Supplementary Information

Heterogeneous bromination of alkenes using Bi(III) polybromide complexes as $\{Br_2\}$ source

S. A. Adonin,[a,b] D.S. Perekalin,[c] Igor D. Gorokh,[b] Denis G. Damsonenko,[a,b] Maxim N. Sokolov[a,b] and Vladimir P. Fedin[a,b]

Materials and methods

All reagents were obtained from commercial sources and used without additional purification. All procedures with $HBr{\cdot}Br_2$ solution were carried out in a well-ventilated fume hood. The NMR spectra were measured on Bruker Avance 400 spectrometer at room temperature.

Synthesis of $(PyH)_3\{[Bi_2Br_9](Br_2)]$ (1)

200 mg (0.66 mmol) of BiOBr were dissolved in 2 ml of 2M HBr. Then 4 ml of solution of Br_2 (1M) in 2M HBr were added. Following that, a solution of pyridine (80 mcl, 1 mmol) in 3 ml of 2M HBr was added. Within 10-15 minutes, deep orange crystals of **1** started to form; the crude product was collected after keeping the reaction mixture overnight. Yield 80%, based on Bi.

Bromination experiments

Polybromide **1** or **2** (0.01 mmol), two different alkenes (0.01 mmol each), 1,3,5-tribromobenzene (3 mg, 0.01 mmol, internal standard) and $CCl_4/CDCl_3$ mixture (0.4 ml + 0.2 ml) were stirred in the dark overnight at room temperature. During the reaction, the Bi(III) polybromide complex remains insoluble but there occurs the colour change from red to pale yellow. The solutions were transferred to NMR tube and ^1H NMR spectrum was recorded to determine the ration of reacted alkenes and produced dibromides.

Iodide-starch test

In a typical experiment, when small amount of dry precipitate (isolated from HBr/Br_2 medium) is put in a solution of NaI or KI and then a drop of starch solution is added, appearance of blue colour corresponds to oxidation of I^- to I_2 by $\{Br_2\}$.

Formation/non-formation of polybromides

Cation	Result	Iodine-starch test (IS)
protonated DABCO (1,4-diazabicyclo[2.2.2]octane)	Yellow solid	Negative
Protonated urotropine	Yellow solid	Negative
H_2(4,4`-bipy)	Yellow solid, identified as $(H_2bipy)_2[Bi_2Br_{10}]$ by PXRD	Negative
H_2(2,2`-bipy)	Yellow solid with some pale orange inclusions	Positive. One of the products of reactions was identified as polybromide (Hbipy)Br_3 by XRD. Most probably, there is a mixture of bromide complex and organic polybromide which gives the positive IS reaction
4-EtPyH	No formation of solid; there forms some instead	n/a
N-BuPy	Depending on the amount of Br_2, there forms either paly yellow solid (IS negative) or deep-red oil	Negative or n/a

X-ray diffractometry

Diffraction data for a single crystals of compound **1** were obtained at 130 K on an automated Agilent Xcalibur diffractometer equipped with a two-dimensional AtlasS2 detector (graphite monochromator, λ(MoKα) = 0.71073 Å, ω scans). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [1]. The structures were solved by a direct method and refined by the full-matrix least squares technique in the anisotropic approximation (except hydrogen atoms) using the SHELX-2014 software [2]. Positions of hydrogen atoms of organic molecules were calculated geometrically and refined in the riding model. Crystallographic data and diffraction experiment details are

given in Table 1. Selected interatomic distances and bond angles are presented in Table 2. Full structural data (atom coordinates, interatomic distances, bond angles, and thermal atomic displacement parameters) have been deposited with the Cambridge Structural Data Base (CCDC-1474709) and can also be obtained from the authors upon request.

[1] CrysAlisPro 1.171.38.41. Rigaku Oxford Diffraction. 2015.

[2] Sheldrick G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* 2008, A64, 112.

Table S1. Crystal data and structure refinement for **1**.

Identification code	**1**
Empirical formula	$C_{15}H_{18}N_3Bi_2Br_{11}$
Formula weight	1537.29
Crystal system	*Monoclinic*
Space group	$P2_1/m$
a, Å	7.8459(2)
b, Å	23.3803(4)
c, Å	9.4868(2)
β, deg.	110.370(3)
V, Å^3	1631.43(7)
Z	2
D_{calcd}, g/cm^3	3.129
μ, mm^{-1}	24.254
F(000)	1360
Crystal size, mm	0.16 × 0.11 × 0.03
θ range for data collection, deg.	3.27–29.54

Index ranges	$-7 \le h \le 9$, $-25 \le k \le 32$, $-12 \le l \le 9$
Reflections collected	8267
Independent reflections	3879
R_{int}	0.0221
Reflections with $I > 2\sigma(I)$	3420
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0252$, $wR_2 = 0.0532$
R indices (all data)	$R_1 = 0.0319$, $wR_2 = 0.0556$
Largest diff. peak / hole, e/Å^3	1.274 / −1.085

Table S2. Selected bond lengths and angles for **1**.

Bond	*d*, Å	Bond	*d*, Å
Bi(1)–Br(1)	2.7094(5)	Bi(1)–Br(5)	3.0015(5)
Bi(1)–Br(2)	2.7776(5)	Bi(1)–Br(6)	3.0444(5)
Bi(1)–Br(3)	2.7064(5)	Br(7)–Br(7)^{ii}	2.3190(9)
Bi(1)–Br(4)	3.0386(5)	Br(2)–Br(7)	3.1385(7)
Angle	ω, deg.	Angle	ω, deg.
Br(1)–Bi(1)–Br(2)	89.002(16)	Br(3)–Bi(1)–Br(4)	93.245(16)
Br(1)–Bi(1)–Br(4)	173.854(15)	Br(3)–Bi(1)–Br(5)	92.609(16)
Br(1)–Bi(1)–Br(5)	93.673(16)	Br(3)–Bi(1)–Br(6)	173.458(15)
Br(1)–Bi(1)–Br(6)	92.934(15)	Br(4)–Bi(1)–Br(6)	82.599(14)
Br(2)–Bi(1)–Br(4)	95.604(16)	Br(5)–Bi(1)–Br(4)	81.545(15)
Br(2)–Bi(1)–Br(5)	176.253(15)	Br(5)–Bi(1)–Br(6)	81.810(15)
Br(2)–Bi(1)–Br(6)	95.446(16)	Bi(1)^{i}–Br(4)–Bi(1)	81.179(16)
Br(3)–Bi(1)–Br(1)	90.819(16)	Bi(1)^{i}–Br(5)–Bi(1)	82.397(17)
Br(3)–Bi(1)–Br(2)	89.972(16)	Bi(1)^{i}–Br(6)–Bi(1)	80.993(15)

Symmetry transformations used to generate equivalent atoms: i) *x*, −*y* + ½, *z*; ii) −*x*, −*y* + 1, −*z*.