Crystallographic characterization of difluoropropargylindium bromide, a reactive fluoroorganometallic reagent∗

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General

NMR spectra were recorded on Varian Inova500 (500 MHz) instruments. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded at 500, 126 and 470 MHz respectively, using CDCl$_3$ as a solvent if not stated. The chemical shifts are reported in δ (ppm) values relative to CHCl$_3$ (δ 7.26 ppm for $^1$H NMR and δ 77.0 ppm for $^{13}$C NMR). Coupling constants are reported in hertz (Hz). The UV-Vis spectrum was recorded on a HP 8453 model.

**Synthesis of difluoropropargyl bromide (1a-1d)**

(3-bromo-3,3-difluoroprop-1-ynyl)-triisopropylsilane (1a)

A mixture of ethynyltriisopropylsilane (10.98 g, 60 mmol) in dry THF (250 mL) was cooled to -78 °C under an argon atmosphere, and then 2.5 M solution of butyllithium in hexane (24 mL, 60 mmol) was added dropwise at -78 °C. After addition, the reaction mixture was stirred for 30 min. Then reaction mixture was cooled to -100 °C, dibromodifluoromethane (15.10 g, 6.6 mL, 72 mmol) was added to the reaction mixture through a canula, (control the speed of addition to make sure the temperature not exceed -90 °C, the reaction produce a lot of heat, a internal thermometer is recommended). After addition, the reaction mixture was allowed to be warmed to -50°C, and then 100 mL sat. NH$_4$Cl solution was added to quench the reaction and then 100 mL hexane was added, the organic layer was washed by water and dried over Na$_2$SO$_4$. After evaporation of the solvent, the crude product was purified by distillation under reduced pressure (about 72 °C / 1 mmHg) to afford 1a (16.6 g, 90%) as a colorless oil. The spectral data of the product is consistent with the literature report. Compounds 1b-1d were synthesized by a similar method.

**Preparation, isolation and physical data of the indium complexes.**

**Preparation of crude indium complex.**

The reactions were carried out under air, using standard organic synthetic techniques. To a 0.15 M solution of 1a in a mixture of water and THF (4:1) is added indium powder (1eq). This mixture was sonicated at 5-10 °C for 6-8h. The temperature in the ultrasound bath was adjusted by addition of ice periodically. An aliquot was analyzed in CDCl$_3$ by $^{19}$F-NMR to monitor the completion of the reaction. After the starting material was consumed, the reaction mixture was extracted by ether and the organic layer was washed by brine and the organic layer was washed by brine, dried over MgSO$_4$ and concentrated to give crude indium complex. The crude indium complex can be used in synthesis without further purification.

**Isolation of indium complexes.**

The crude indium complex (which was prepared from 5 mmol compound 1a and was dissolved in 5 mL ether) was charged into a column packed with SiO$_2$ (80 g) in ether, and eluted with ether (300 mL) followed by 5% methanol in ether (300 mL). DMSO (1 mL) was added to the two fractions collected, after evaporation of solvent two white solids were obtained, then they were filtered, washed with hexane, and dried in vacuum giving 5a (750 mg, 37%) and 6a (400 mg, 13%) as white solids.

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1 For the detailed synthesis and spectroscopic data of 1, see: B. Xu, M. Mae, J.A. Hong, Y. Li, G.B. Hammond, *Synthesis*, 2005, 803.

2 The preparation of indium complexes was conducted by a slightly modified procedure of our previous published paper (ref 6 in manuscript).
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$^a$ Not determined because it is not solid at room temperature

**Bis(1,1-difluoro-3-(triethylsilyl)prop-2-ynyl)indium(III) bromide (5b)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.63 (q, $J = 7.5$ Hz, 12 H), 1.00 (t, $J = 7.5$ Hz, 18 H), 2.75 (s, 12H, DMSO); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 4.3, 7.6, 39.2 (DMSO), 94.1, 103.2, 131.1 (t, $J = 285$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 88.8 (s, 2F).

**Bis(1,1-difluoro-6-methylhept-2-ynyl)indium(III) bromide (5c)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.87-0.92 (m, 12 H), 1.42-1.51 (m, 4H), 1.67-1.71 (m, 2H), 2.29-2.32 (m, 2H), 2.38-2.42 (m, 2H), 2.72 (s, 12H, DMSO); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 17.0, 22.2, 27.1, 37.2, 40.4 (DMSO), 78.6 (t, $J = 25.7$ Hz), 92.3, 132.2 (t, $J = 285$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 86.9 (s, 2F).

**Bis(1,1-difluoro-3-(triphenyl)prop-2-ynyl)indium(III) bromide (5d)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.62 (q, $J = 8.0$ Hz, 6 H), 0.99 (t, $J = 8.0$ Hz, 9 H), 2.75 (s, 12H, DMSO); $^{13}$C NMR (126 MHz, $d$-DMF) $\delta$ 45.1 (s, DMSO), 94.1, 112.9, 133.2, (t, $J = 276$ Hz), 135.3, 137.5, 140.2; $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 89.1 (s, 2F).

**Bis(1,1-difluoro-3-(triethylsilyl)prop-2-ynyl)indium(III) bromide (6b)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.62 (q, $J = 8.0$ Hz, 6 H), 0.99 (t, $J = 8.0$ Hz, 9 H), 2.75 (s, 12H, DMSO); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 3.9, 7.3, 39.2 (DMSO), 95.0, 103.0, 131.2 (t, $J = 285$ Hz); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 91.1 (s, 2F).

**Bis(1,1-difluoro-6-methylhept-2-ynyl)indium(III) bromide (6c)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 0.83 (d, $J = 6.5$ Hz, 6H), 1.39-1.42 (m, 2H), 1.60-1.68 (m, 1H), 2.26-2.28 (m, 2H), 2.62 (s, 12H, DMSO); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 89.1 (s, 2F).

**Bis(1,1-difluoro-3-(triphenyl)prop-2-ynyl)indium(III) bromide (6d)**

$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.62 (s, 12H, DMSO), 7.28-7.41 (m, 9 H), 7.69-7.71 (m, 6H); $^{19}$F NMR (470 MHz, CDCl$_3$) $\delta$ 91.1 (s, 2F).
Fig. 1 $^{19}$F-NMR of TIPS indium complexes (before and after the column)

Crude indium complex from 1a

Fraction 1, complex 5a

Fraction 2, complex 6a

$^{13}$C-NMR of TIPS-indium complex 5a.
UV-Vis spectrum of 6d

The use the indium complexes in synthesis.

The crude indium complex can react with electronophile to yield 3 or 4 depending on the nature of the electrophile (E) used.

Preparation of 3a from crude indium complex 2
The crude indium complex (prepared from compound 1a 1.0 mmol) was dissolved in 5 mL ether and benzaldehyde 1.0 mmol was added, the reaction mixture was refluxed for 2h. Then 10 ml saturated NH$_4$Cl solution was added to quench the reaction. After stirring for 5 min at room temperature, the resulting aqueous mixture was extracted with ether (three times); the extract washed with brine (three times) and then dried over MgSO$_4$. The solvent was removed under reduced pressure, and the crude product was purified by flash silica gel chromatography (hexane to 10 % ethyl acetate in hexane) to give the product 3a (51%) as a colorless oil. (The analytical data was consistent with ref 7 in manuscript)

Preparation of 4a from crude indium complex 2
The freshly prepared indium complex 4 (prepared from compound 1a (3.20g, 9.7 mmol)) was dissolved in 50 ml THF, then reaction mixture was cooled to -78 °C, then a solution of Br$_2$ (3.10 g, 19.4 mmol) in 10 mL THF was added dropwise to the reaction mixture under stirring. The reaction mixture was warmed to -20 °C and was stirring for another 0.5 h at -20 °C. Then 10 mL saturated Na$_2$S$_2$O$_3$ solution was added to quench the reaction. After stirring for 5 min at about 0 °C, the resulting aqueous mixture was extracted with ether (three times); the extract washed with brine (three times) and then dried over Na$_2$SO$_4$. The solvent was removed by rotavapor, and the crude product was purified by flash silica gel chromatography (pure hexane) to give the bromoallene product 4a (2.44 g, 76%) as colorless oil. (The yield varied from 67-81% from compound 1a (2 steps), the obtained fluoroallene 4a is not very stable in solution, but neat 4a can be stored in freezer for more than 1 month, the analytical data was consistent with ref 8 in manuscript)
The reaction of isolated indium with electrophiles.

The isolated indium complexes 5 and 6 have the same reaction pattern as the crude indium complex with electrophiles and the isolated indium complexes 5 and 6 have the same reaction pattern with electrophiles. The reaction of indium complexes 5a and 6a with benzaldehyde and bromine was investigated by $^{19}$F-NMR.