1894.80
temp/°C	150(2)	180(2)
wavelength/Å	0.71073	0.71073
cryst syst	monoclinic	triclinic
space group	*C*2/*c*	$P\bar{1}$
a/Å	33.1340(8)	11.4280(2)
b/Å	13.3310(3)	14.4554(3)
c/Å	25.5320(7)	22.7656(6)
α/deg	90	78.7470(10)
β/deg	95.021(1)	88.0570(10)
γ/deg	90	67.0470(10)
V/Å^3	11234.4(5)	3392.75(13)
Z	8	2
density (calcd)/mg/m^3	1.692	1.855
abs coeff/mm^{-1}	6.734	6.054
F(000)	5456	1820
cryst size/mm	0.30 × 0.18 × 0.06	0.40 × 0.30 × 0.20
θ range for data collection/deg	3.42 to 26.04	1.94 to 25.00
no. reflns collected	32601	16211
no. independent reflns	10290 [*R*(int) = 0.0846]	11716 [*R*(int) = 0.1078]
abs correction	semiempirical from equivalents	semiempirical from equivalents
data completeness	92.9	97.9
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	10290/0/586	11716/0/654
goodness-of-fit on F^2	1.027	0.992
final *R* indices [$I > 2\sigma$(I)]	R1 = 0.0586; wR2 = 0.1500	R1 = 0.0651; wR2 = 0.1345
R indices (all data)	R1 = 0.0955; wR2 = 0.1714	R1 = 0.1102; wR2 = 0.1524
largest diff peak and hole/e·Å^{-3}	3.197 and −1.720	2.129 and −3.522

Scheme 1. Proposed Solution Behavior of 2



PPh_3 ligands. As expected from steric and electronic arguments[17] the phosphine ligands lie trans to one another, while the three ethene ligands circle the Ir center, lying perpendicular to the Ir−P axis. The anion is not interacting with the metal center (closest Ir−Br distance 5.250 Å). In solution this is also the case, with BH(2−6) resolved as a clear doublet [*J*(HB) = 166 Hz] in the ^{11}B NMR spectrum. A single peak at *δ* 0.0 is observed in the ^{31}P{^{1}H} NMR spectrum. In the room temperature ^{1}H NMR spectrum the coordinated ethene ligands are observed as a very broad (fwhm ca. 100 Hz) integral 12 H resonance at *δ* 3.21 in the presence of a slight excess of ethene, which itself is also observed as a very broad signal, suggesting exchange between free and bound olefin. This can be arrested by cooling to −25 °C, at which point sharp signals are observed for bound (*δ* 3.09, 12 H) and free (*δ* 5.39) ethene. Placing **5** under a dynamic vacuum overnight results in loss of one ethene molecule to afford red [$(PPh_3)_2Ir(\eta^2\text{-}C_2H_4)_2$][*closo*-$CB_{11}H_6Br_6$] (**6**).[8]

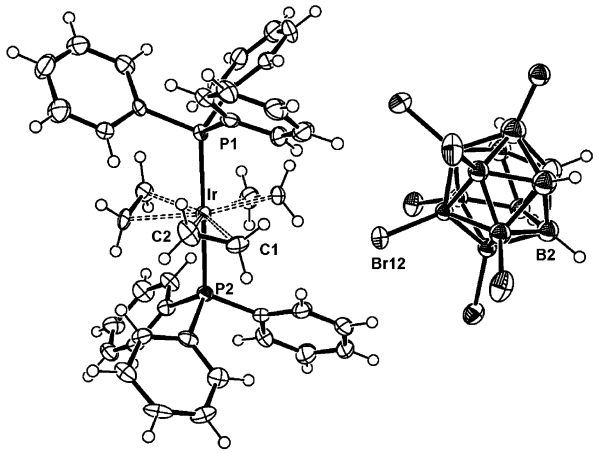


Figure 2. ORTEP plot of complex **5**. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ir−P1 2.379(2), Ir−P2 2.370(2), P1−Ir−P2 177.74(8). The three solvent molecules ($HCCl_3$) in the asymmetric unit are not shown.

In situ spectroscopically characterized analogues of **5** with different anions, such as [$(PPh_3)_2Ir(\eta^2\text{-}C_2H_4)_x$]-[$BF_4$], have been previously reported by Crabtree [*x* = 2][8] and Brown [*x* = 3].[18] In the latter case this complex is unstable, even at −30 °C. This is in contrast with **5**, which is stable in chlorinated solvents for days at room temperature. This again demonstrates the significant stability advantages of using [*closo*-$CB_{11}H_6Br_6$]$^-$ over traditional counterions.[3,4,19] Consistent with this, for the iridium systems [$(PPh_3)_2$Ir(COD)][BF_4][20] or [(PHOX)Ir-(COD)][PF_6],[7] addition of hydrogen in the absence of

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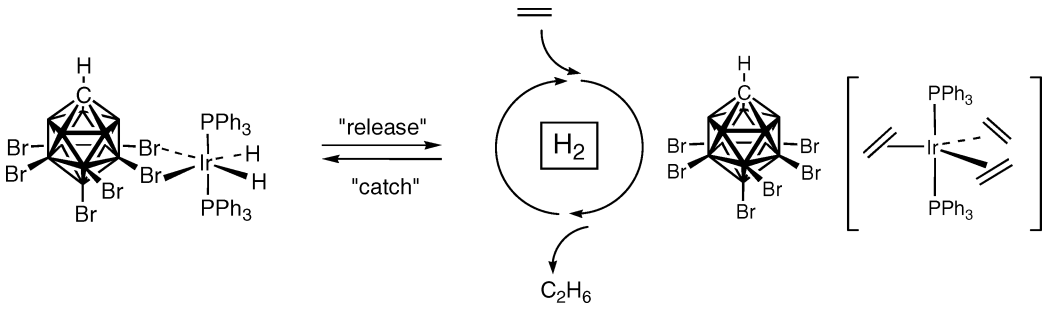
Scheme 2: "Release and Catch" of the [*closo*-$CB_{11}H_6Br_6]^-$ Anion in the Hydrogenation of Ethene



olefin (or when the olefin is completely consumed in the catalytic cycle) affords bi- and trimetallic Ir−hydride decomposition products that are catalytically inactive. The mechanism for decomposition has been suggested to be the combination of reactive 14-electron $\{L_2Ir(H)_2\}^+$ fragments. Similarly, in our hands, addition of H_2 to $[(Ph_3P)_2Ir(COD)][BAr_F]$ (**7**), which contains a weakly coordinating anion but not one that can readily stabilize a coordinatively unsaturated metal center, results in the formation of the bimetallic Ir−hydride decomposition complex $[\{(PPh_3)_2Ir(H)\}_2(\mu\text{-}H)_3][BAr_F]$, as observed by Crabtree for the $[BF_4]^-$ salt.[20] In contrast, for **2** the "weakly coordinating" [*closo*-$CB_{11}H_6Br_6]^-$ anion affords enough stabilization to stop decomposition in the absence of olefin, but still can move away easily to allow the olefin to coordinate to the metal (complex **5**) when needed. Addition of H_2 to complex **5** in CD_2Cl_2 solution rapidly regenerates **2**, completing the hydrogenation cycle. The cycle of ethene addition followed by hydrogenation may be repeated in an NMR tube for a number of cycles without noticeable decomposition.

The role of the weakly coordinating [*closo*-$CB_{11}H_6Br_6]^-$ anion in stabilizing the catalyst to decomposition is further demonstrated by the catalytic hydrogenation of a more relevant substrate: cyclohexene. For this internal olefin, **2** effects complete reduction after 30 min (ca. 1 atm of H_2, 1 mol %, GC yield, unoptimized conditions). After all the olefin had been consumed complex **2** was the only organometallic product observed, with other hydrides, that would indicate the formation of decomposition products, not detected in the ^1H NMR spectrum. The hydrogenation cycle may be repeated, with addition of cyclohexene to the used catalyst solution and subsequent hydrogenation having been repeated five times with no apparent loss in catalytic activity. Thus, for this particular system, the [*closo*-$CB_{11}H_6Br_6]^-$ anion *both* acts in a weakly coordinating capacity allowing hydrogenation of the olefin to proceed under mild conditions ("release" Scheme 2) and also has a significant role in stabilizing the catalyst to decomposition once all the substrate has been consumed ("catch" Scheme 2), allowing the catalyst to be reused.

Conclusions

Complexes **2** and **5** represent structurally characterized intermediates in the catalytic cycle of olefin hydrogenation by cationic group 9 complexes. Moreover, complex **2** appears to be *reuseable* in ethene and cyclohexene reductions. This attractive property can be attributed to the weakly coordinating [*closo*-$CB_{11}H_6Br_6]^-$ anion, which allows the metal fragment to act as an effective catalyst but then returns to stabilize it after hydrogenation is complete and all the olefin has been consumed. This is in direct contrast to anions such as $[BAr_F]^-$ and $[BF_4]^-$ that cannot stabilize the metal in the absence of olefin, and inactive hydride-bridged dimers result. Complex **2** is also similar to the 14-electron $\{P_2Ir(H)_2\}^+$ complexes reported by Caulton[21] that are stabilized by agostic C−H interactions rather than the anion. That the anion in **2** can move away to reveal a reactive metal center, but also returns to stabilize the complex when needed, suggests that the chemistry of **2** and related compounds should be of interest, and studies to this end are currently underway.

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Supporting Information Available: ^{11}B NMR spectra for **2** and **5**; full data collection details, bond lengths and angles, and CIF data for **2** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data files have been deposited with the Cambridge Crystallographic Data Service (CCDC, 12 Union Road, Cambridge CB2 1EZ (UK); phone (+44) 1223-336-408; fax (+44) 1223 336 033, e-mail deposit@ccdc.cam.ac.uk).

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