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Dibromoindium(III) cations as a π -Lewis acid: characterization of $[\text{IPr}\cdot\text{InBr}_2]\text{[SbF}_6]$ and its catalytic activity towards alkynes and alkenes^{†‡}

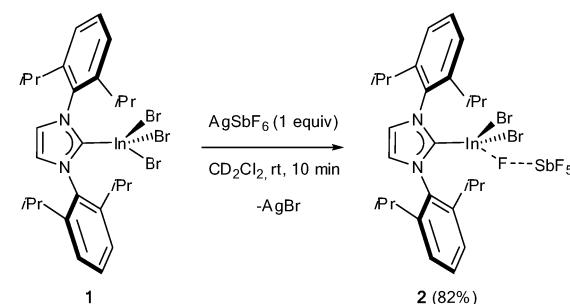
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$[\text{IPr}\cdot\text{InBr}_2]\text{[SbF}_6]$ (2) (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) has been synthesized and characterized in the solid state. This complex proved to be a very active catalyst for hydroarylations, transfer hydrogenations,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

Indium(III) salts of type InX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{NTf}_2$) are enjoying increasing use in homogeneous molecular organic catalysis.¹ In particular, Corey *et al.* showed that InBr_3 and InI_3 have 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, $\text{Y} = \text{SbF}_6$ or $\text{B}[\text{C}_6\text{H}_5\text{-3,5-(CF}_3\text{)}_2]_4$) 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 $[\text{InX}_2][\text{Y}]$ species could not be separated from AgY . The higher activity of InX_2^+ has been explained by the participation of the two vacant p-orbitals of indium in the coordination of the orthogonal π -orbitals of the alkyne cascade initiator in a criss-crossed geometry. On the other hand, we have shown that complexes of type $\text{L}\cdot\text{GaCl}_2^+$, 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 $(\kappa^1\text{-L})_n\text{InX}_2^+$ displaying monocoordinating ligands have been characterized in the solid state.⁶ Most compounds actually display $\kappa^2\text{-L}$ bidentate ligands and are 8- or 12-electron species of type $(\kappa^2\text{-L})\cdot\text{InX}_2^+$ or $(\kappa^2\text{-L})_2\text{InX}_2^+$.⁷ To the best of our knowledge, none of them have found applications in molecular catalysis. On the other hand, a

6-electron complex of type $(\kappa^1\text{-L})\cdot\text{InX}_2^+$ 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, $[\text{IPr}\cdot\text{GaCl}_3]$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) is bench-stable.⁸ In that respect, it would be particularly interesting to use $[\text{IPr}\cdot\text{InBr}_3]$ (1) instead of the hygroscopic InBr_3 Lewis acid.⁹ This air-stable species is one of the very few indium complexes 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 $[\text{L}\cdot\text{InBr}_2]^+$ cations as a π -Lewis acid would be at hand.

Addition of one equiv. of AgSbF_6 to (1) in CD_2Cl_2 at room temperature led to the immediate formation of a grey precipitate (Scheme 1). Energy dispersive spectroscopy was used to qualitatively analyze the chemical composition of this precipitate, which reveals mainly the presence of AgBr . All ^1H signals of the carbene moiety were found to be shifted, notably the signal corresponding to the olefinic backbone of the imidazolium ring, which was found at 7.60 ppm after the addition of the silver salt instead of 7.35 ppm for (1). The ^{19}F NMR spectra showed a broad signal at -123.6 ppm, which is typical of a fluorine-bridged $[\text{M}\cdots\text{F}\cdots\text{SbF}_5]$ fragment in which each fluorine undergoes rapid exchange.^{5,11} Thus, this reaction is likely to provide the desired complex 2 of



Scheme 1 Reaction of $[\text{IPr}\cdot\text{InBr}_3]$ with AgSbF_6 .

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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. CCDC 1044808. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5cc00740b



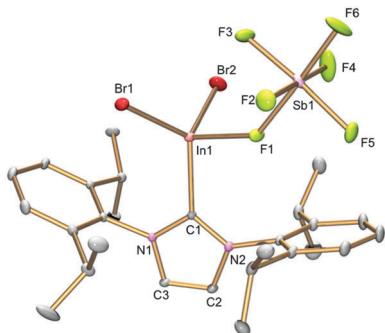


Fig. 1 Crystal structure of **2** (thermal ellipsoids at 30% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): In1–Br1 2.4333(5), In1–Br2 2.4425(5), In1–F1 2.189(2), In1–C1 2.178(2), Sb1–F1 1.954(2), Sb1–F2 1.851(2), Sb1–F3 1.867(2), Sb1–F4 1.842(4), Sb1–F5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

formula $[\text{IPr-InBr}_2][\text{SbF}_6]$, which could also be described as the fluorine-bridged $[\text{IPr-InBr}_2(\mu\text{-F})\text{SbF}_6]$.

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 (Fig. 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 ($\kappa^1\text{-L}$)- InX_2^+ complex.

The catalytic activity of **2** as a π -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

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 trace amounts 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 only in 12% yield (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 $\text{InBr}_3/\text{AgSbF}_6$ (entry 5). It is worth noting 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. Cationic species **2** 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 to be quite close to those of the two-component experiment. In toluene, the $1/\text{AgSbF}_6$ 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 just represent a stable alternative to the hygroscopic InBr_3 . In some cases, the $[\text{IPr-InBr}_2]^+$ cation proved to be 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).

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 the hydrogen transfer agent.^{5e} This reaction does not work with the neutral indium species InBr_3 and **1** (entries 1 and 2), or with AgSbF_6 alone. Yet it becomes very efficient with InBr_2^+ or $[\text{IPr-InBr}_2]^+$ (entries 3 and 4), both displaying similar activities.

Two other alkenes were also reduced using the *in situ* generated $[\text{IPr-InBr}_2]^+$ cation as the catalyst and 1,4-CHD as the 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.

Table 1 $\text{In}(\text{III})$ -catalyzed dihydroarylation of arenyne **3** with anisole

Entry	[In]	AgY	Solvent	4 : 5 ^a (% conv.)	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 amounts. ^d No reaction. ^e **4** is isolated in 75% yield.

Table 2 $\text{In}(\text{III})$ -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)

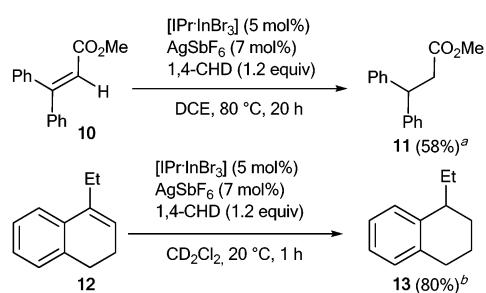
^a Isolated yields.



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.

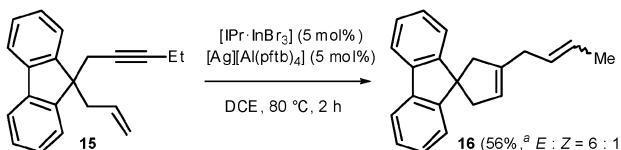
Scheme 2 In(III)-catalyzed transfer hydrogenation of alkenes **10** and **12** (^a isolated yield; ^b determined by ¹H NMR using *p*-anisaldehyde as an internal standard).Table 4 In(III)-catalyzed hydrogenative cyclizations of arenyne **3**

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.

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 InBr₂⁺, 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-InBr₂]⁺ and the isolated yield was improved to 73% (entry 4).

Lastly, the cycloisomerization of the enyne **15** was attempted (Scheme 3).^{4c,17} When carried out with a catalytic mixture of [IPr-GaCl₃] and AgSbF₆ or [IPr-InBr₃] and AgSbF₆, full conversion was reached but the desired product **16** was obtained in low amounts and admixed with a complex mixture of unidentified products. Another cationizing agent was then tested, silver polyfluoro-*tert*-butoxyaluminate [Ag][Al(pftb)₄] (pftb = OC(CF₃)₃),

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

which displays one of the most weakly coordinating anions known.¹⁸ While the joint use of [IPr-GaCl₃] and [Ag][Al(pftb)₄] still gave rise to decomposition, **16** could be obtained very cleanly with [IPr-InBr₃] 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.

In conclusion, this work demonstrates that the hygroscopic InBr₃ salt can be advantageously replaced by the bench-stable [IPr-InBr₃] complex to generate the catalytically active [IPr-InBr₂]⁺ cation upon treatment with AgSbF₆. This species, which is a rare type of cationic (κ^1 -L)-InX₂⁺ complex, has been characterized in the solid state and proved to be a powerful π -Lewis acid. In various cases, we could show its superior activity compared to InBr₂⁺, even with alkyne substrates, even though it displays a single vacant site. We also found one type of reaction for which [IPr-InBr₂]⁺ proves to be more selective than the previously described [IPr-GaCl₂]⁺, provided it is generated from [IPr-InBr₃] and [Ag][Al(pftb)₄] instead of AgSbF₆. This interesting counterion effect is being explored in our laboratory.

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