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Cis-Bromination of Encapsulated Alkenes

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Contents

1. Experimental Section

Chart 1. Compounds and their labels.[a]

1 $[(L^{Me})Co^{II}_2(\mu\text{-}Cl)]^{1+}$

2 $[(L^{Me})Co^{II}_2(\mu\text{-}O_2CCH{=}CH_2)]^{1+}$

3 $[(L^{Me})Co^{III}_2(\mu\text{-}O_2CCH{=}CH_2)]^{3+}$

4 $[(L^{Me})Co^{III}_2(\mu\text{-}O_2CCHBrCH_2Br)]^{3+}$

5 $[(L^{Me})Co^{II}_2(\mu\text{-}O_2CCHBrCH_2Br)]^{1+}$

6 $[(L^{Me})Co^{III}_2(\mu\text{-}O_2CCH{=}CHPh)]^{3+}$

7 $[(L^{Me})Co^{III}_2(\mu\text{-}\textit{threo}\text{-}O_2CCHBrCHBrPh)]^{3+}$

8 $[(L^{Me})Co^{II}_2(\mu\text{-}\textit{threo}\text{-}O_2CCHBrCHBrPh)]^{1+}$

9 $PhCHBrCHBrCO_2H$ (threo *dl* pair)

10 $PhCHBrCHBrCO_2H$ (erythro *dl* pair)

11 $[(L^{Me})Co^{II}_2(\mu\text{-}\textit{erythro}\text{-}O_2CCHBrCHBrPh)]^{1+}$

12 $[(L^{Me})Co^{III}_2(\mu\text{-}\textit{erythro}\text{-}O_2CCHBrCHBrPh)]^{3+}$

[a] The complexes were isolated as ClO_4^- or BPh_4^- salts.

General: Unless otherwise noted the preparations of the metal complexes were carried out under an argon atmosphere by using standard Schlenk techniques. The compounds $H_2L^{Me}{\cdot}6HCl$, $[(L^{Me})Co_2(\mu\text{-}Cl)]ClO_4$ (**1**$\cdot ClO_4$) and $[(L^{Me})Co^{III}_2(\mu\text{-}O_2CCH{=}CHPh)](ClO_4)_3$ (**6**$\cdot(ClO_4)_3$) were prepared as described in the literature (see B. Kersting, G. Steinfeld, *Inorg. Chem.* **2002**, *41*, 1140-1150). All other compounds and reagents were purchased from Aldrich. Melting points were determined in capillaries and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX-200 or a Varian 300 unity spectrometer. Elemental analysis were performed on a Vario EL analyzer (Elementaranalysensysteme GmbH). All compounds crystallize with solvent molecules (see crystal structures of **8**$\cdot BPh_4\cdot CH_3CN\cdot H_2O$ and **11**$\cdot ClO_4\cdot$2MeOH), but the compounds slowly loose their solvent molecules upon standing in air. This is why the observed microanalytical

data do not always fit exactly with the calculated values (for the solvent-free compounds). The analytical data of the $Co^{III}Co^{III}$ complexes **3**·$(ClO_4)_3$, **4**·$(ClO_4)_3$**,** **7**·$(ClO_4)_3$ and **12**·$(ClO_4)_3$, on the other hand, can be improved if water molecules of solvent of crystallization are included in the calculations. This is appropiate since the crystal structure of complex **6**·$(ClO_4)_3$ (crystallized in a manner similar to **3**, **4**, **7** and **12**) shows an acetonitrile and three water molecules of solvent of crystallization (see *Inorg. Chem.* **2002**, *41*, 1140-1150)). Therefore the $Co^{III}Co^{III}$ complexes are formulated with water molecules of solvent of crystallization. The observed and calculated values lie in an acceptable range. CHN analysis IR spectra were taken on a Bruker VECTOR 22 FT-IR-spectrophotometer as KBr pellets. Electronic absorption spectra were recorded on a Jasco V-570 UV/vis/near IR spectrophotometer. Cyclic voltammetry measurements were carried out at 25 °C with an EG&G Princeton Applied Research potentiostat/galvanostat model 263 A. The cell contained a Pt working electrode, a Pt wire auxiliary electrode, and a Ag wire as reference electrode. Concentrations of solutions were 0.10 M in supporting electrolyte ($n$$Bu_4NPF_6$) and ca. 1×10^{-3} M in sample. Cobaltocene was used as internal standard. Under our experimental conditions $E(Cp_2Co^+/Cp_2Co) = -1.345$ V vs Cp_2Fe^+/Cp_2Fe. All potentials were converted to the SCE reference using tabulated values (Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877–910).

2,3-Dibromo-propionic acid. To an ice cold solution of acrylic acid (3.00 g, 41.6 mmol) in carbon disulfide (5 mL) was added bromine (6.65 g, 41.6 mmol). The reaction mixture was stirred for 3 h during which time colorless crystals of the title compound precipitated. Yield: 4.30 g (45 %). M.p. 63-64°C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.23 (s *br*, 1H, OH), 4.49 (m, 1H, C*H*), 3.91 (m, 1H, C*H*), 3.69 (m, 1H, C*H*).

Caution ! *Perchlorate salts of transition metal complexes are hazardous and may explode.*

Only small quantities should be prepared and great care taken.

[(L^{Me})Co^{II}_2(μ-$O_2CCH=CH_2$)](ClO_4) (2·ClO_4). A solution of sodium acrylate (19 mg, 0.20 mmol) in methanol (5 mL) was added to a solution of the perchlorate salt **1**·ClO_4 (92 mg, 0.10 mmol) in methanol (30 mL). The mixture was stirred for 2 h during which time the color of the solution turned from brown to pale red. A solution of $LiClO_4 \cdot 3H_2O$ (400 mg, 2.50 mmol) in methanol (2 mL) was added. The resulting pale red microcrystalline solid was isolated by filtration, washed with methanol and dried in air. This material was recrystallized once from a mixed ethanol/acetonitrile (1:1) solvent system. Yield: 84 mg (88 %). M.p. 358-360° C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 444 (450), 463 (sh, 340), 523 (189), 544 (sh, 142), 1250 nm (34 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1639 [ν(C=C)], 1578 [$\nu_{as}(RCO_2^-)$], 1430 [$\nu_s(RCO_2^-)$], 1090 vs [$\nu(ClO_4^-)$]. CV (CH_3CN, 295 K, 0.1 M $^nBu_4NPF_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.22 (0.14 V), $E^2_{1/2}$ = +0.59 (ΔE_p 0.14 V). The tetraphenylborate salt, [(L^{Me})Co^{II}_2(μ-$O_2CCH=CH_2$)](BPh_4) (**2**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **2**·ClO_4 (96 mg, 0.10 mmol) in methanol (40 mL). The resulting pale red solid was recrystallized from a mixed ethanol/acetonitrile solution. Yield: 101 mg (86 %). M.p. 298° C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 443 (645), 462 (sh, 512), 523 (271), 543 (sh 204), 1247 nm (51 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1638 [ν(C=C)], 1577 [$\nu_{as}(RCO_2^-)$], 1430 [$\nu_s(RCO_2^-)$], 732, 703 (BPh_4^-). Elemental analysis calcd (%) for $C_{65}H_{87}BCo_2N_6O_2S_2$ (M_w 1177.23): C 66.32, H 7.45, N 7.14, S 5.45; found: C 65.58, H 6.67, N 6.78, S 5.17.

[(L^{Me})Co^{III}_2(μ-$O_2CCH=CH_2$)](ClO_4)$_3$ (3·(ClO_4)$_3$). A solution of bromine (80 mg, 0.50 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **2**·ClO_4 (191 mg, 0.20 mmol) in acetonitrile (25 mL). During addition the temperature was kept at 0° C by external cooling with an ice-bath. The resulting dark brown solution was stirred for further 2 min to ensure complete oxidation of the educt. The reaction mixture was then evaporated to dryness by using a rotary evaporator and the brown-black residue redissolved in acetonitrile (10 mL). This latter procedure was repeated twice to remove the excess oxidant. Then the residue was dissolved in 20 mL of acetonitrile and a solution of $LiClO_4·3H_2O$ (400 mg, 2.50 mmol) in ethanol (20 mL) was added to give the title compound as a black microcrystalline precipitate. The crystals were quickly filtered, washed with a little ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 157 mg (68 %). M.p. 218-220°C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 468 (10584), 641 nm (2339 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1635 [ν(C=C)], 1519 [ν_{as}(C–O)], 1428 [ν_s(C–O)], 1090 vs [$\nu(ClO_4^-)$]. ^{1}H NMR (200 MHz, CD_3CN, resonances in the region 2.0 to 4.5 ppm are broad and were not assigned): δ = 7.31 (s, 4 H, ArH), 5.3-5.2 (m, 3H, $CH=CH_2$), 1.23 (s, 18H, $C(CH_3)_3$). CV (CH_3CN, 295 K, 0.1 M ^{n}Bu$_4$NPF$_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.22 (0.11 V), $E^2_{1/2}$ = +0.60 (ΔE_p 0.12 V). Elemental analysis calcd (%) for $C_{41}H_{67}Cl_3Co_2N_6O_{14}S_2·2H_2O$ (M_w 1192.39): C 41.30, H 6.00, N 7.05, S 5.38; found: C 40.96, H 6.00, N 6.89, S 4.98.

[(L^{Me})Co^{III}_2(μ-$O_2CCHBrCH_2Br$)](ClO_4)$_3$ (4·(ClO_4)$_3$). To a stirred solution of **3**·(ClO_4)$_3$ (116 mg, 0.100 mmol) in acetonitrile (20 mL) was added a solution of bromine (160 mg, 1.00 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 4 days at ambient temperature. To remove the excess oxidant the reaction mixture was evaporated to dryness

and the brown-black residue redissolved in acetonitrile (10 mL). This latter procedure was repeated twice. Then the residue was dissolved in 20 mL of acetonitrile and a solution of $LiClO_4 \cdot 3H_2O$ (400 mg, 2.50 mmol) in ethanol (20 mL) was added to give the title compound as a black microcrystalline precipitate. The crystals were filtered, washed with a little ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 103 mg (78 %). M.p. 204-205°C (decomp.). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1559 [$\nu_{as}(RCO_2^-)$], 1386 [$\nu_s(RCO_2^-)$], 1090 vs [$\nu(ClO_4^-)$]. ^{1}H NMR (200 MHz, CD_3CN, resonances in the region 4.3 to 2.5 ppm are broad and were not assigned): δ = 7.39 (s, 4 H, ArH), 1.27 (s, 18H, $C(CH_3)_3$). CV (CH_3CN, 295 K, 0.1 M $^nBu_4NPF_6$, ν = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.31 (0.14 V), $E^2_{1/2}$ = +0.70 (ΔE_p 0.12 V). Elemental analysis calcd (%) for $C_{41}H_{67}Br_2Cl_3Co_2N_6O_{14}S_2 \cdot 2H_2O$ (M_w 1352.20): C 36.42, H 5.29, N 6.22, S 4.74; found: C 36.77, H 4.89, N 5.95, S 4.23. Oxidation of complex **5**·(ClO_4) with bromine (vide below) also yields this compound.

[(L^{Me})Co^{II}_2(μ-$O_2CCHBrCH_2Br$)](ClO_4) (5·ClO_4). To a solution of **4**·$(ClO_4)_3$ (132 mg, 0.100 mmol) in acetonitrile (40 mL) was added a solution of $NaBH_4$ (5 mg) in methanol (2 mL). The resulting pale-red reaction mixture was diluted with ethanol (40mL) and then concentrated in vacuo to about one fifth of its original volume, whereupon the product precipitated as pale-red microcrystals. The crystals were filtered, washed with a little ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 48 mg (43 %). M.p. 328° C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 448 (551), 468 (sh, 443), 525 (194), 544 (sh, 149), 1246 nm (38 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1627 [ν_{as}(C–O)], 1394 [ν_s(C–O)]. CV (CH_3CN, 295 K, 0.1 M $^nBu_4NPF_6$, ν = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.30 (0.11 V), $E^2_{1/2}$ = +0.69 (ΔE_p 0.12 V). Elemental analysis calcd (%)

for $C_{41}H_{67}Br_2ClCo_2N_6O_6S_2$ (M_w 1117.27): C 44.08, H 6.04, N 7.52, S 5.74; found: C 44.15, H 6.07, N 7.44, S 5.34. The tetraphenylborate salt, $[(L^{Me})Co^{II}_2(\mu\text{-}O_2CCHBrCH_2Br)](BPh_4)$ (**5**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **5**·ClO_4 (112 mg, 0.10 mmol) in methanol (40 mL). The resulting pale red solid was recrystallized from a mixed ethanol/acetonitrile solution. Yield: 123 mg (92 %). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1627 [$\nu_{as}(RCO_2^-)$], 1394 [$\nu_s(RCO_2^-)$], 732, 704 [$\nu(BPh_4^-)$]. Elemental analysis calcd (%) for $C_{65}H_{87}BBr_2Co_2N_6O_2S_2$ (M_w 1337.04): C 58.39, H 6.56, N 6.29, S 4.80; found: C 60.14, H 6.86, N 6.35, S 4.80. The reaction of complex **1**·ClO_4 with the sodium salt of 2,3-dibromo-propionic acid also gives complex **5**·ClO_4 (73 %).

$[(L^{Me})Co^{III}_2(\mu\text{-}threo\text{-}O_2CCHBrCHBrPh)](ClO_4)_3$ (7·$(ClO_4)_3$). To a stirred solution of **6**·$(ClO_4)_3$ (123 mg, 0.100 mmol) in acetonitrile (20 mL) was added a solution of bromine (160 mg, 1.00 mmol) in acetonitrile (2 mL). The reaction mixture was stirred for 6 h at ambient temperature. The reaction mixture was then evaporated to dryness by using a rotary evaporator and the brown-black residue redissolved in acetonitrile (10 mL). This latter procedure was repeated twice to remove the excess oxidant. A solution of $LiClO_4 \cdot 3H_2O$ (400 mg, 2.50 mmol) in ethanol (20 mL) was finally added to give the title compound as a black microcrystalline precipitate. The crystals were filtered, washed with a little ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 97 mg (70 %). M.p. 197°C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 467 (7697), 653 nm (1640 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1560 [$\nu_{as}(RCO_2^-)$], 1384 [$\nu_s(RCO_2^-)$], 1097 vs [$\nu(ClO_4^-)$]. ^{1}H NMR (200 MHz, CD_3CN, resonances in the region 2.0 to 4.5 ppm are broad and were not assigned): δ = 7.42 (s, 4 H, ArH), 7.17 (d, 1H, ^3J = 2 Hz,PhCHBr), 7.13 (m, 2H, Ar*H*), 7.11-7.04 (m, 3H, Ar*H*), 5.00 (d,

1H, ^3J = 2 Hz, C*H*BrCO$_2$), 1.18 (s, 18H, C(CH$_3$)$_3$). CV (CH$_3$CN, 295 K, 0.1 M ^{n}Bu$_4$NPF$_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.32 (0.13 V), $E^2_{1/2}$ = +0.69 (ΔE_p 0.18 V). $C_{47}H_{71}Br_2Cl_3Co_2N_6O_{14}S_2 \cdot 2H_2O$ (M_w 1428.29): C 39.52, H 5.29, N 5.88, S 4.49; found: C 39.06, H 5.38, N 5.82, S 4.04.

[(L^{Me})Co$^{II}_2$(*μ-threo*-O$_2$CCHBrCHBrPh)](ClO$_4$) (8·ClO$_4$). To a solution of **7**·(ClO$_4$)$_3$ (139 mg, 0.100 mmol) in acetonitrile (40 mL) was added a solution of NaBH$_4$ (5 mg, 0.132 mol) in methanol (2 mL). The resulting pale-red reaction mixture was diluted with ethanol (40mL) and then concentrated in vacuo to about one fifth of its original volume, whereupon the product precipitated as pale-red microcrystals. The crystals were filtered, washed with a little ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 90 mg (75 %). M.p. 276–278° C (decomp.). UV/Vis (CH$_3$CN): λ_{max} (ε) = 445 (467), 467 (sh, 400), 523 (170), 542 (sh, 121), 565 (sh, 64), 1262 nm (33 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1627 [ν_{as}(C–O)], 1394 [ν_s(C–O)]. CV (CH$_3$CN, 295 K, 0.1 M ^{n}Bu$_4$NPF$_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.32 (0.08 V), $E^2_{1/2}$ = +0.70 (ΔE_p 0.12 V). The tetraphenylborate salt, [(L^{Me})Co$^{II}_2$(*μ-threo*-O$_2$CCHBrCH$_2$BrPh)](BPh$_4$) (**8**·BPh$_4$), was prepared by adding NaBPh$_4$ (342 mg, 1.00 mmol) to a solution of **8**·ClO$_4$ (119 mg, 0.100 mmol) in methanol (40 mL). The resulting pale red solid was recrystallized from a mixed ethanol/acetonitrile solution. Yield: 123 mg (87 %). M.p. 276-278° C (decomp.). UV/Vis (CH$_3$CN): λ_{max} (ε) = 449 (530), 470 (sh, 480), 524 (210), 544 (sh, 160), 1246 nm (40 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1627 [ν_{as}(RCO$_2^-$)], 1394 [ν_s(RCO$_2^-$)], 732, 704 [ν(BPh$_4^-$)]. Elemental analysis calcd (%) for $C_{71}H_{91}BBr_2Co_2N_6O_2S_2$ (M_w 1413.14): C 60.35, H 6.49, N 5.95, S 4.54; found: C 60.70, H 7.00, N 5.95, S 4.04. This compound was additionally characterized by X-ray crystallography. The hydrolysis of **8**·ClO$_4$ produces *threo*-2,3-dibromo-

3-phenyl-propionic acid (vide infra).

DL-*threo*-2,3-dibromo-3-phenylpropionic acid (9). This acid was prepared by hydrolysis of the dicobalt(II) complex [(L^{Me})Co_2(*μ-threo*-O_2CCHBrCHBrPh)]ClO_4 (**8**·ClO_4). To a solution of **8**·ClO_4 (1.19 g, 1.00 mmol) in methanol 100 mL was added 6 M HCl (10 mL). The reaction mixture was stirred for further 12 h to ensure complete hydrolysis of the starting material. After the solution was evaporated to dryness, water (60 mL) and ether (20 mL) were added to the residue and the resulting suspension was acidified with 6M HCl (5 mL). The mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with ether (2 × 20 mL). The organic extracts were combined and dried with magnesium sulfate. Evaporation of the solvent gave DL-*threo*-2,3-dibromo-3-phenylpropionic acid **9** as a white foamy solid. Yield: 250 mg (81 %). ^{1}H NMR (200 MHz, CD_3OD): δ 7.54-7.49 (m, 2H, Ar*H*), 7.40-7.32 (m, 3H, ArH), 5.39 (d, 1H, ^3J = 10.2 Hz, PhC*H*Br), 4.96 (d, 1H, ^3J = 10.2 Hz, C*H*BrCO_2H).

DL-*erythro*-2,3-dibromo-3-phenylpropionic acid (10). DL-*erythro*-2,3-dibromo-3-phenylpropionic acid was prepared according to the literature procedure (A. Michael, *Chem. Ber*. **1901**, *34*, 3664-3666). Yield 80 %. M.p. 205-206° C (lit. 200-205°). ^{1}H NMR (200 MHz, CD_3OD): δ 7.54-7.46 (m, 2H, Ar*H*), 7.45-7.37 (m, 3H, ArH), 5.42 (d, 1H, ^3J = 11.7 Hz, PhC*H*Br), 5.04 (d, 1H, ^3J = 11.7 Hz, C*H*BrCO_2H).

[(L^{Me})Co^{II}_2(*μ-erythro*-O_2CCHBrCHBrPh)](ClO_4) (11·ClO_4). A solution of sodium D,L-*erythro*-2,3-dibromo-3-phenyl-propionate (66 mg, 0.20 mmol) in methanol (5 mL) was added to a solution of the perchlorate salt **1**·ClO_4 (92 mg, 0.10 mmol) in methanol (30 mL). The mixture was stirred for 2 h during which time the color of the solution turned from brown to

pale red. A solution of $LiClO_4 \cdot 3H_2O$ (800 mg, 5.00 mmol) in methanol (2 mL) was added. The resulting pale red microcrystalline solid was isolated by filtration, washed with methanol and dried in air. Yield: 95 mg (80 %). M.p. 272–274° C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 449 (634), 466 (sh, 482), 527 (205), 546 (176), 1246 nm (36 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1623 [$\nu_{as}(RCO_2^-)$], 1393 [$\nu_s(RCO_2^-)$], 1097 [$\nu(ClO_4^-)$]. CV (CH_3CN, 295 K, 0.1 M $^nBu_4NPF_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.30 (0.08 V), $E^2_{1/2}$ = +0.68 (ΔE_p 0.12 V). This compound was additionally characterized by X-ray crystallography. The tetraphenylborate salt, [(L^{Me})Co^{II}_2(*μ-erythro*-$O_2CCHBrCHBrPh$)](BPh_4) (**9**·BPh_4), was prepared by adding $NaBPh_4$ (342 mg, 1.00 mmol) to a solution of **9**·ClO_4 (119 mg, 0.100 mmol) in methanol (40 mL). The resulting pale red solid was recrystallized from a mixed ethanol/acetonitrile solvent system. Yield: 120 mg (85 %). M.p. 243° C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 450 (703), 468 (sh, 524), 527 (230), 546 (198), 1250 nm (39 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1622 [$\nu_{as}(RCO_2^-)$], 1393 [$\nu_s(RCO_2^-)$], 732, 703 [$\nu(BPh_4^-)$]. Elemental analysis calcd (%) for $C_{71}H_{91}BBr_2Co_2N_6O_2S_2$ (M_w 1413.14): C 60.35, H 6.49, N 5.95, S 4.54; found: C 60.46, H 6.39, N 6.00, S 4.45.

[(L^{Me})Co^{III}_2(*μ-erythro*-$O_2CCHBrCHBrPh$)](ClO_4)$_3$ (12·(ClO_4)$_3$). A solution of bromine (80 mg, 0.50 mmol) in acetonitrile (5 mL) was added dropwise to a solution of **11**·ClO_4 (239 mg, 0.20 mmol) in acetonitrile (25 mL). During addition the temperature was kept at 0° C. The resulting dark brown solution was stirred for a further 2 min to ensure complete oxidation of **11**·ClO_4. The reaction mixture was then evaporated to dryness and the brown-black residue redissolved in acetonitrile (10 mL). This latter procedure was repeated twice to remove the excess oxidant. A solution of $LiClO_4 \cdot 3H_2O$ (400 mg, 2.50 mmol) in ethanol (20 mL) was finally added to precipitate the title compound. The black crystals were filtered, washed with

ethanol and dried in air. An analytical sample was obtained by recrystallisation from a mixed acetonitrile/ethanol (1:1) solvent system. Yield: 203 mg (73 %). M.p. 196–198°C (decomp.). UV/Vis (CH_3CN): λ_{max} (ε) = 471 (11819), 652 (2655 $M^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\nu}$ = 1550 [ν_{as}(C–O)], 1390 [ν_s(C–O)], 1090 vs [$\nu(ClO_4^-)$]. ^{1}H NMR (CD_3CN): δ = 7.43-7.15 (m, 4+5H, ArH), 4.77 (d, ^3J = 11.9 Hz, 1H, PhC*H*Br), 4.52 (d, ^3J = 11.9 Hz, 1H, C*H*BrCO_2^-), 1.19 (s br, 18H, C(C*H*$_3$)$_3$). CV (CH_3CN, 295 K, 0.1 M ^{n}Bu$_4$NPF$_6$, v = 100 mV/s; E (V) vs SCE): $E^1_{1/2}$ = +0.30 (0.12 V), $E^2_{1/2}$ = +0.68 (ΔE_p 0.12 V). Elemental analysis calcd (%) for $C_{47}H_{71}Br_2Cl_3Co_2N_6O_{14}S_2 \cdot 2H_2O$ (M_w 1428.29): C 39.52, H 5.29, N 5.88, S 4.49; found: C 39.79, H 5.78, N 5.57, S 4.07.

2. Crystal structure determinations

Single crystals of **8**·$BPh_4 \cdot CH_3CN \cdot H_2O$ and of **11**·ClO_4·2MeOH suitable for X-ray structure analysis were grown from an acetonitrile/methanol (1:1) mixed solvent system. The crystals were mounted on glass fibers using perfluoropolyether oil. Intensity data were collected at 210(2) K, using a Bruker SMART CCD diffractometer. Graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) was used throughout. The data were processed with SAINT and corrected for absorption using SADABS (transmission factors: 1.00–0.78 for **8** and 1.00–0.78 for **11**). The structures were solved by direct methods using the program SHELXS-86, and refined by full-matrix least-squares techniques against F^2 using SHELXL-97. PLATON was used to search for higher symmetry. Unless otherwise noted all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to idealized positions and given isotropic thermal parameters 1.2 times (1.5 times for CH_3 groups) the thermal parameter of the atoms to which they were attached.

Crystal data for **8**·$BPh_4 \cdot CH_3CN \cdot H_2O$: $C_{73}H_{96}BBr_2Co_2N_7O_3S_2$ (M_r = 1472.18); crystal size 0.42

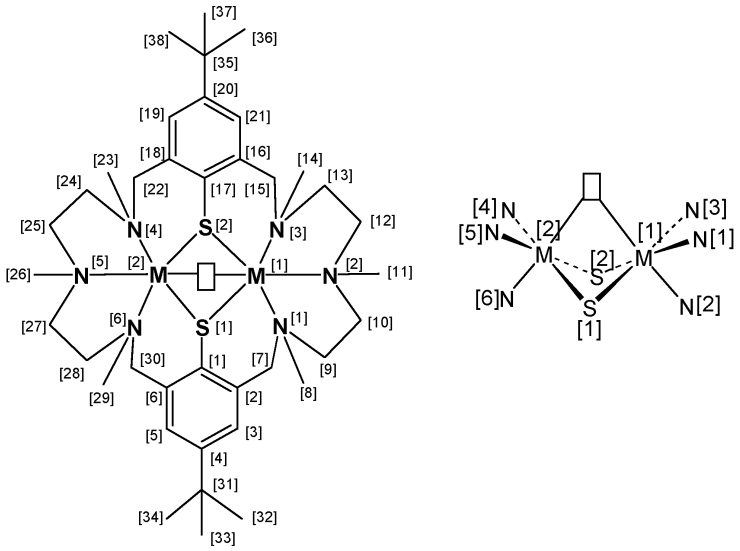
× 0.30 × 0.30 mm^3; triclinic, space group *P*1-bar (no. 2), with a = 13.444(3), b = 16.860(3), c = 18.293(4) Å, α = 96.89(3)°, β = 104.32(3)°, γ = 103.80(3)°, Z = 2, V = 3830.4(14) $Å^3$, ρ_{calcd} = 1.276 $g \cdot cm^{-3}$, $2\theta_{max}$ = 58.56°, μ(Mo-K_α) = 1.578 mm^{-1}, 35025 reflections measured, 18152 unique (R_{int} = 0.0943), 5725 observed reflections [$I > 2\sigma(I)$]. The following groups were found to be disordered over two positions: one *t*-butyl group of the macrocyclic ligand, the carboxylato coligand, the acetonitrile and the water molecules of solvent of crystallisation. The C, N, O and Br atoms of the disordered groups were refined isotropically. A split atom model was applied for the disordered *t*Bu group and the carboxylato coligand. The site occupancies of the two orientations were refined as 0.65(1)/0.35(1) [for C(36a/b), C(37a/b), C(38a/b)] and 0.53(1)/0.47(1) [for Br(1a/b), C(41a/b), Br(2a/b), C(42a/b)-C47(a/b)]. One of the phenyl rings C(42a)-C(47a) was found from Fourier maps, the other one was calculated (routine AFIX 66 in SHELXL 97) and refined as a rigid group. The solvent (acetonitrile and water) molecules are disordered over two positions at half occupancy. No hydrogen atoms were calculated for the disordered moieties, except for the *t*-butyl group. Final residuals: R1 = 0.0696, wR2 = 0.1866 [for 5725 reflections with $I > 2\sigma(I)$], R1 = 0.2158, wR2 = 0.2460 (for all data); 800 parameter; largest difference peak/hole: 1.011/–0.958 $e \cdot A^{-3}$. **[CCDC 202751]**

Crystal data for **11**·ClO_4·2MeOH: $C_{49}H_{79}Br_2ClCo_2N_6O_8S_2$ (M_r = 1257.43); crystal size 0.30 × 0.30 × 0.30 mm^3; monoclinic, space group $P2_1/c$ (no. 14), with a = 15.712(3), b = 27.223(5), c = 14.095(3) Å, β = 113.80(3)° , Z = 4, V = 5516(2) $Å^3$, ρ_{calcd} = 1.514 $g \cdot cm^{-3}$, $2\theta_{max}$ = 58.12°, μ(Mo-K_α) = 2.230 mm^{-1}, 34915 reflections measured, 13402 unique (R_{int} = 0.1071), 4288 observed reflections [$I > 2\sigma(I)$]. Final residuals: R1 = 0.0612, wR2 = 0.1381 [for 4288 reflections with $I > 2\sigma(I)$], R1 = 0.2195, wR2 = 0.2047 (for all data); 631 parameter; largest difference peak/hole: 0.769/–1.249 $e \cdot A^{-3}$. **[CCDC 202752]**

Crystallographic data (excluding structure factors) for the structure(s) reported in this paper

have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-202751 and 202752. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk.

3. Figures of the molecular structures of the complexes



Scheme 1. The atomic labeling scheme used for the complexes reported in this paper. The box represents the free coordination site of the complexes. For atomic labeling of the coligands see Figures S1-S2.

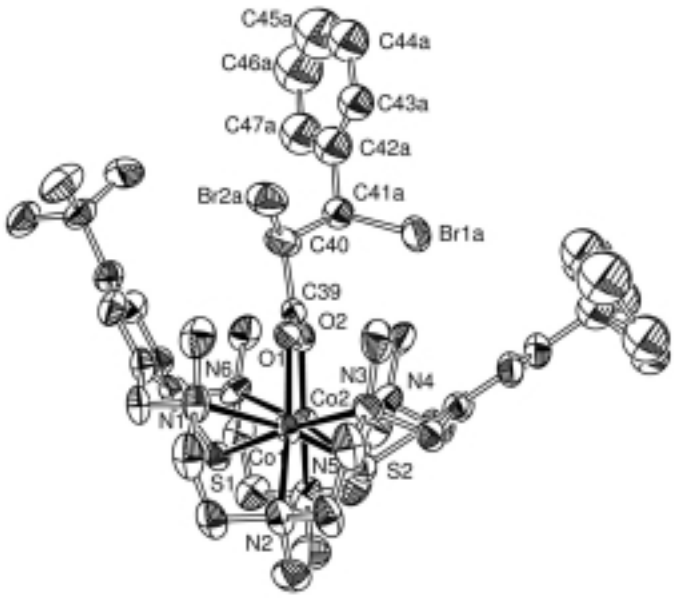


Figure S1. Structure of the dicobalt(II) complex **8** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only one orientation of the disordered carboxylate ligand is displayed.

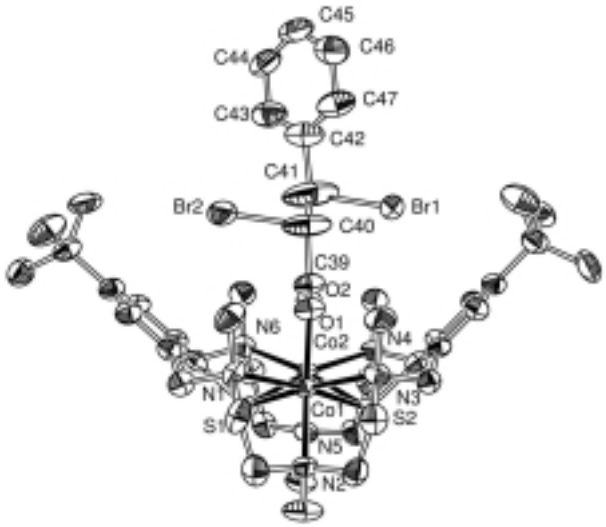


Figure S2. Structure of the dicobalt(II) complex **11** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

4. Table S1. Selected bond lengths [Å] of cobalt complexes 8 and 11.

	8 (M = Co)	**11** (M = Co)
M(1)–O(1)	2.046(5)	2.033(5)
M(1)–N(1)	2.356(6)	2.254(6)
M(1)–N(2)	2.207(6)	2.164(6)
M(1)–N(3)	2.253(6)	2.261(6)
M(1)–S(1)	2.528(2)	2.443(2)
M(1)–S(2)	2.431(2)	2.499(2)
M(2)–O(2)	2.042(5)	2.048(5)
M(2)–N(4)	2.259(6)	2.302(6)
M(2)–N(5)	2.176(7)	2.159(6)
M(2)–N(6)	2.348(5)	2.250(7)
M(2)–S(1)	2.527(2)	2.451(2)
M(2)–S(2)	2.466(2)	2.454(2)

5. Kinetic measurements

The temperature dependence of the bromination of compound **6**·$(ClO_4)_3$ was examined using ^{1}H NMR spectroscopy. The reaction was carried out at four different temperatures (300, 310, 320, 330 K). All reactions were run under pseudo-first-order conditions with [Br_2] in a ca 15-fold molar excess over [**6**·$(ClO_4)_3$]. In a typical experiment 1.0 mL of a ca 6×10^{-3} M solution of complex **6**·ClO_4 in CD_3CN was mixed with 15-20 mg of Br_2 and immediately transferred to an ^{1}H NMR tube. The spectra were recorded at appropiate intervals of time. Figures S3 and S4 show two representative ^{1}H NMR spectra.

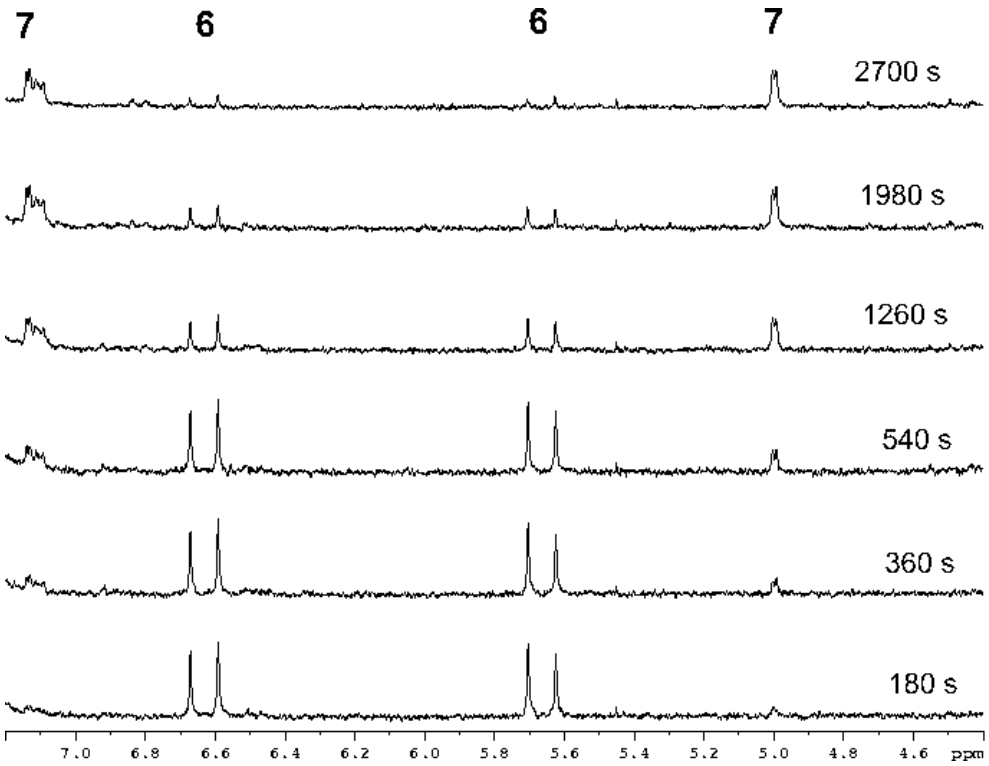


Figure S3. ^{1}H NMR spectra recorded as a function of time at 200 MHz and 330 K for a mixture of **6**·$(ClO_4)_3$ ($6.25 \cdot 10^{-3}$ M) and Br_2 (0.098 M) in CD_3CN solution in the 7.20-4.40 ppm region.

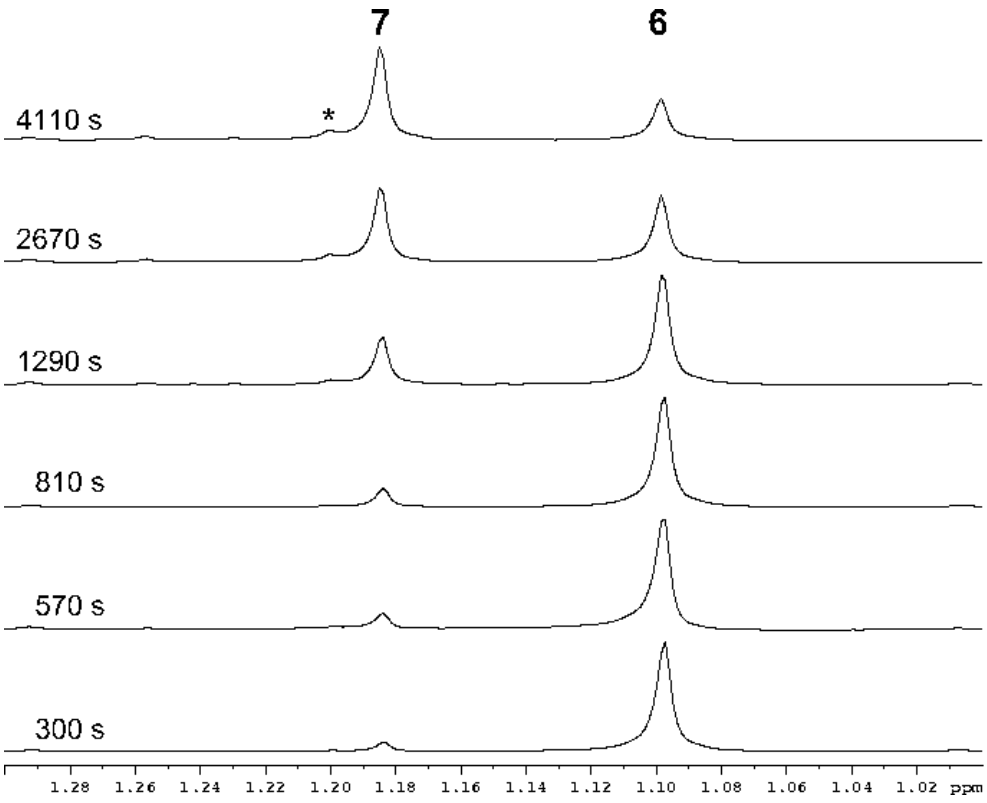


Figure S4. ^{1}H NMR spectra obtained as a function of time at 200 MHz and 300 K for a mixture of **6**·$(ClO_4)_3$ (6.17 M) and Br_2 (0.13 M) in CD_3CN solution in the *t*-butyl region (1.30-1.00 ppm). The feature at δ = 1.21 ppm (marked with an asterisk) is due to compound **12**.

The reaction was followed by monitoring the decrease in intensity of the ^{1}H NMR signal for the *t*-butyl protons of **6** at δ = 1.10 and the increase in intensity of the ^{1}H NMR signal for the *t*-butyl protons of **7** at δ = 1.18 ppm. The relative concentrations of **6** and **7** were determined by integration of the signals. Table S2 lists the experimental data.

Table S2. Relative concentrations of compound **6** as a function of time and temperature.

Exp. 1 conditions: T = 300 K $[Br_2]$ =6.83×10^{-2} M $[\mathbf{6}_{t=0}]$ = 4.39×10^{-3} M		Exp. 2 conditions: T = 300 K $[Br_2]$ =13.27×10^{-2} M $[\mathbf{6}_{t=0}]$ = 6.17×10^{-3} M		Exp. 3 conditions: T = 310 K $[Br_2]$ = 8.52×10^{-2} M $[\mathbf{6}_{t=0}]$ = 4.43×10^{-3} M		Exp. 4 conditions: T = 310 K $[Br_2]$ = 9.99×10^{-2} M $[\mathbf{6}_{t=0}]$ = 5.99×10^{-3} M	
t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$
0	1.000	0	1.000	0	1.000	0	1.000
900	0.877	300	0.922	300	0.907	198	0.924
1800	0.786	470	0.878	600	0.851	384	0.883
2700	0.702	570	0.867	1200	0.734	558	0.848
3600	0.624	690	0.837	1800	0.644	738	0.806
4500	0.555	810	0.812	2400	0.559	918	0.775
5400	0.494	930	0.788	3000	0.474	1098	0.738
6300	0.440	1050	0.764	3600	0.423	1278	0.701
7200	0.394	1170	0.741	4200	0.359	1458	0.667
8100	0.348	1290	0.720	4800	0.308	1638	0.633
9000	0.303	1560	0.672	5400	0.265	1878	0.595
10800	0.241	1710	0.644	6000	0.221	2058	0.567
12600	0.184	1950	0.609	6600	0.188	2256	0.542
14100	0.155	2190	0.565	7320	0.156	2388	0.516
		2400	0.539	8100	0.126	2670	0.478
		2670	0.502	8700	0.113	3018	0.434
		2910	0.471	9900	0.087	3318	0.403
		3150	0.439	10500	0.069	3618	0.371
		3390	0.418			3948	0.343
		3630	0.388				
		3780	0.362				
		4110	0.348				
		4290	0.327				

Exp. 5 conditions: T = 320 K $[Br_2]$ =7.53×10^{-2} M $[\mathbf{6}_{t=0}]$ = 4.47×10^{-3} M		Exp. 6 conditions: T = 320 K $[Br_2]$ =10.51×10^{-2} M $[\mathbf{6}_{t=0}]$ = 6.09×10^{-3} M		Exp. 7 conditions: T = 330 K $[Br_2]$ =7.43×10^{-2} M $[\mathbf{6}_{t=0}]$ = 4.50×10^{-3} M		Exp. 8 conditions: T = 330 K $[Br_2]$ = 9.76×10^{-2} M $[\mathbf{6}_{t=0}]$ = 6.25×10^{-3} M	
t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$	t /s	$\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]}$
0	1.000	0	1.000	0	1.000	0	1.000
420	0.902	246	0.904	600	0.799	180	0.908
600	0.847	366	0.855	720	0.756	360	0.833
1500	0.668	552	0.798	1320	0.614	540	0.760
2400	0.532	726	0.746	1920	0.491	720	0.691
3300	0.416	906	0.701	2520	0.394	900	0.631
4200	0.330	1146	0.633	3120	0.322	1092	0.570
5100	0.258	1266	0.598	3720	0.256	1260	0.525
6000	0.207	1446	0.562	4320	0.211	1440	0.483
6900	0.164	1626	0.523	4920	0.169	1620	0.444
7800	0.133	1806	0.490	5520	0.136	1806	0.387
8700	0.106	1986	0.445			1980	0.361
9600	0.080	2172	0.418			2160	0.329
		2346	0.387			2352	0.312
		2526	0.359			2520	0.275
		2706	0.341			2700	0.251

For each experiment, a plot of -*ln*([**6**(t)]/([**6**(t)] + [**7**(t)]) vs *t* is linear, indicating that the pseudo-first order rate law in equation 1 is obeyed (R. G. Wilkins, Kinetics and Mechanism of Reactions of Transition Metal Complexes, 2nd.ed, VCH, Weinheim, **1991**). Figure S5 shows a representative example (Experiment 3).

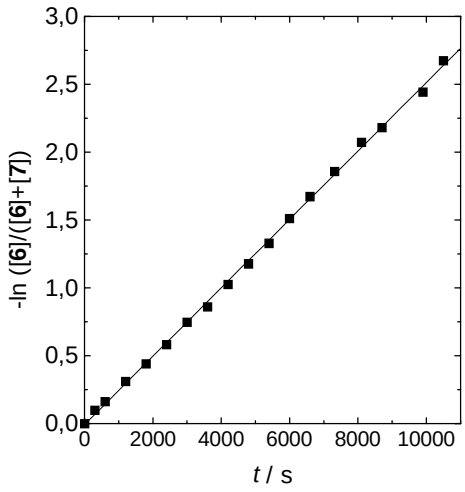


Figure S5. Plot of -ln([**6**]/[**6**]+[**7**]) vs *t*.

The values of *k*' were obtained from linear regression analysis of the dependence of the rate law, and the concentration-independent rate constants *k* from equation 2. Table S3 lists the concentration-independent rate constants *k*.

$$-\ln\frac{[\mathbf{6}(t)]}{[\mathbf{6}_{t=0}]} = -\ln\frac{[\mathbf{6}(t)]}{[\mathbf{6}(t)]+[\mathbf{7}(t)]} = k[\mathrm{Br}_2]\cdot t = k'\cdot t \qquad (1)$$

$$k = k'/[\mathrm{Br}_2] \qquad (2)$$

Table S3. Concentration independent rate constants *k*.

experiment	T /K	$k(T)$ / $l\cdot\mathrm{mol}^{-1}\mathrm{s}^{-1}$
1	300	1.93×10^{-3}
2	300	1.96×10^{-3}
3	310	2.94×10^{-3}
4	310	2.75×10^{-3}
5	320	3.47×10^{-3}
6	320	3.82×10^{-3}
7	330	4.89×10^{-3}
8	330	5.23×10^{-3}

The activation enthalpy, $\Delta H^{\ddagger}$, and the activation entropy, $\Delta S^{\ddagger}$, of the reaction can be obtained by plotting ln(k/T) vs 1/T (Figure S4).

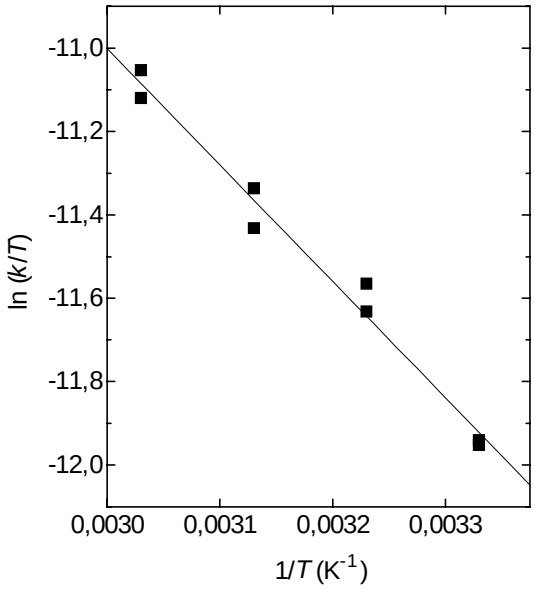


Figure S4. Eyring plot for the bromination of **6**·$(ClO_4)_3$.

The slope [= $-(2.8 \pm 0.1) \times 10^3$ K] and the intercept [= -2.62 ± 0.50] were determined by regression analysis. The corresponding $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were calculated with the Eyring equation [Eq (3)].

$$\ln\left(\frac{k_{\exp}}{T}\right) = -\frac{\Delta H^{\ddagger}}{RT} + \left(\frac{\Delta S^{\ddagger}}{R} + \ln\frac{k_B}{h}\right) \qquad (3)$$

$$\Delta H^{\ddagger} = -R \cdot (-2.80 \pm 0.10) \cdot 10^3 = 23.3 \pm 0.8 kJmol^{-1}$$

$$\Delta S^{\ddagger} = R \cdot \left(\left(-2.62 \pm 0.50\right) - 23.76\right) = -220 \pm 4\, Jmol^{-1}K^{-1}$$