(Supporting Information)

Remarkable Substituent Effects on the Oxidizing Ability of Triarylbismuth Dichlorides in Alcohol Oxidation

Yoshihiro Matano, Teppei Hisanaga, Hisatsugu Yamada, Shingo Kusakabe, Hazumi Nomura, and Hiroshi Imahori*

Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan and Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan

Contents

General. All melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded using $CDCl_3$ as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane and *J* values are given in Hz. FABMS spectra were measured using *m*-nitrobenzyl alcohol as a matrix. Column chromatography was performed on silica gel or on a fast flow liquid chromatography system fitted with a silica gel column. CH_2Cl_2 was distilled from CaH_2 before use. $CDCl_3$ was distilled from CaH_2 and stored over 4Å molecular sieves. Toluene was distilled from sodium and stored over 4Å molecular sieves.

Spectral and analytical data of 1h-u.

Tris(4-methoxy-2-methylphenyl)bismuth Dichloride (**1h**): mp 210–220 °C (decomp.); ^{1}H NMR δ 2.70 (s, 9H, Me), 3.85 (s, 9H, OMe), 6.95–6.99 (m, 6H), 7.94 (d, 3H, *J* = 8.4 Hz); FABMS *m/z* 607 (M^+−Cl). Anal. Calcd for $C_{24}H_{27}BiCl_2O_3$: C, 44.81; H, 4.23. Found: C, 45.04; H, 3.93.

Tris(2,4-dimethylphenyl)bismuth Dichloride (**1i**): mp 170–174 °C (decomp.) (lit. 169 °C,[5b]); ^{1}H NMR δ 2.40 (s, 9H, Me), 2.69 (s, 9H, Me), 7.28 (dd, 3H, *J* = 8.4, 2.8 Hz), 7.33 (d, 3H, *J* = 2.8 Hz), 7.90 (d, 3H, *J* = 8.4 Hz); FABMS *m/z* 559 (M^+−Cl).

Tris(4-chloro-2-methylphenyl)bismuth Dichloride (**1j**): mp 154–156 °C (decomp.); ^{1}H NMR δ 2.70 (s, 9H, Me), 7.47 (dd, 3H, *J* = 8.4, 2.4 Hz), 7.53 (d, 3H, *J* = 2.4 Hz), 7.94 (d, 3H, *J* = 8.4 Hz); FABMS *m/z* 619 (M^+−Cl). Anal. Calcd for $C_{21}H_{18}BiCl_5$: C, 38.41; H, 2.76. Found: C, 38.28; H, 2.63.

Tris(2-methyl-4-nitrophenyl)bismuth Dichloride (**1k**): mp 159–162 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 9H, Me), 8.21 (d, 3H, *J* = 8.8 Hz), 8.36 (dd, 3H, *J* = 8.8, 2.4 Hz), 8.45 (d, 3H, *J* = 2.4 Hz); FABMS *m/z* 652 (M^+−Cl). Anal. Calcd for $C_{21}H_{18}BiCl_2N_3O_6$: C, 36.65; H, 2.64; N, 6.11. Found: C, 36.87; H, 2.66; N, 5.86.

Tris(2-ethylphenyl)bismuth Dichloride (**1l**): mp 127–129 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 1.37 (t, 9H, *J* = 7.2 Hz, Me), 3.03 (q, 6H, *J* = 7.2 Hz, CH_2), 7.48 (dt, 3H, *J* = 2.0, 7.6 Hz), 7.52 (dt, 3H, *J* = 1.6,

7.6 Hz), 7.66 (dd, 3H, *J* = 2.0, 7.6 Hz), 8.01 (dt, 3H, *J* = 1.6, 7.6 Hz); FABMS *m*/*z* 559 (M^+−Cl). Anal. Calcd for $C_{24}H_{27}BiCl_2$: C, 48.42; H, 4.57. Found: C, 48.13; H, 4.54.

Tris[2-(trifluoromethyl)phenyl]bismuth Dichloride (**1m**): mp 127–129 °C (decomp.); ^{1}H NMR ($CDCl_3$) δ 7.74 (t, 3H, *J* = 7.8 Hz), 7.84 (dt, 3H, *J* = 1.6, 7.8 Hz), 8.00 (dd, 3H, *J* = 7.6, 1.6 Hz), 8.22 (d, 3H, *J* = 8.0 Hz); FABMS *m*/*z* 679 (M^+−Cl). Anal. Calcd for $C_{21}H_{12}BiCl_2F_9$: C, 35.27; H, 1.69. Found: C, 35.03; H, 1.89.

(4-Methoxyphenyl)bis(4-methylphenyl)bismuth Dichloride (**1n**): mp 127-129 °C (lit.[5a] 120-122 °C); ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 6H, Me), 3.85 (s, 3H, OMe), 7.12 (d, 2H, *J* = 8.6 Hz), 7.44 (d, 4H, *J* = 8.2 Hz), 8.35 (d, 4H, *J* = 8.2 Hz), 8.45 (d, 2H, *J* = 8.6 Hz); FABMS *m*/*z* 533 (M^+−Cl). Anal. Calcd for $C_{21}H_{21}BiCl_2O$: C, 44.31; H, 3.72. Found: C, 44.29; H, 3.73.

Bis(4-methoxyphenyl)(phenyl)bismuth Dichloride (**1o**): glassy solid; ^{1}H NMR ($CDCl_3$): δ 3.85 (s, 6H, OMe), 7.13 (d. 4H, *J* = 9.1 Hz), 7.53 (d, 1H, *J* = 7.2 Hz), 7.64 (t, 2H, *J* = 7.2 Hz), 8.45 (d, 4H, *J* = 9.1 Hz), 8.44–8.47 (m, 2H); FABMS *m*/*z* 535 (M^+−Cl). A good analytical data for **1o** was not obtained, although the spectral data indicated its high state of purity.

Bis(4-chlorophenyl)(4-methoxyphenyl)bismuth Dichloride (**1p**): mp 133–135 °C; ^{1}H NMR ($CDCl_3$): δ 3.86 (s, 3H, OMe), 7.15 (d, 2H, *J* = 9.0 Hz), 7.61 (d, 4H, *J* = 8.8 Hz), 8.43 (d, 2H, *J* = 9.0 Hz), 8.45 (d, 4H, *J* = 8.8 Hz); FABMS *m*/*z* 573 (M^+−Cl). Anal. Calcd for $C_{19}H_{15}BiCl_4O$: C, 37.40; H, 2.48. Found: C, 36.94; H, 2.09.

Bis(4-chlorophenyl)(4-trifluoromethylphenyl)bismuth Dichloride (**1q**): mp 118–120 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ 7.64 (d, 4H, *J* = 6.9 Hz), 7.91 (d, 2H, *J* = 8.1 Hz), 8.49 (d, 4H, *J* = 6.9 Hz), 8.65 (d, 2H, *J* = 8.1 Hz); FABMS *m*/*z* 611 (M^+−Cl). Anal. Calcd for $C_{19}H_{12}BiCl_4F_3$: C, 35.21; H, 1.87. Found: C, 34.99; H, 1.86.

(4-Methoxy-2-methylphenyl)bis(2-methylphenyl)bismuth Dichloride (**1r**): mp 172–174 °C (decomp.); ^{1}H NMR ($CDCl_3$): δ 2.71 (s, 3H, Me), 2.74 (s, 6H, Me), 3.86 (s, 3H, OMe), 6.97–7.00 (m,

2H), 7.42–7.54 (m, 6H), 7.97 (d, *J* = 8.8 Hz, 1H), 8.02 (dd, *J* = 1.6, 7.6 Hz, 2H); FABMS *m*/*z* 547 (M^+–Cl). Anal. Calcd for $C_{22}H_{23}BiCl_2O$: C, 45.30; H, 3.97. Found: C, 45.19; H, 3.85.

(2,4-Dimethylphenyl)bis(2-methylphenyl)bismuth Dichloride (**1s**): mp 156–161 °C; ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H, Me), 2.70 (s, 3H, Me), 2.74 (s, 6H, Me), 7.26–7.54 (m, 8H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 7.2 Hz, 2H); FABMS *m*/*z* 531 (M^+–Cl). Anal. Calcd for $C_{22}H_{23}BiCl_2$: C, 46.58; H, 4.09. Found: C, 46.11; H, 4.03.

(4-Chloro-2-methylphenyl)bis(2-methylphenyl)bismuth Dichloride (**1t**): mp 92–95 °C; ^{1}H NMR ($CDCl_3$): δ 2.72 (s, 3H, Me), 2.74 (s, 6H, Me), 7.44–7.57 (m, 8H), 7.98–8.03 (m, 3H); FABMS *m*/*z* 551 (M^+–Cl). Anal. Calcd for $C_{21}H_{20}BiCl_3$: C, 42.92; H, 3.43. Found: C, 42.63; H, 3.63.

(4-Chlorophenyl)bis(2-methylphenyl)bismuth Dichloride (**1u**): mp 163–165 °C; ^{1}H NMR ($CDCl_3$): δ 2.67 (s, 6H, Me), 7.40–7.51 (m, 6H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 7.6 Hz, 2H), 8.81 (d, *J* = 8.8 Hz, 2H); FABMS *m*/*z* 537 (M^+–Cl). Anal. Calcd for $C_{20}H_{18}BiCl_3$: C, 41.87; H, 3.16. Found: C, 41.62; H, 3.24.

^{1}H NMR data of 2. The structures of **2** were characterized by ^{1}H NMR. In all compounds, the protonated DBU group ($[DBUH]^+$) was observed at δ 1.6–3.5 (total 16 H) and at around δ 10–11 (br-s, 1H, NH). The protons due to the aryl ligands are summarized below.

2a: δ 7.27 (t, 2H, *J* =7.4 Hz), 7.53 (t, 4H, *J* = 7.4 Hz), 8.60 (d, 4H, *J* = 7.4 Hz).

2b: δ 3.78 (s, 6H, OMe), 7.03 (d, 4H, *J* = 8.8 Hz), 8.47 (d, 4H, *J* = 8.8 Hz).

2c: δ 2.28 (s, 6H, Me), 7.32 (d, 4H, *J* = 7.6 Hz), 8.49 (d, 4H, *J* = 7.6 Hz).

2d: δ 7.45 (d, 4H, *J* = 8.4 Hz), 8.52 (d, 4H, *J* = 8.4 Hz).

2e: δ 7.71 (d, 4H, *J* = 7.6 Hz), 8.74 (d, 4H, *J* = 7.6 Hz).

2f: δ 8.25 (d, 4H, *J* = 8.6 Hz), 8.69 (d, 4H, *J* = 8.6 Hz).

2g: δ 2.58 (s, 6H), 7.31 (dd, 2H, *J* = 7.6, 7.3 Hz), 7.44 (dd, 2H, *J* = 7.6, 7.3 Hz), 7.48 (d, 2H, *J* = 7.6

Hz), 8.49 (d, 2H, *J* = 7.6 Hz),

2h: □2.47 (s, 6H, Me), 3.79 (s, 6H, OMe), 6.95 (d, 2H, *J* = 7.2 Hz), 6.97 (s, 2H), 8.27 (d, 2H, *J* = 7.2 Hz).

2i: □2.30 (s, 6H, Me), 2.48 (s, 6H, Me), 7.29 (d, 2H, *J* = 7.4 Hz), 7.30 (s, 2H), 8.36 (d, 2H, *J* = 7.4 Hz).

2j: □2.59 (s, 6H, Me), 7.28 (dd, 2H, *J* = 7.6, 1.6 Hz), 7.38 (d, 2H, *J* = 1.6 Hz), 8.32 (d, 2H, *J* = 7.6 Hz).

2k: □2.47 (s, 6H), 8.03 (d, 2H, *J* = 8.8 Hz), 8.18 (s, 3H), 8.40 (d, 3H, *J* = 8.8 Hz).

2l: □1.24 (t, 6H, *J* = 7.3 Hz), 2.65 (q, 4H, *J* = 7.3 Hz), 7.35 (d, 2H, *J* = 7.2 Hz), 7.40–7.50 (m, 4H), 8.30 (br-s, 2H).

2m: □7.47 (t, 3H, *J* = 7.4 Hz), 7.67 (t, 3H, *J* = 7.4 Hz), 7.90 (d, 3H, *J* = 7.8 Hz), 8.70 (d, 3H, *J* = 7.6 Hz).

2n: □2.32 (s, 3H, Me), 3.78 (s, 3H, OMe), 7.05 (d, 2H, *J* = 8.4 Hz), 7.36 (d, 2H, *J* = 7.6 Hz), 8.43 (d, 2H, *J* = 8.4 Hz), 8.45 (d, 2H, *J* = 7.6 Hz).

2o: □3.78 (s, 3H, OMe), 7.03 (d, 2H, *J* = 8.4 Hz), 7.25 (t, 2H, *J* = 7.6 Hz), 7.51 (t, 1H, *J* = 7.6 Hz), 8.49 (d, 2H, *J* = 8.4 Hz), 8.55 (d, 2H, *J* = 7.6 Hz).

2p: □3.78 (s, 3H, OMe), 7.05 (d, 2H, *J* = 8.8 Hz), 7.44 (d, 2H, *J* = 8.0 Hz), 8.45 (d, 2H, *J* = 8.8 Hz), 8.51 (d, 2H, *J* = 8.0 Hz).

2q: □7.47 (d, 2H, *J* = 8.0 Hz), 7.71 (d, 2H, *J* = 7.8 Hz), 8.57 (d, 2H, *J* = 8.0 Hz), 8.73 (d, 2H, *J* = 7.8 Hz).

2r: □2.57 (s, 3H, Me), 2.58 (s, 3H, Me), 3.78 (s, 3H, OMe), 6.90 (dd, 1H, *J* = 8.4, 2.4 Hz), 6.97 (d, 1H, *J* = 2.4 Hz), 7.30 (t, 1H, *J* = 7.6 Hz), 7.40–7.50 (m, 2H), 8.33 (d, 1H, *J* = 8.4 Hz), 8.50 (d, 1H, *J* = 7.6 Hz).

2s: □2.31 (s, 3H, Me), 2.55 (s, 3H, Me), 2.57 (s, 3H, Me), 7.29 (d, 1H □2, *J* = 7.6 Hz), 7.34 (s, 1H), 7.40–7.50 (m, 2H), 8.34 (d, 1H, *J* = 7.6 Hz), 8.48 (d, 1H, *J* = 7.6 Hz).

2t: □2.57 (s, 3H, Me), 2.63 (s, 3H, Me), 7.30 (d, 1H, *J* = 7.6 Hz), 7.31 (d, 1H, *J* = 7.6 Hz), 7.40 (d, 1H,

J = 7.6 Hz), 7.40–7.50 (m, 2H), 8.39 (d, 1H, *J* = 7.6 Hz), 8.45 (d, 1H, *J* = 7.6 Hz).

2u: □2.67 (s, 3H, Me), 7.15–7.25 (m, 1H), 7.40–7.45 (m, 2H), 7.50 (d, 2H, *J* = 8.4 Hz), 8.36 (dd, 1H, *J* = 7.6, 1.6 Hz), 8.58 (d, 2H, *J* = 8.4 Hz).