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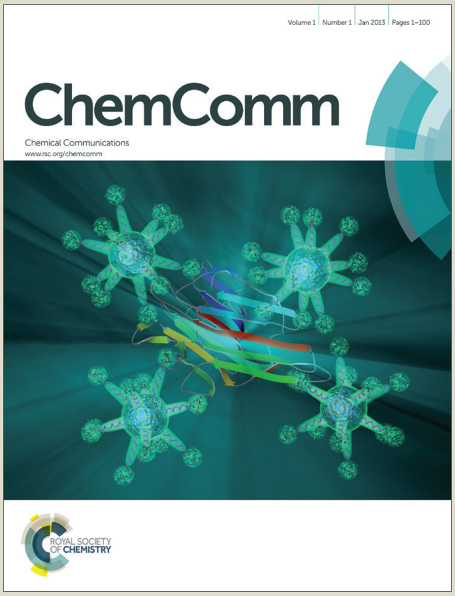

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# Dibromoindium(III) Cation as π-Lewis Acid: Characterization of [IPr·InBr$_2$][SbF$_6$] and Catalytic Activity Towards Alkynes and Alkenes

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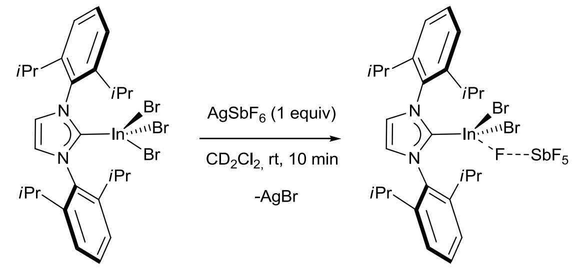
**[IPr·InBr$_2$][SbF$_6$] (2) (IPr = 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene) has been synthetized and characterized in the solid state. This complex proved to be a very active catalyst for hydroarylations, transfer hydrogenations, and cycloisomerizations.**

Indium(III) salts of type InX$_3$ (X = Cl, Br, I, OTf, NTf$_2$) are enjoying increasing use in homogeneous molecular organic catalysis.[1] In particular, Corey et al. showed that InBr$_3$ and InI$_3$ have a strong affinity for alkynes and trigger elegant cationic polycyclizations.[2] In a recent paper, this team reported that a catalytic mixture of InI$_3$ and AgY (10 mol% each, Y = SbF$_6$ or B[C$_6$H$_3$-3,5-(CF$_3$)$_2$]$_4$) was an even more active initiator for such cyclizations than InI$_3$ or InBr$_3$.[3,4] These two components are supposed to give rise to InX$_2^+$ cations, yet no analysis could be performed on the weakly soluble material, and the putative [InX$_2$][Y] species could not be separated from AgX. The higher activity of InX$_2^+$ has been explained by the participation of the two vacant p-orbital of indium in the coordination of the orthogonal π-orbitals of the alkyne cascade initiator in a crisscrossed geometry. On the other hand, we have shown that complexes of type L·GaCl$_2^+$, where L is a N-heterocyclic carbene (NHC), are more active than GaCl$_3$ towards alkynes, even though they display only one vacant orbital.[5] We reasoned that the synthesis and characterization of a well-defined indium complex of the (NHC)·InX$_2^+$ series and the evaluation of its π-acidity would shed light on that matter and advance the field for additional reasons: firstly, only a few indium(III) complexes of type (κ$^1$-L)$_n$·InX$_2^+$ displaying monocoordinating ligands have been characterized in the solid state.[6] Most compounds actually display κ$^2$-L bidentate ligands and are 8- or 12-electron species of type (κ$^2$-L)·InX$_2^+$ or (κ$^2$-L)$_2$·InX$_2^+$.[7] To the best of our knowledge, none of them has found application in molecular catalysis. On the other hand, a 6-electron complex of type (κ$^1$-L)·InX$_2^+$ should display interesting Lewis acid properties due to its unsaturated character. We are not aware of any such compound characterized in the solid state. Secondly, the formation of a donor-acceptor adduct between a NHC and a main group Lewis acid can give rise to easy-to-handle species. For instance, whereas GaCl$_3$ is highly hygroscopic, [IPr·GaCl$_3$] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is bench-stable.[8] In that respect, it would be particularly interesting to use [IPr·InBr$_3$] (**1**) instead of the hygroscopic InBr$_3$ Lewis acid.[9] This air-stable species is one of the very few indium complex supported by NHC ligands.[10] If the bromide abstraction can be achieved and provide a well-defined species, a unique opportunity to study the behavior of [L·InBr$_2$]$^+$ cations as π-Lewis acids would be at hand.

Addition of one equiv. of AgSbF$_6$ to [IPr·InBr$_3$] (**1**) in CD$_2$Cl$_2$ at room temperature led to the immediate formation of a grey precipitate. Energy dispersive spectroscopy was used to qualitatively analyze the chemical composition of this precipitate which reveals mainly the presence of AgBr. All $^1$H signals of the carbene moiety were found shifted, notably the singlet corresponding to the olefinic backbone of the imidazolium ring, which was found at 7.60 ppm after addition of the silver salt instead of 7.35 ppm in **1**. The $^{19}$F NMR spectra showed a broad signal at -123.6 ppm, which is typical of a fluorine-bridged [M···F···SbF$_5$] fragment in which each fluorine is in rapid exchange.[5f,11] Thus, this reaction is likely to provide the desired complex **2** of formula [IPr·InBr$_2$][SbF$_6$], which could also be described as the fluorine-bridged [IPr·InBr$_2$($\mu$-F)SbF$_5$].



**1** **2** (82%)

**Scheme 1.** Reaction of [IPr·InBr$_3$] with AgSbF$_6$.

After filtration of the precipitate and slow evaporation, colorless crystals suitable for X-ray diffraction were collected (82% isolated yield). X-ray structure analysis confirmed the general structural assignment (Figure 1).[12] In **2**, the In1–Br bond distances are significantly shorter than in **1** (2.4379(5) Å (av) vs 2.496(2) Å (av)). The same is true for the In1–C1 bond (2.178(2) Å vs 2.204(8) Å (av)). The In1–F1 distance (2.189(2) Å) is quite long for a standard In–F bond (expected around 2.05 Å).[13] As a result of the sharing of F1 between In1 and Sb1, the Sb1–F1 bond is also longer than the other five Sb–F bonds (1.954(2) Å vs 1.856(3) Å (av)). Thus, complex **1** represents a rare example of a perfluoroanion monocoordinated to a p-block metal,[5f,14] and, as noted above, a rare example of a well-defined ($\kappa^1$-L)·$InX_2^+$ complex.

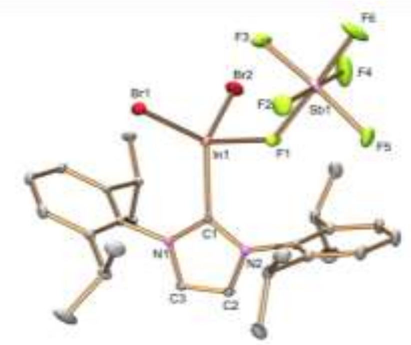
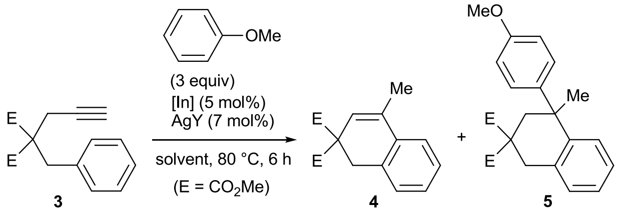


**Figure 1.** Crystal structure of **2** (thermal ellipsoids at 30% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): In1-Br1 2.4333(5), In1-Br2 2.4425(5), In1-F1 2.189(2), In1-C1 2.178(2), Sb1-F1 1.954(2), Sb1-F2 1.851(2), Sb1-F3 1.867(2), Sb1-F4 1.842(4), Sb1-F5 1.855(2), Sb1-F6 1.865(2); In1-F1-Sb1 137.1(1).

The catalytic activity of **2** as a $\pi$-Lewis acid was evaluated and compared to that of simple indium salts. The reaction of arenyne **3** with anisole was used as a prototype of a cationic cascade since it involves the activation of an alkyne to give **4** and then the activation of the alkene moiety of **4** to give the tandem product **5** (Table 1).[15]

**Table 1.** In(III)-catalyzed dihydroarylation of arenyne **3** with anisole.



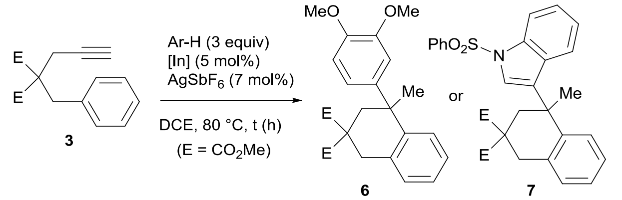
| Entry | [In] | AgY | Solvent | 4:5 (% conv)[a] | Yield of 5 (%)[b] |
|---|---|---|---|---|---|
| 1 | InCl$_3$ | - | DCE | - | -[c] |
| 2 | InBr$_3$ | - | DCE | 32/13 | 12 |
| 3 | InBr$_3$ | AgSbF$_6$ | DCE | 18/81 | 65 |
| 4 | **1** | - | DCE | - | -[d] |
| 5 | **1** | AgSbF$_6$ | DCE | 20/80 | 62 |
| 6 | **2** | - | DCE | 29/71 | 68 |
| 7 | **1** | AgSbF$_6$ | Toluene | 78/13 | 15[e] |
| 8 | **1** | AgSbF$_6$ | THF | - | -[d] |
| 9 | **1** | AgBF$_4$ | DCE | - | -[d] |
| 10 | **1** | AgPF$_6$ | DCE | - | -[d] |

[a] Determined by GC. [b] Isolated yields. [c] Trace. [d] No reaction. [e] **4** is isolated in 75% yield.

The reaction was first carried out in 1,2-dichloroethane (DCE) at 80 °C. With a catalytic amount of the poorly soluble InCl$_3$, only traces of products were monitored by gas chromatography (entry 1). With the soluble InBr$_3$, product **5** was obtained as the minor component of the mixture and isolated in 12% yield only (entry 2). The joint use of InBr$_3$ and AgSbF$_6$ provided **5** as the major product in 65% isolated yield (entry 3).[16] Complex **1** showed no catalytic activity (entry 4). On the other hand, a catalytic mixture of **1** and AgSbF$_6$ gave similar results as InBr$_3$/AgSbF$_6$ (entry 5). It is worthy of note that in the two-component reactions, the indium complex (InBr$_3$ or **1**) and AgSbF$_6$ were premixed at room temperature for 5 min to ensure the formation of the corresponding cationic species (a precipitate forms instantly). Moreover, AgSbF$_6$ shows no activity in this reaction. That the cationic species **2** is generated under these catalytic conditions was further evidenced by using it directly (entry 6). The products distribution and the isolated yield of **5** were found quite close to those of the two-component experiment. In toluene, the **1**/AgSbF$_6$ system was much less effective (entry 7) and in THF, no reaction took place (entry 8). Replacement of AgSbF$_6$ by AgBF$_4$ or AgPF$_6$ was also detrimental to the reactivity (entries 9 and 10).

Complex **1** does not only represent a stable alternative to the hygroscopic InBr$_3$. In some cases, the [IPr·InBr$_2$]$^+$ cation proved more active than InBr$_2^+$. When 1,2-dimethoxybenzene or 1-(phenylsulfonyl)indole were used instead of anisole in the transformation of **3**, full conversion was reached faster and the isolated yields of **6** and **7** were better with the former (Table 2).

**Table 2.** In(III)-catalyzed bimolecular dihydroarylation of arenyne **3** with 1,2-dimethoxybenzene and 1-(phenylsulfonyl)indole.

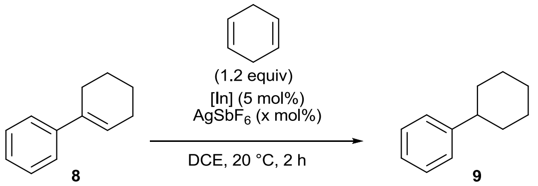


| Entry | [In] | Ar-H | t (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | $InBr_3$ | 1,2-dimethoxybenzene | 24 | **6** (45) |
| 2 | **1** | 1,2-dimethoxybenzene | 2 | **6** (82) |
| 3 | $InBr_3$ | 1-(phenylsulfonyl)indole | 24 | **7** (69) |
| 4 | **1** | 1-(phenylsulfonyl)indole | 16 | **7** (83) |

[a] Isolated yields.

We next examined whether catalytic transfer hydrogenation of alkenes was possible (Table 3). The reduction of cyclohexenylbenzene **8** was attempted using 1,4-cyclohexadiene (1,4-CHD) as hydrogen transfer agent.[5e] This reaction does not work with the neutral indium species $InBr_3$ and **1** (entries 1 and 2), nor with $AgSbF_6$ alone. Yet it becomes very efficient with $InBr_2^+$ or $[IPr{\cdot}InBr_2]^+$ (entries 3 and 4), both displaying similar activities.

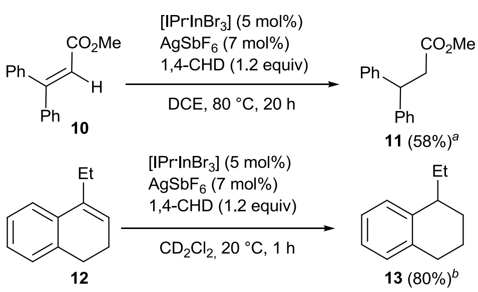
**Table 3.** In(III)-catalyzed transfer hydrogenation of cyclohexenylbenzene **8**.



| Entry | [In] | x | Conv of **9** (%)[a] |
|---|---|---|---|
| 1 | $InBr_3$ | 0 | 1 |
| 2 | **1** | 0 | 0 |
| 3 | $InBr_3$ | 7 | 99 |
| 4 | **1** | 7 | 94 |

[a] Conversion determined by GC.

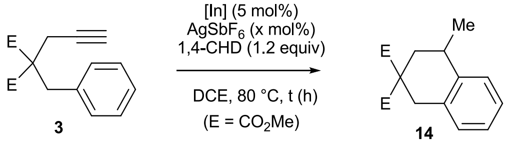
Two other alkenes were also reduced using the in situ generated $[IPr{\cdot}InBr_2]^+$ cation as catalyst and 1,4-CHD as hydrogen transfer agent (Scheme 2). For the transformation of the acyclic substrate **10**, a temperature of 80 °C had to be applied. With the more reactive cyclic alkene **12**, the reaction took place at rt.



**Scheme 2.** In(III)-catalyzed transfer hydrogenation of alkenes **10** and **12** ([a] Isolated yield; [b] determined by $^1H$ NMR using *p*-anisaldehyde as internal standard).

Hydrogenative cyclization of **3** in the presence of 1,4-CHD was also tested (Table 4). Again, the activity of the neutral indium species was marginal (entries 1 and 2). With $InBr_2^+$, the transformation required 6 h to reach completion at 80 °C and the isolated yield of **14** was 58% (entry 3). On the other hand, the reaction was over in 2 h with $[IPr{\cdot}InBr_2]^+$ and the isolated yield was improved to 73% (entry 4).

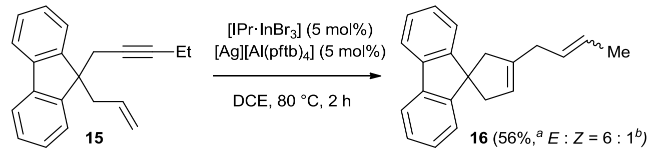
**Table 4.** In(III)-catalyzed hydrogenative cyclizations of arenyne **3**.



| Entry | [In] | x | t (h) | Yield of **14** (%)[a] |
|---|---|---|---|---|
| 1 | $InBr_3$ | 0 | 24 | 12 |
| 2 | **1** | 0 | 24 | 0 |
| 3 | $InBr_3$ | 7 | 6 | 58 |
| 4 | **1** | 7 | 2 | 73 |

[a] Isolated yields.

Lastly, the cycloisomerization of the enyne **15** was attempted (Scheme 3).[4c,17] When carried out with a catalytic mixture of $[IPr{\cdot}GaCl_3]$ and $AgSbF_6$ or $[IPr{\cdot}InBr_3]$ and $AgSbF_6$, full conversion was reached but the desired product **16** was obtained in low amount and admixed with a complex mixture of unidentified products. Another cationizing agent was then tested: silver polyfluoro-*tert*-butyloxyaluminate $[Ag][Al(pftb)_4]$ (pftb = $OC(CF_3)_3$) which displays one of the most weakly coordinating anions known.[18] While the joint use of $[IPr{\cdot}GaCl_3]$ and $[Ag][Al(pftb)_4]$ still gave rise to decomposition, **16** could be obtained very cleanly with $[IPr{\cdot}InBr_3]$ and $[Ag][Al(pftb)_4]$.[19] This result shows that the NHC indium complex can surpass the gallium one and reveals an interesting counterion effect in this chemistry.



**Scheme 3.** In(III)-catalyzed cycloisomerization of enyne **15** ([a] Isolated yield; [b] determined by GLC analysis).

In conclusion, this work demonstrates that the hygroscopic $InBr_3$ salt can be advantageously replaced by the bench-stable $[IPr{\cdot}InBr_3]$ complex to generate the catalytically active $[IPr{\cdot}InBr_2]^+$ cation upon treatment with $AgSbF_6$. This species, which is a rare type of cationic $(\kappa^1\text{-L}){\cdot}InX_2^+$ complex, has been characterized in the solid state and proved to be a powerful $\pi$-Lewis acid. In various cases, we could show its superior activity compared to $InBr_2^+$, even with alkyne substrates, even though it displays a single vacant site. We also found one type of reaction for which $[IPr{\cdot}InBr_2]^+$ proves more selective than the previously described $[IPr{\cdot}GaCl_2]^+$, provided it is generated from $[IPr{\cdot}InBr_3]$ and $[Ag][Al(pftb)_4]$ instead of $AgSbF_6$. This interesting counterion effect is being explored in our laboratory.

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## Notes and references

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† Dedicated to Prof. A. M. Echavarren on the occasion of his 60th birthday.

†† Electronic Supplementary Information (ESI) available: Synthetic procedures and crystallographic details for **2**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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[15] This reaction also works well with GaCl$_3$ (see ref 5a) or [IPr·GaCl$_2$][SbF$_6$] (see ref 5b). On the other hand, the aluminium counterparts of these species are not active.

[16] Silver salts are not active in the reactions presented herein. The use of a slight excess of AgY compared to the indium complex is to ensure complete cationization. The yields are usually slightly better with a 5/7 ratio than with a 5/5 one.

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