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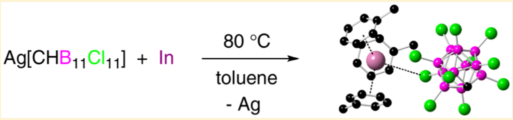
Synthesis and Reactivity of Indium(I) 1-Carba-*closo*-undecachlorododecaborate

Khalid M. Osman,[†] Douglas R. Powell,[‡] and Rudolf J. Wehmschulte*,[†]

[†]Department of Chemistry, Florida Institute of Technology, 150 West University Boulevard, Melbourne, Florida 32901, United States
[‡]Department of Chemistry and Biochemistry, University of Oklahoma, 101 Stephenson Parkway, Norman, Oklahoma 73019-5251, United States

Supporting Information



ABSTRACT: The arene-solvated indium(I) species $[In(C_7H_8)_3][CHB_{11}Cl_{11}]$ (**1**) and $[In(C_6H_5Br)_{1.5}][CHB_{11}Cl_{11}]$ (**2**) were obtained by a redox reaction involving the silver salt $Ag[CHB_{11}Cl_{11}]$ and indium powder at 80 °C in a toluene or bromobenzene solution. These thermally stable compounds react with triphenylphosphine and the N-heterocyclic carbene 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene under reduction of indium(I) to indium metal and oxidation of the ligands to phosphonium and imidazolium cations contrary to the more commonly observed disproportionation reactions. The presence of 2 equiv of carbene led to deprotonation of the anion to give the dianion $[CB_{11}Cl_{11}]^{2-}$. Interactions of In^+ with soft donor ligands such as phosphines, olefins, alkynes, and aromatics are weak, and a crystalline solid was only obtained with the nonvolatile phosphinoacetylene $Mes_2PC{\equiv}CPh$ (Mes = 2,4,6-$Me_3C_6H_2$). The structure of this compound displays In···C interactions involving the triple bond and the π system of one mesityl group but no In···P contact. Solutions of **2** in fluorobenzene also showed moderate activity as the catalyst for intramolecular hydroamination of primary and secondary aminopentenes. The new compounds were characterized by multinuclear NMR spectroscopy and X-ray diffraction for compounds **1**, **2**, and **4**−**6**.

INTRODUCTION

As a fifth period element, indium possesses a relatively stable 1+ oxidation state next to its typical 3+ oxidation state.[1] Although indium(I) halides are stable and commercially available, their use in synthetic chemistry is not widespread because of their insolubility in nonpolar or weakly polar solvents and their tendency to undergo disproportionation reactions in polar solvents.[2,3] Numerous room temperature stable molecular indium(I) compounds have been reported to date,[2,4,5] but they are usually supported by large substituents including Cp* (Me_5C_5),[6] nacnac (β-diketiminate, $[CH(CR{=}NAr)_2]^-$),[7] or Ar* (a bulky aryl substituent such as 2,6-$Dipp_2C_6H_3$, where Dipp = 2,6-$i$$Pr_2C_6H_3$).[8] This changed with the synthesis of indium(I) triflate (InOTf) in 2004[9] and the arene-solvated In^I cations $[In(arene)_{2\text{ or }3}][Al\{OC(CF_3)_3\}_4]$ in 2010[10] and 2012.[11] Both compounds are thermally stable and readily soluble in either toluene (InOTf) or the more polar aromatic solvents fluorobenzene and difluorobenzene. A related compound with isolated In^+ cations, $In[B\{C_6H_3(CF_3)_2\text{-}3,5\}_4]$, was reported in 2008,[12] but the structural and chemical properties were not communicated.

Because of the low oxidation state and the presence of two 5s electrons, In^I centers can act as both weak Lewis acids and bases. Complexes of phosphines,[11] an N-heterocyclic carbene (NHC),[13] amines,[14] and a crown ether[15] with either arene-solvated In^+ ions or InOTf have been observed, and species such as Cp^*In[16] or even In^+[12] have been used as donor ligands in transition-metal complexes. As part of a project to investigate stabilization of low-oxidation-state indium and gallium compounds with ambiphilic ligands, i.e., ligands that possess donor and acceptor centers, we have prepared two new arene-solvated cationic indium(I) species with the undecachlorinated carbadodecaborate counterion $[CHB_{11}Cl_{11}]^-$ and have investigated their coordination behavior toward a variety of substrates. Most notably, reactions with triphenylphosphine and an NHC led to outcomes different from those reported for the related salt $[In(C_6H_5F)_{2,3}][Al\{OC(CF_3)_3\}_4]$.[11,13]

EXPERIMENTAL SECTION

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or a Vacuum Atmospheres drybox. Solvents were freshly distilled under N_2 from sodium, potassium, or calcium hydride and degassed twice prior to use, or they were dispensed from a commercial solvent purification system. The compounds $Ag[CHB_{11}Cl_{11}]$,[17] $PhC{\equiv}CPMes_2$,[18] $B(C_6H_4PPh_2\text{-}2)_3$,[19] and 1,3-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr)[20] were prepared according to literature procedures. All other reagents were obtained from commercial suppliers and used as received. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. ^1H NMR chemical shift values were determined relative to the residual protons in $CDCl_3$, C_6D_6 or C_6D_5Br as the internal reference (δ 7.27, 7.16, or 6.95). ^{13}C NMR spectra were referenced to the solvent signal (C_6D_6, δ 128.39; C_6D_5Br, δ 122.45), ^{11}B NMR spectra to a solution of $F_3B{\cdot}OEt_2$ in C_6D_6 as the external standard (δ 0), and ^{31}P NMR spectra to a solution of Ph_3P in C_6D_6 as the external standard (δ −6).

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[In(C_7H_8)$_3$][$CHB_{11}Cl_{11}$] (1). A Schlenk flask was charged with Ag[$CHB_{11}Cl_{11}$] (0.78 g, 1.20 mmol), indium metal (0.28 g, 2.40 mmol), and toluene (50 mL). The suspension was stirred at 80 °C for 24 h. Upon cooling to room temperature, light-brown needle-shaped crystals formed. The crystals were isolated and dried under vacuum. Yield: 0.73 g, 64%. ^{1}H NMR (400.13 MHz, C_6D_5Br): δ 7.13 (t, J = 7.3 Hz, *m*-H(tol), 2H), 7.06 (d, J = 7.2 Hz, *p*-H(tol), 1H), 7.01 (d, partially obscured by C_6D_5Br, *o*-H(tol), 2H), 2.75 (s, $CHB_{11}Cl_{11}$, 1H), 2.16 (s, CH_3(tol), 3H). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_5Br): δ 138.11 (*i*-*C*), 129.51 (*o*-*C*), 128.67 (*m*-*C*), 125.89 (*p*-*C*), 47.98 (br, $CHB_{11}Cl_{11}$), 21.61 (*o*-CH_3). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −2.1 (s, 1B), −9.4 (s, 5B), −12.2 (s, 5B). Crystals of **1** slowly lose toluene upon storage under inert conditions. This is why this sample only has one toluene per indium (see also Figure S1).

[In(C_6H_5Br)$_{1.5}$][$CHB_{11}Cl_{11}$] (2). A small grease-free Schlenk flask equipped with a Teflon valve was charged with Ag[$CHB_{11}Cl_{11}$] (0.19 g, 0.30 mmol), indium powder (0.07 g, 0.60 mmol), and bromobenzene (ca. 3 mL). The suspension was stirred at 80 °C for 24 h, and a few crystals were formed after cooling to room temperature. The crystals were dissolved with brief heating with a heat gun. The brownish supernatant liquid was filtered through a medium-porosity frit and concentrated to ca. 0.5 mL under vacuum, and subsequent cooling to −20 °C for 2 days afforded small colorless crystals of **2**. Yield: 0.14 g, 59%. The low yield is due to the small-scale and mechanical losses. ^{1}H NMR (400.13 MHz, C_6D_5Br): δ 7.29, 7.02, 6.94 (C_6H_5Br signals, partially obscured by the solvent), 2.75 (s, $CHB_{11}Cl_{11}$, 1H). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_5Br): δ 131.59 (*o*-*C*),130.13 (*m*-*C*), 126.94 (*p*-*C*), 122.70 (*i*-*C*), 48.12 (br, $CHB_{11}Cl_{11}$). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −2.2 (s, 1B), −9.4 (s, 5B), −12.1 (s, 5B).

Semiquantitative Assessment of the Absence of Silver in Samples of 1 and 2. Late transition metals are known to form well-defined complexes with the tridentate ambiphilic ligand B($C_6H_4PPh_2$-2)$_3$.[21] A complex of AgCl with the related ligand B($C_6H_4PiPr_2$-2)$_3$ has been isolated, and its ^{31}P NMR spectrum shows two characteristic doublets due to Ag−P coupling with both common silver isotopes, ^{107}Ag and ^{109}Ag.[22] Solid B($C_6H_4PPh_2$-2)$_3$ (21 mg, 27 μmol) was added to a solution of Ag[$CHB_{11}Cl_{11}$] in C_6D_5Br (0.4 mL) in an NMR tube inside a glovebox, and after brief shaking of the tube, a clear yellow solution was obtained. ^{1}H NMR (400.13 MHz, C_6D_5Br): δ 7.4−6.8 (m, br, aromatic H), 2.85 (s, CHB_{11}). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −1.8 (s, 1B), −9.2 (s, 5B), −12.3 (s, 5B). ^{31}P{^{1}H} NMR (161.97 MHz, C_6D_5F): δ 14.2 (2d, J(^{109}Ag−P) = 300 Hz, J(^{107}Ag−P) = 345 Hz). The addition of B($C_6H_4PPh_2$-2)$_3$ to solutions of **1** and **2** in fluorobenzene resulted in the immediate precipitation of an as-yet-unidentified orange precipitate, and the ^{31}P NMR spectrum of the mother liquor only showed the signal of the uncomplexed ligand. Thus, a significant contamination of compounds **1** and **2** with silver can be ruled out.

[Ph_3PH][$CHB_{11}Cl_{11}$] (3). A solution of **1** (0.09 g, 0.09 mmol) in fluorobenzene (10 mL) was added to a solution of PPh_3 (0.06 g, 0.23 mmol) in fluorobenzene (10 mL) at room temperature. After the addition, a black precipitate began to form. The supernatant liquid was filtered twice through a medium-porosity glass frit to give a clear solution. The solution was concentrated under reduced pressure to 5−10 mL, and cooling at −20 °C for 14 days afforded small yellow crystals. ^{31}P {^{1}H} NMR (161.97 MHz, C_6D_5F): δ 5.8 (s, br, $w_{1/2}$ ~ 110 Hz, [$HPPh_3$]$^+$), −5.5 (s, br, $w_{1/2}$ ~ 184 Hz, PPh_3), relative intensity ~ 1:0.39. ^{31}P NMR (161.97 MHz, C_6D_5F): δ 5.8 (d, br, $^1J_{PH}$ = 501 Hz). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −1.9 (s, 1B), −9.3 (s, 5B), −12.4 (s, 5B).

[IPr·H][$CHB_{11}Cl_{11}$] (4). To a mixture of IPr (0.01 g, 0.03 mmol) and **2** (0.03 g, 0.03 mmol) in a small grease-free Schlenk flask was added fluorobenzene (2 mL) at room temperature. A small amount of a black precipitate formed immediately. The reaction mixture was briefly heated with a heat gun (ca. 10 s), whereupon more precipitate formed. The mixture was filtered through a medium-porosity sintered-glass frit and cooled at −20 °C for 9 days to afford yellowish crystals of **4**. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 8.37 (s, NC*H*N, 1H), 7.75 (s, =C*H*, 2H), 7.67 (t, J = 7.8 Hz, *p*-H, 2H), 7.43 (d, J = 7.8 Hz, *m*-H, 4H), 3.12 (s, CHB_{11}, 1H), 2.40 (sept, J = 6.8 Hz, C*H*(CH_3)$_2$, 4H), 1.34 (d, J = 6.8 Hz, CH(CH_3)$_2$, 12H), 1.24 (d, J = 6.8 Hz, CH(CH_3)$_2$, 12H). This sample also contains ca. 1 equiv of fluorobenzene and a significant amount of silicone grease (see Figure S9).

[IPr·H]$_2$[$CB_{11}Cl_{11}$] (5). A solution of IPr (0.09 g, 0.22 mmol) in fluorobenzene (10 mL) was added to a solution of **1** (0.10 g, 0.11 mmol) in fluorobenzene (10 mL) at room temperature. A small amount of a black precipitate formed and was separated by filtration through a medium-porosity sintered-glass frit. The solution was concentrated to ca. 10 mL under vacuum, and subsequent cooling at −20 °C for 7 days afforded yellowish crystals of **5**. ^{1}H NMR (400.13 MHz, C_6D_5Br): δ 7.10 (m), 6.88 (m), 2.51 (m, br, C*H*(CH_3)$_2$, 4 H), 1.10 (t, J = 7.7 Hz, CH(CH_3)$_2$, 24 H). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_5Br): δ 145.26 (C_q), 133.58 (C_q), 130.82, 130.14, 130.07, 124.16, 123.67, 115.46, 115.25, 28.85 (*C*H(CH_3)$_2$), 24.47 (CH_3), 23.79 (CH_3). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −1.5 (s, 1B), −9.1 (s, 5B), −12.3 (s, 5B).

[In(PhC≡CPMes$_2$)][$CHB_{11}Cl_{11}$]·0.5C_6H_5F (6·0.5C_6H_5F). A small grease-free Schlenk flask equipped with a Teflon valve was charged with **1** (0.05 g, 0.05 mmol), PhC≡CPMes$_2$ (0.02 g, 0.05 mmol), and fluorobenzene (ca. 2 mL). The resulting orange solution was stored at −20 °C for 2 days to afford small crystals of **6**. ^{1}H NMR (400.13 MHz, C_6D_5Br): δ 7.07 (m, Ph, 4H), 6.88 (t, J = 8.8 Hz, *p*-Ph, 1H), 6.71 (d, $^4J_{PH}$ = 3.3 Hz, *m*-Mes, 4H), 2.79 (s, $CHB_{11}Cl_{11}$, 1H), 2.45 (s, *o*-CH_3^{Mes}, 12H), 2.12 (s, *p*-CH_3^{Mes}, 6H). ^{13}C{^{1}H} NMR (100.61 MHz, C_6D_5Br): δ 142.16 (d, J_{PC} = 20.5 Hz), 131.72 (s), 130.63 (d, J_{PC} = 8.7 Hz), 129.05 (d, J_{PC} = 3.1 Hz), 128.59 (s), 126.90 (s), 125.86 (s), 124.2 (d, J_{PC} = 3.0 Hz), 115.33 (d, J_{PC} = 20.9 Hz), 47.70 (br, $CHB_{11}Cl_{11}$), 23.14 (br, *o*-CH_3^{Mes}), 21.16 (*p*-CH_3^{Mes}). ^{11}B NMR (128.38 MHz, C_6D_5Br): δ −2.0 (s, 1B), −9.3 (s, 5B), −12.1 (s, 5B). ^{31}P{^{1}H} NMR (161.97 MHz, C_6D_5Br): δ −56.2 ($w_{1/2}$ ~ 58 Hz).

Hydroamination Reactions. All work was carried out in J. Young type NMR tubes, which were charged with 20−31 μmol of aminopentene, 10 mol % of catalyst **2**, hexamethylbenzene as the internal standard (3 mg, 18 μmol), fluorobenzene (0.8 mL), and a C_6D_6-filled narrow tube for NMR lock. The samples, which were clear solutions initially, were placed in a temperature-controlled oil bath (T = 130(2) °C), and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. During the reactions, a small amount of a dark powder precipitated. The aminopentenes **A**−**C** (Scheme 1 and Table 1) were prepared according to literature procedures,[23−25] and the products were identified by comparison with reported spectra.[23−25]

Scheme 1

Table 1. Catalytic Conversion of Aminopentenes A−C

compound	R	amount (μmol)	time (h)	conversion (%)	yield (%)
A		31	25	95	96
B	H	27	11	98	95
C	CH_3	20	94	97	90

X-ray Crystallography. Crystals of compounds **1**, **2**, and **4**−**6** were grown as described above (Table 2). The data were collected using a diffractometer with a Bruker APEX CCD area detector and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(2) K. The data were corrected for absorption by the empirical method,[26] and the structures were solved and refined using the *SHELXS* and *SHELXL* packages.[27]

In the structure of **1**, the metal and two of the three toluenes were disordered. The occupancies of In1 and C1B−C7C were refined to 0.587(2) and 0.413(2) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered

Table 2. Abbreviated Crystal Data and Structure Refinement for **1**, **2**, and **4**−**6**

	1	**2**	**4**	$\mathbf{5}\cdot 2C_6F_5$	$\mathbf{6}\cdot 0.5C_6F_5$
empirical formula	$C_{22}H_{25}B_{11}Cl_{11}In$	$C_{39.62}H_{33.69}B_{44}Br_{5.94}Cl_{44}In_4$	$C_{28}H_{38}B_{11}Cl_{11}N_2$	$C_{67}H_{85}B_{11}Cl_{11}F_2N_4$	$C_{30}H_{30.5}B_{11}Cl_{11}F_{0.5}InP$
fw	913.10	3478.96	911.46	1493.25	1055.19
cryst syst	monoclinic	triclinic	triclinic	orthorhombic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$
a [Å]	14.9640(17)	10.0115(16)	10.578(2)	18.0266(14)	12.0234(9)
b [Å]	13.5109(15)	20.330(3)	12.099(3)	32.407(2)	13.6914(10)
c [Å]	18.387(2)	28.620(5)	17.099(4)	13.2700(10)	14.0875(10)
α [deg]	90	105.9143(17)	87.879(3)	90	92.3625(14)
β [deg]	99.9712(19)	94.6438(17)	86.955(3)	90	109.8192(13)
γ [deg]	90	90.319(3)	76.496(4)	90	101.0265(13)
V [Å^3]	3661.3(7)	5581.1(16)	2124.2(8)	7752.2(10)	2127.2(3)
Z	4	2	2	4	2
$F(000)$	1792	3286	924	3100	1042
data/restraints/param	7204/602/534	29544/658/1265	14150/0/479	15748/430/921	12937/0/506
wR2(F^2) (all data)[a]	0.1489	0.2560	0.2216	0.0959	0.0586
R1(F) (obsd data)[b]	0.0550	0.0874	0.0671	0.0453	0.0234
largest diff peak and hole [e/Å^3]	3.214 and −4.265	1.648 and −2.223	1.214 and −0.979	0.377 and −0.534	0.930 and −0.410

[a] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^{\ 2})^2]\}^{1/2}$. [b] $R1 = \sum||F_0| - |F_c||/\sum|F_o|$.

toluenes and the displacement parameters of the metals were required. The crystal of **2** was twinned by a 2-fold rotation about the [210] direction with a refined twin ratio of 0.3800(12). One of the In atoms was disordered over three locations. The occupancies for In4, In4′, and In5 were refined to 0.560(13), 0.377(13), and 0.063(3), respectively. Atom In5 was too close to the F-labeled bromobenzene, so this bromobenzene was refined with an occupancy of 0.937(3). Restraints on the geometry of the F-labeled bromobenzene and the displacement parameters of several atoms were required. The structure of **4** was refined as a three-component twin. The second domain was obtained by a 2-fold rotation about the (001) axis with a twin ratio of 0.3461(14). The third domain was obtained by a 90° rotation about the (210) axis with a twin ratio of 0.0515(4). One of the fluorobenzene molecules in the structure of **5** was disordered. The occupancies of atoms C1D−F7D refined to 0.811(5) and 0.189(5) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered atoms were required.

■ RESULTS AND DISCUSSION

Heating a solution of Ag[$CHB_{11}Cl_{11}$] in toluene or bromobenzene with indium powder at 80 °C for 24 h resulted in the clean formation of the arene-solvated indium(I) salts **1** and **2** as colorless crystals after concentration and cooling (eq 1). Contrary to the synthesis of the reported salt [In($C_6H_5F)_{2,3}$][Al{OC($CF_3)_3$}$_4$], which required activation through a high-intensity ultrasound bath,[11] compounds **1** and **2** were obtained by thermal activation alone. However, it should also be mentioned that our attempts to generate the perfluorotetraphenyl borate species [In(arene)$_n$][B($C_6F_5)_4$] by the thermal redox route have been unsuccessful so far. Compounds **1** and **2** are practically insoluble in benzene and only slightly soluble in toluene at room temperature. Both are readily soluble in fluoro- and bromobenzene at room temperature and in benzene/fluorobenzene and benzene/bromobenzene mixtures at elevated temperatures. They also possess a high thermal stability, which was demonstrated by no observed degradation after heating a toluene solution of **1** for 11 days at 80 °C. However, isolated crystals of **1** and **2** slowly lose some of the coordinated arenes upon storage at room temperature under inert conditions.

$$\mathrm{Ag[CHB_{11}Cl_{11}]} + \mathrm{In} \xrightarrow[\text{arene}\atop 24\ \text{h}]{80\ ^\circ\text{C}} \mathrm{[In(arene)_{\mathit{n}}][CHB_{11}Cl_{11}]} + \mathrm{Ag} \qquad (1)$$

$$\text{arene} = C_7H_8,\ n = 3,\ \mathbf{1}$$
$$= C_6H_5Br,\ n = 1.5,\ \mathbf{2}$$

The structure of **1** (Figure 1) consists of an In^I cation coordinated to three toluene molecules in a slightly distorted η^6 fashion and additionally very weakly to one Cl center of the anion. The [In($C_7H_8)_3$]$^+$ moiety in **1** closely resembles the [In($C_6H_5F)_3$]$^+$ moiety in [In($C_6H_5F)_3$][Al{OC($CF_3)_3$}$_4$], which was described as "bowl-like".[11] The average In···toluene centroid distances in **1** are close to the In···fluorobenzene centroid distances with values of 2.995 and 3.108 Å (due to a disorder) versus 3.007 Å in the latter. Similarly, there is only one weak interaction with the anion in each case (In···Cl = 3.796 and 3.446 Å; In···F = 3.349 Å), which are very close to the sum of the van der Waals radii (In−Cl = 3.63 Å; In−F = 3.40 Å).[28]

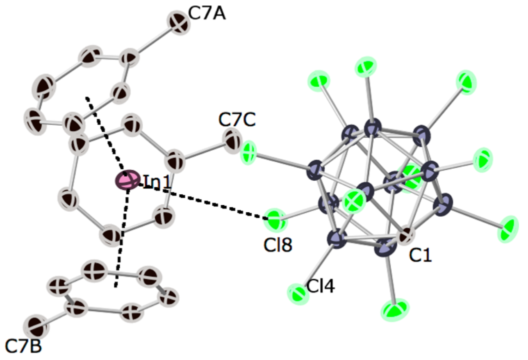


Figure 1. Thermal ellipsoid (50%) plot of **1**. H atoms are omitted for clarity. Selected distances (Å): In1···centroid A, 2.875(1); In1···centroid B, 3.124(3); In1···centroid C, 2.987(1); In1···Cl8, 3.796(1).

The structure of compound **2** contains only 1.5 molecules of bromobenzene per In^I cation on average, and there are four distinct In$^+$ coordination environments. Possibly because of the lower π-electron density of bromobenzene compared to toluene, the [$CHB_{11}Cl_{11}$]$^-$ anion competes successfully for coordination sites. In1 is coordinated to three anions with seven In···Cl contacts ranging from 3.207(4) to 3.662 (5) Å and to three C centers from a bromobenzene molecule in a distorted η^3 fashion (Figure 2). The environments of In2 (Figure S20) and In4, which are disordered over two positions (Figure S21), are very similar to that of In1, whereas In3 is coordinated to three anions with seven In···Cl interactions ranging from 3.217(5) to 3.671(4) Å and two bromobenzene molecules with In···Br distances of 3.795(4) and 4.035(5) Å (Figure 3), just above the sum of the van der Waals radii (3.76 Å for the latter[28]). Whereas M···X contacts with halobenzenes have been observed previously for strongly Lewis acidic metal centers,[29] this has not yet been reported for indium(I) compounds.

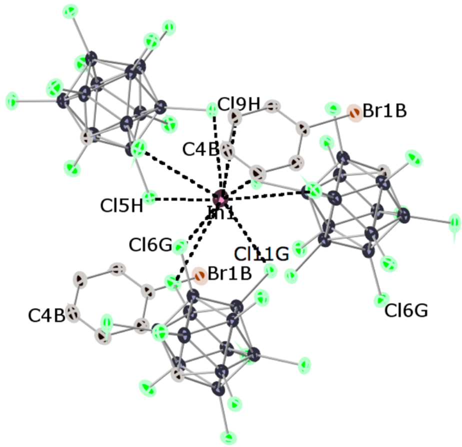


Figure 2. Thermal ellipsoid (50%) plot of the coordination environment of In1 in **2**. H atoms are omitted for clarity. Selected distances (Å): In1···C4B, 3.225(17); In1···C3B, 3.486(16); In1···C5B, 3.558(18); In1···Cl11G, 3.207(4); In1···Cl8G, 3.231(5); In1···Cl5H, 3.348(5); In1···Cl7G, 3.354(5); In1···Cl4H, 3.388(5); In1···Cl9H, 3.426(4); In1···Cl6G, 3.662(5).

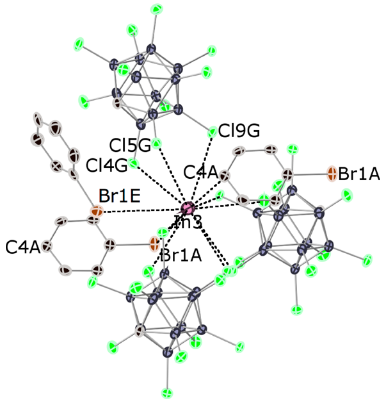


Figure 3. Thermal ellipsoid (50%) plot of the coordination environment of In3 in **2**. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): In3···C4A, 3.77(8); In3···Br1A, 3.79(8); In3···Br1E, 4.0(1); In3···Cl6H, 3.217(5); In3···Cl10H, 3.301(5); In3···Cl5G, 3.490(5); In3···Cl4G, 3.513(6); In3···Cl11H, 3.628(5); In3···Cl9G, 3.642(5); In3···Cl9H, 3.671(4); In3···Cl11H, 3.766(6); In3···Cl7H, 3.780(5).

Having facile access to In^I cations, the coordination chemistry of these ions was explored. Initially, reactions with phosphines and NHCs were investigated for comparison with the reported reactivity of the related compound $[In(C_6H_5F)_{2,3}][Al\{OC(CF_3)_3\}_4]$. This compound afforded the species $[In_2(PPh_3)_7][Al\{OC(CF_3)_3\}_4]$ and $[In(PtBu_3)_2][Al\{OC(CF_3)_3\}_4]$ when reacted with the phosphines PPh_3 and $PtBu_3$[11] and $[In(IPr)_2][Al\{OC(CF_3)_3\}_4]$ in the reaction with the NHC IPr.[13] The $In-PR_3$ interaction in solution is rather weak, as judged by only a very minor shift of the ^{31}P NMR signals of the coordinated phosphines compared to those of the free phosphines. Interestingly, neither **1** nor **2** afforded phosphine or carbene complexes under reaction and storage conditions similar to those reported for $[In(C_6H_5F)_{2,3}][Al\{OC(CF_3)_3\}_4]$. Instead, a dark fine powder precipitated (indium metal), and phosphonium and imidazolium salts were the only crystalline compounds that could be isolated. The phosphonium salt **3** was identified by ^{11}B and ^{31}P NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum shows two broadened singlets at δ 5.8 and −5.5 in a 2.6:1 ratio, suggesting a mixture of **3** and free PPh_3. The signal at δ 5.8 becomes a doublet with a P−H coupling constant of 501 Hz in the fully coupled spectrum, whereas the signal at δ −5.5 only broadens slightly. The reported ^{31}P NMR data of the phosphonium salt $[Ph_3PH][O_3SCF_3]$ with δ 3.9 and $^1J_{P-H} = 531$ Hz in a $CDCl_3$ solution[30] and δ 6.9 and $^1J_{P-H} = 518$ Hz in a C_6D_6 solution (see the Supporting Information) support the proposed identity of **3**.

The reaction of **2** with the carbene IPr in a 1:1 ratio resulted in isolation of the salt **4** (Figure S22), whereas the reaction of **1** with 2 equiv of IPr afforded the salt **5**, which contains the deprotonated dianion $[CB_{11}Cl_{11}]^{2-}$ (Figure 4). The experimental procedure for synthesis of the known carbene complex $[In(IPr)_2][Al\{OC(CF_3)_3\}_4]$ also mentions the formation of a small amount of a black precipitate, but the expected indium carbene comlex was obtained.[13] It is not yet clear why the analogous indium carbene complex with the $[CHB_{11}Cl_{11}]^-$ anion instead of the $[Al\{OC(CF_3)_3\}_4]^-$ anion could not be isolated. Indium(I) carbene complexes appear to be thermally labile because heating of the above-mentioned solution of a 1:1 mixture of **2** and IPr resulted in the formation of additional black powder and eventually the isolation of **4**. The presence of excess carbene, which is a strong base, led to deprotonation of the $[CHB_{11}Cl_{11}]^-$ anion to give the salt **5**. Previously, the bases $nBuLi$[31] and $KOtBu$[32] have been applied to deprotonate the $[CHB_{11}Cl_{11}]^-$ anion.

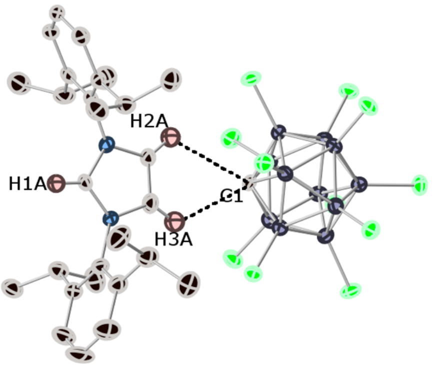


Figure 4. Thermal ellipsoid (50%) plot of a part of the structure of **5** showing the interaction of one of two imidazolium ions with the deprotonated carbon of the dianion. H atoms except H1A, H2A, and H3A are omitted for clarity. Selected distances (Å) and angles (deg): C1···H2A, 2.711(4); C1···H3A, 2.538(4); H2A−C1−H3A, 56.1.

Although disproportionation into indium metal and indium(II) or (III) compounds is a common decomposition pathway of indium(I) compounds,[2] the reactions of **1** and **2** with the phosphine PPh_3 and the carbene IPr appear to be "normal" redox reactions, in which the In^I ion is reduced and the ligands are oxidized. A putative first step would be oxidation of the donor ligands to their respective radical cations. These reactive species could pick up a H atom from the solvent to afford the observed phosphonium and imidazolium cations. This observation is contrary to the more typical redox behavior of indium(I) compounds, which consists of reduction of the ligand and oxidation of the In^I center as seen in, e.g., the reaction of InOTf with diazabutadiene (α-diimine) ligands.[33]

Because good and soft donor ligands led to redox reactions, the reactions of **2** with the weaker π-donor ligands 1-hexene, 2-methyl-1-pentene, 5-bromopentene, phenylacetylene, and hexamethylbenzene were investigated in a small scale using J. Young type NMR tubes. The addition of 1–23 equiv of substrate to a solution of **2** in fluoro- or bromobenzene resulted in no visible change, and the ^1H NMR spectra of the reaction mixtures did not show any changes either, even after prolonged heating at 80 °C (see the Supporting Information). The apparently weak In···ligand interactions and the low boiling point of most of the substrates did not allow for concentration of the reaction mixture to incipient crystallization. In order to obtain a crystalline sample, the nonvolatile phosphinoacetylene $Mes_2PC{\equiv}CPh$ (Mes = 2,4,6-$Me_3C_6H_2$) was chosen as a ligand. As an additional benefit, the presence of at least two donor centers, the phosphorus and the triple bond, could permit identification of the preferred donor type for In^I cations. Cooling a fluorobenzene solution of a 1:1 mixture of **1** and $Mes_2PC{\equiv}CPh$ at −20 °C for 2 days afforded colorless crystals of the adduct **6**. Its structure (Figure 5) consists of two $[In(PhC{\equiv}CPMes_2)]^+$ units bridged by two anions. In addition to five long In···Cl contacts [3.285(1)–3.839(4) Å], each In center is coordinated in an η^2 fashion to one triple bond and in an η^6 fashion to one of the two mesityl substituents of the same phosphine. The In···P distance with a value of 4.168(4) Å is longer than the sum of the van der Waals radii (3.73 Å),[28] and the lone pair on the P center points away from the In ion. The In···C distances involving the triple bond and one mesityl ring range from 3.061(2) to 3.413(3) Å, and the In···triple bond interaction is of sufficient strength to bend the acetylene group toward the In ion, as evidenced by the P–C–C angle with a value of 167.7(1)°. The In···mesityl centroid distance is 2.829(2) Å and thus significantly shorter than related distances in, e.g., **1** (2.995 Å) and $[In(C_6H_5F)_3][Al\{OC(CF_3)_3\}_4]$ (3.007 Å),[11] possibly a combination of the effects of the phosphinoacetylene acting as a "bidentate" ligand and the higher electron density of the mesityl ring with respect to toluene of fluorobenzene.

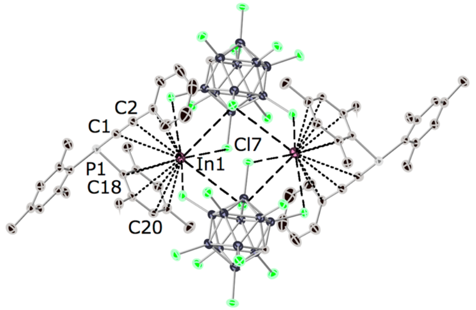
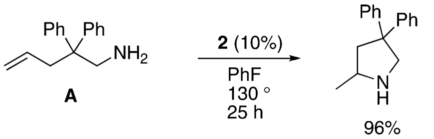


Figure 5. Thermal ellipsoid (50%) plot of the structure of **6**. H atoms are omitted for clarity. Selected distances (Å) and angles (deg): P1–C1, 1.7734(15); C1–C2, 1.210(2); In1···C18, 3.111(3); In1···C19, 3.061(2); In1···C20, 3.104(2); In1···C21, 3.209(3); In1···C22, 3.239(3); In1···C23, 3.218(2); In1···C1, 3.4131(3); In1···C2, 3.223(3); In1···Cl7, 3.285(2); In1···Cl12, 3.288(2); In1···Cl3, 3.340(3); C2–C1–P1, 167.74(13).

Finally, the activity of In^+ cations as catalysts for the intramolecular hydroamination of three aminopentenes was investigated. Cationic aluminum(III)[25] and zinc(II)[34] compounds have shown moderate activities, so that it was of interest how a cationic weak and soft Lewis acid such as In^+ would fare. It was found that the reactivity of **2** is comparable to that of $[AlEt_2][CH_6B_{11}I_6]$ for the primary amine **A** (25 h at 130 °C for **2** versus 28 h at 135 °C for the aluminum compound[25]) but significantly slower for the secondary amines **B** and **C**. Considering that a small amount of a dark powder precipitates upon heating a solution of **2** with the aminopentenes, it is not yet clear whether the reaction is really catalyzed by a solvated In^+ cation or by an indium(III) species.



(2)

SUMMARY

Arene-solvated In^I cations with the $[CHB_{11}Cl_{11}]^-$ counterion can be obtained through a redox reaction at elevated temperatures, and these compounds are thermally stable. Coordination attempts with electron-rich phosphine and carbene ligands led to reduction of the In cation to indium metal and concomitant oxidation of the ligands to phosphonium and imidazolium ions. In the reaction with a trifunctional ligand, coordination of the In ion with π systems is preferred over coordination to a P-donor center. Solutions of compound **2** also showed a moderate activity for the intramolecular hydroamination of primary and secondary aminopentenes. Current efforts focus on the use of ligands with N- and O-donor atoms because such ligands have been shown to support the 1+ oxidation state of indium.[5] Furthermore, if ligand oxidation is the pathway of indium reduction in phosphine and carbene complexes, the more difficult oxidation of N- or O-donor centers should shut down this decomposition route.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b01629.

Additional experimental details, NMR spectra of compounds **1**–**6** and the progress of the hydroamination reactions, and additional figures of the crystal structures (PDF)

X-ray data in the form of CIF files (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: rwehmsch@fit.edu.

Notes

The authors declare no competing financial interest.

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