Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Base-free glucose dehydration catalysed by NHC-stabilised heterohalo cyclopentadienyl Cr(III) complexes

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## Supporting Information

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1. Crystal data and structure refinement for **1**-**7** (**Tables S1**,**S2**)

**Table S1**

| Complex | 1[a] | 2 | 3 | 4 |
|---|---|---|---|---|
| **Emp. formula** | $C_{16}H_{17}N_2Cl_{1.82}Br_{0.18}Cr$ | $C_{22}H_{21}N_2Cl_{1.36}Br_{0.64}Cr$ | $C_{16}H_{17}N_2ClBrCr$ | $C_{24}H_{25}N_2Cl_{1.35}Br_{0.65}Cr$ |
| **Form. weight (g.mol$^{-1}$)** | 368.11 | 464.71 | 404.67 | 493.15 |
| **Crystal system** | monoclinic | monoclinic | orthorhombic | orthorhombic |
| **Space group** | $P2_1/c$ | $P2_1/c$ | $Pbca$ | $P2_12_12_1$ |
| **Crystal descr.** | blue blade | blue blade | blue needle | blue block |
| **a (Å)** | 22.494(6) | 11.578(3) | 7.8759(5) | 9.9270(1) |
| **b (Å)** | 6.2985(2) | 20.917(5) | 16.9413(11) | 14.6703(1) |
| **c (Å)** | 22.856(6) | 16.763(4) | 25.1308(16) | 15.1733(2) |
| **α (°)** | 90 | 90 | 90 | 90 |
| **β (°)** | 95.878(6) | 91.965(5) | 90 | 90 |
| **γ (°)** | 90 | 90 | 90 | 90 |
| **Volume (Å$^3$)** | 3221.1(2) | 4057.2(2) | 3353.2(4) | 2209.7(4) |
| **Z** | 8 | 8 | 8 | 4 |
| **Abs. coeff. (m.mm$^{-1}$)** | 1.447 | 2.010 | 3.219 | 1.865 |
| **F(000)** | 1506.0 | 1892.0 | 1624.0 | 1011.0 |
| **Independent refl.** | 4518 | 7419 | 5221 | 4546 |
| **Completeness (%)** | 98.4 | 100.0 | 99.4 | 100.0 |
| **Data/Restr/Para** | 4518/0/205 | 7419/0/491 | 5221/0/200 | 4546/0/264 |

| | | | | |
|---|---|---|---|---|
| **Goodness of fit on $F^2$** | 1.121 | 0.990 | 0.982 | 1.055 |
| **Final $R_1$ indexes** | 0.1568 | 0.0722 | 0.0695 | 0.0211 |
| **$wR_2$ indices (all data)** | 0.3369 | 0.1436 | 0.1954 | 0.0481 |
| **Largest diffr. peak and hole ($e.Å^{-3}$)** | 1.07/-0.90 | 0.57/-0.42 | 1.41/-1.23 | 0.25/-0.28 |

[a] Data not suitable for CCD deposition; used for comparison purposes only

**Table S2**

| **Complex** | **5** | **6** | **7** |
|---|---|---|---|
| **Emp. formula** | $C_{23}H_{23}N_2Cl_{1.24}Br_{0.76}Cr$ | $C_{18}H_{22}N_4Cl_{5.0}Br_{0.8}Cr_2$ | $C_{23}H_{23}N_2Cl_2Cr$ |
| **Form. weight ($g.mol^{-1}$)** | 484.23 | 493.15 | 450.33 |
| **Crystal system** | orthorhombic | monoclinic | monoclinic |
| **Space group** | $P2_12_12_1$ | $P2_1$ | $P2_1/c$ |
| **Crystal descr.** | blue block | blue block | blue block |
| **a (Å)** | 9.920(4) | 7.7436(1) | 9.3840(6) |
| **b (Å)** | 14.406(6) | 7.0456(9) | 14.9768(1) |
| **c (Å)** | 14.898(6) | 11.7412(2) | 14.9659(1) |
| **α (°)** | 90 | 90 | 90 |
| **β (°)** | 90 | 92.740(4) | 92.549(2) |
| **γ (°)** | 90 | 90 | 90 |
| **Volume ($Å^3$)** | 2129.0(2) | 639.85(2) | 2101.3(2) |
| **Z** | 4 | 1 | 4 |
| **Abs. coeff. ($m.mm^{-1}$)** | 2.135 | 2.596 | 0.810 |
| **F(000)** | 987.0 | 322.0 | 932.0 |
| **Independent refl.** | 4388 | 2831 | 4752 |
| **Completeness (%)** | 99.8 | 99.9 | 99.6 |
| **Data/Restr/Para** | 4388/0/255 | 2831/1/141 | 4752/0/253 |
| **Goodness of fit on $F^2$** | 1.066 | 1.097 | 0.904 |
| **Final $R_1$ indexes** | 0.0439 | 0.0738 | 0.0446 |
| **$wR_2$ indices (all data)** | 0.1035 | 0.2152 | 0.1419 |
| **Largest diffr. peak and hole ($e.Å^{-3}$)** | 0.82/-0.40 | 1.29/-1.08 | 0.66/-0.68 |

2. Selected bond lengths and angles for **1**-**7** (**Table S3**)

| **Description** | **1** | **2** | **3** | **4** | **5** | **6** | **7** |
|---|---|---|---|---|---|---|---|
| **Cr1-C1** | 2.107(2) | 2.102(7) | 2.108(3) | 2.132(2) | 2.127(5) | - | 2.117(3) |
| **Cr1-Cg[a]** | 1.886(5) | 1.897(9) | 1.891(9) | 1.904(5) | 1.902(7) | 1.895(6) | 1.888(9) |
| **Cr1-X1[b]** | 2.321(6) | 2.3548(2) | 2.3254(9) | 2.3584(7) | 2.3730(2) | 2.324(4) | 2.3225(9) |
| **Cr1-X2[b]** | 2.328(5) | 2.3988(2) | 2.3471(9) | 2.3933(6) | 2.4066(2) | 2.360(3) | 2.3242(9)[d] |
| **Cr1-C1-Cl1** | 97.239(2) | 96.450(2) | 97.804(3) | 100.486(2) | 82.817(3) | - | 97.478(3) |
| **Cr1-C1-Br1** | 100.114(2) | 99.832(2) | 97.724(3) | 98.161(2) | 99.652(3) | - | 98.551(3)[e] |
| **$C_\beta$-$C_\alpha$-N1-C1[c]** | 127.841(2) | -77.168(5) | - | 128.727(2) | -127.029(6) | - | -72.823(4) |
| **$C_\beta$-$C_\alpha$-N2-C1[c]** | - | -132.343(5) | 112.056(5) | -134.143(2) | 81.480(6) | - | 112.804(3) |
| **$C_\gamma$-$C_\beta$-$C_\alpha$-N1[c]** | 119.699(2) | -54.622(6) | - | -74.162(2) | 71.272(5) | - | 152.008(3) |
| **$C_\gamma$-$C_\beta$-$C_\alpha$-N2[c]** | - | -124.305(6) | 175.804(5) | 71.238(2) | -163.136(5) | - | -179.548(3) |

[a] Cg = centroid of cyclopentadienyl moiety. [b] X1, X2 = Cl, Br. [c] $C_\alpha$, $C_\beta$, and $C_\gamma$ denotes the primary, secondary, and tertiary carbon atoms attached to the NX (X = 1, 2) atom, in the former respective order. [d] The Cr1-Cl2 bond distance refers. [e] The Cr1-C1-Cl2 bond angle refers.

3. Schematic representation of the oxidation and reduction processes (**Figure S1**)

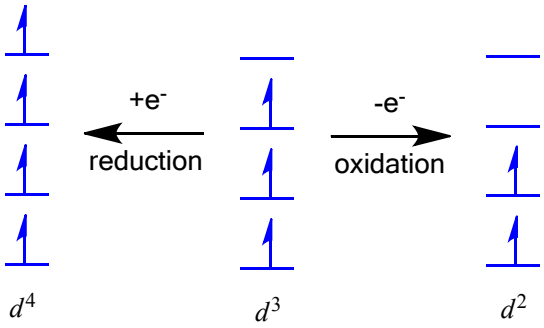


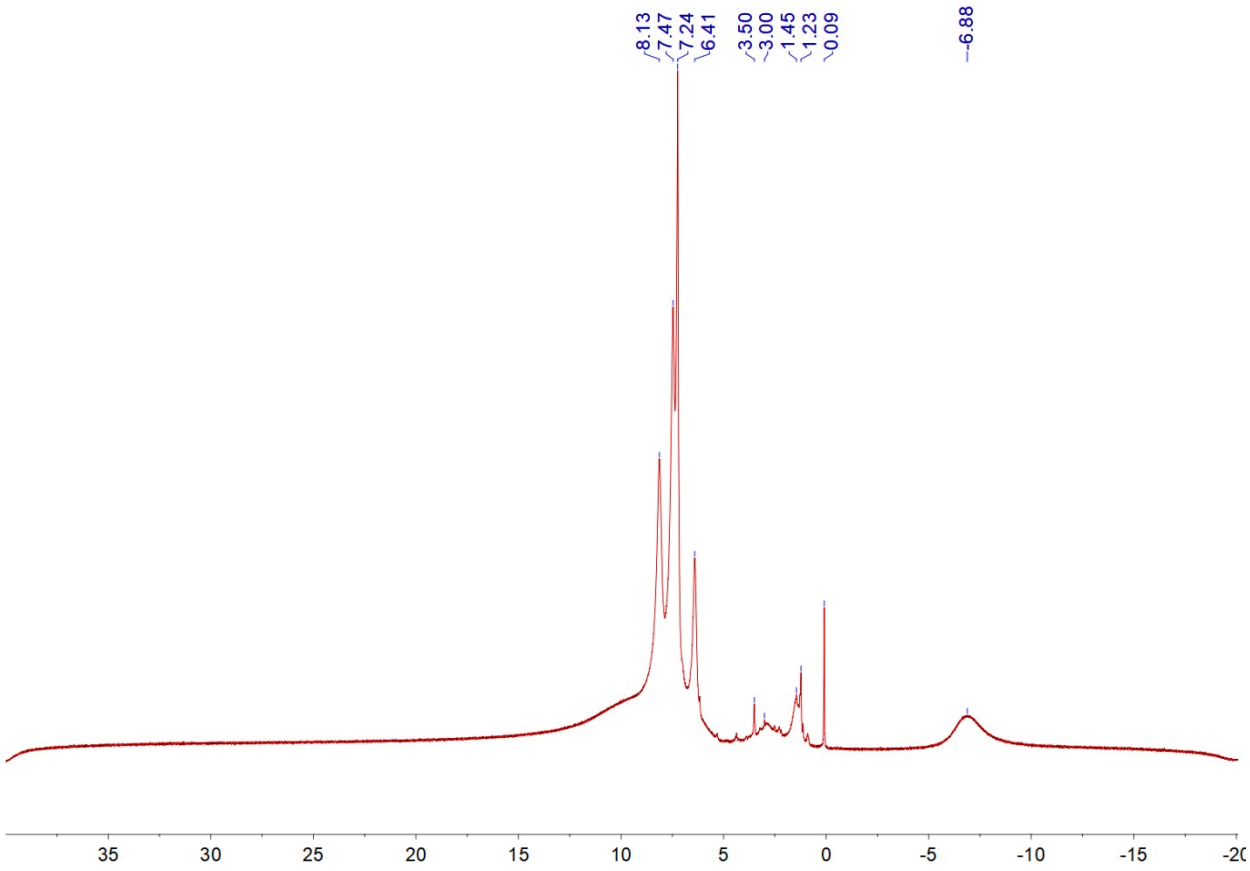

**Figure S1:** Schematic representation of the oxidation and reduction process of the Cr(III)-NHC complexes [CpCrBrCl(NHC)] (**1**–**5**). The blue arrows represent electrons (up arrow is an alpha up-spin electron).

4. Glucose dehydration using **1**-**6** (**Table S4**)

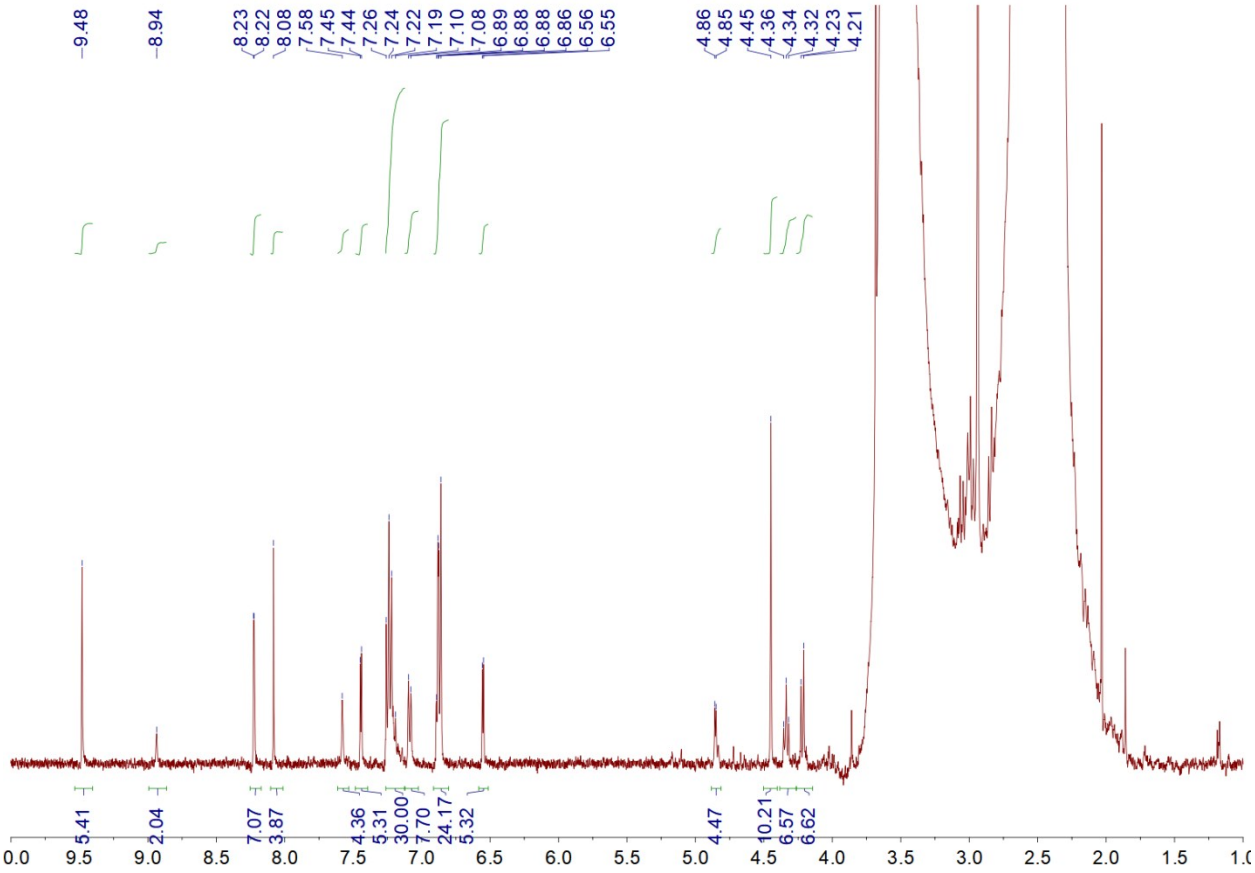
| Entry | Catalyst (5 mol%) | Conversion (%) | HMF Yield (%) | Other (%) | TOF ($h^{-1}$) |
|---|---|---|---|---|---|
| 1 | - | 14.9 | 3.8 | 11.1 | 0.0 |
| 2 | $CrCl_3(THF)_3$ | 89.8 | 89.8 | 0.0 | 9.9 |
| 3 | **2** (room temperature) | 34.0 | 34.0 | 0.0 | 0.2 |
| 4 | **2** (3 mol%) | 48.1 | 34.8 | 13.3 | 1.22 |
| 5 | **2** (10 mol%) | 92.3 | 73.1 | 19.2 | 3.00 |
| 6 | **2** | 68.6 | 68.6 | 0.00 | 2.62 |
| 7 | **2** (THF) | 64.7 | 51.3 | 13.4 | 3.82 |
| 8 | **1** | 71.7 | 37.2 | 34.5 | 3.69 |
| 9 | **3** | 76.0 | 35.5 | 40.5 | 3.13 |
| 10 | **4** | 60.3 | 56.3 | 4.0 | 2.02 |
| 11 | **5** | 51.7 | 48.3 | 3.4 | 2.08 |
| 12 | **6** | 80.6 | 76.0 | 4.6 | 5.44 |

General conditions: (+)-D-glucose (0.11 mmol), [Cr] (6 mol%), DMSO (4 mL), anisole (0.11 mmol), 120 °C.

5. $^{1}$H-NMR spectrum of **6**



6. $^{1}$H-NMR spectrum of glucose dehydration reaction mixture




General conditions: (+)-D-glucose (0.11 mmol), [**1**] (6 mol%), anisole (0.11 mmol), 120 °C. Aliquot taken after 1 hour reaction time, analysed using $d_6$-DMSO.