Electronic supplementary information

Vanadyl calix[6]arene complexes: Synthesis, structural studies and ethylene homo-(co-)polymerization capability

Carl Redshaw,[a*] Mark Walton,[b] Kenji Michiue,[c] Yimin Chao,[b] Alex Walton,[d] Pertti Elo,[e]

Victor Sumerin,[e] Chengying Jiang[f] and Mark R.J. Elsegood[f]

[a] *Department of Chemistry, University of Hull, Hull, HU6 7RX, U.K.*
[b] *School of Chemistry, University of East Anglia, Norwich, NR4 7TJ, U.K.*
[c] *Process Technology Center*, *Mitsui Chemicals Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan*
[d] *School of Physics & Astronomy, University of Leeds, Leeds, LS2 9JT, UK.*
[e] *Borealis Polymers Oy, P.O. Box 330, Porvoo, FI-06101, Finland*
[f] *Chemistry Department, Loughborough University, Loughborough, Leicestershire, LE11 3TU, U.K.*

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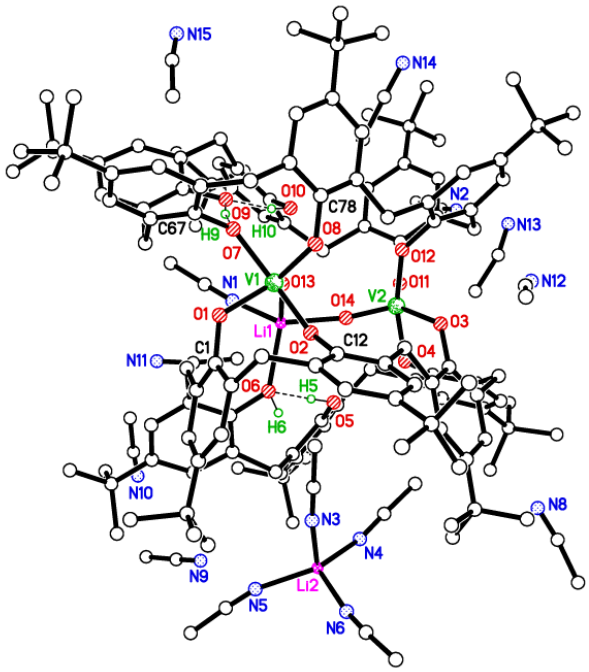
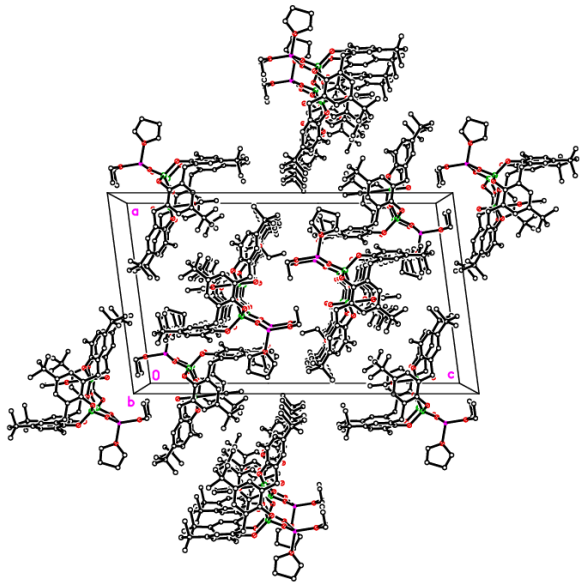


Figure S1. Structure of the salt $[Li(MeCN)_4][V_2(O)_2Li(MeCN)(L^6H_2)_2]\cdot 9.67MeCN$ (**2**.9.67MeCN) showing the atom numbering scheme. Hydrogen atoms except those involved in H-bonds have been omitted for clarity.



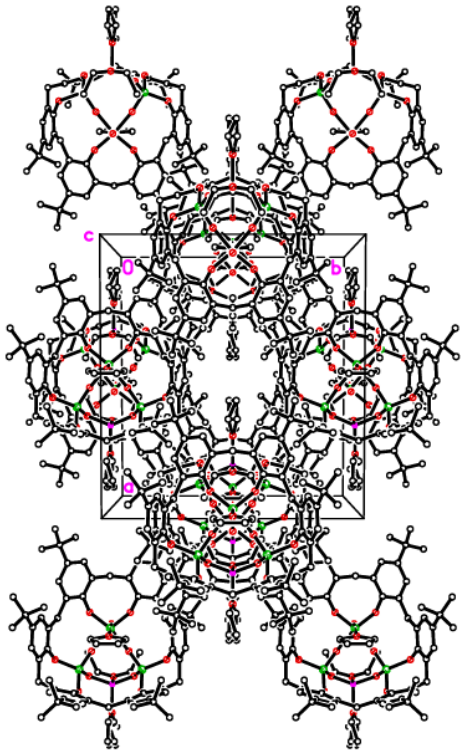


Figure S2. Packing of molecules of **4**.

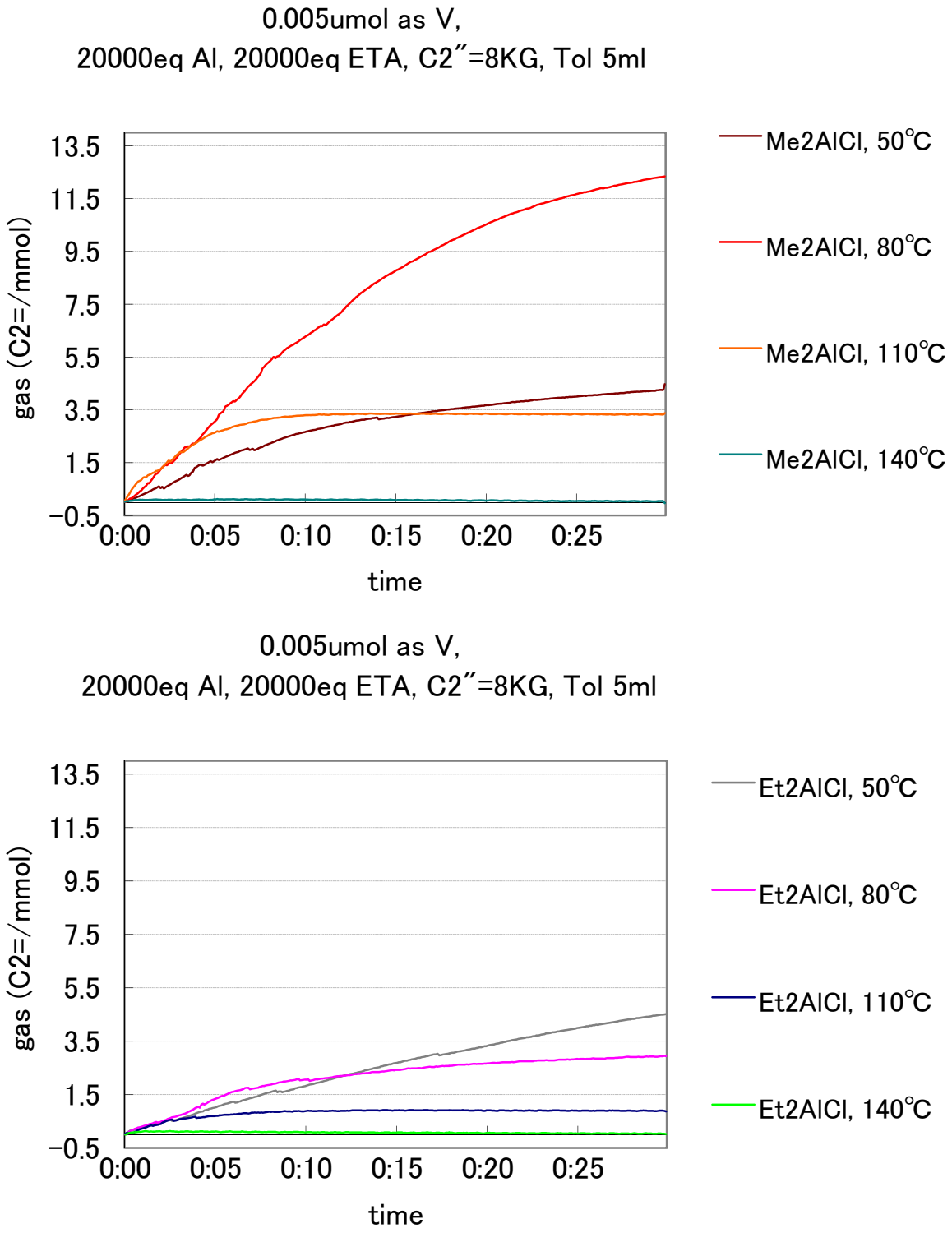


Figure S3. Ethylene uptake for **1** *versus* temp. Top using DMAC and bottom DEAC as co-catalyst.

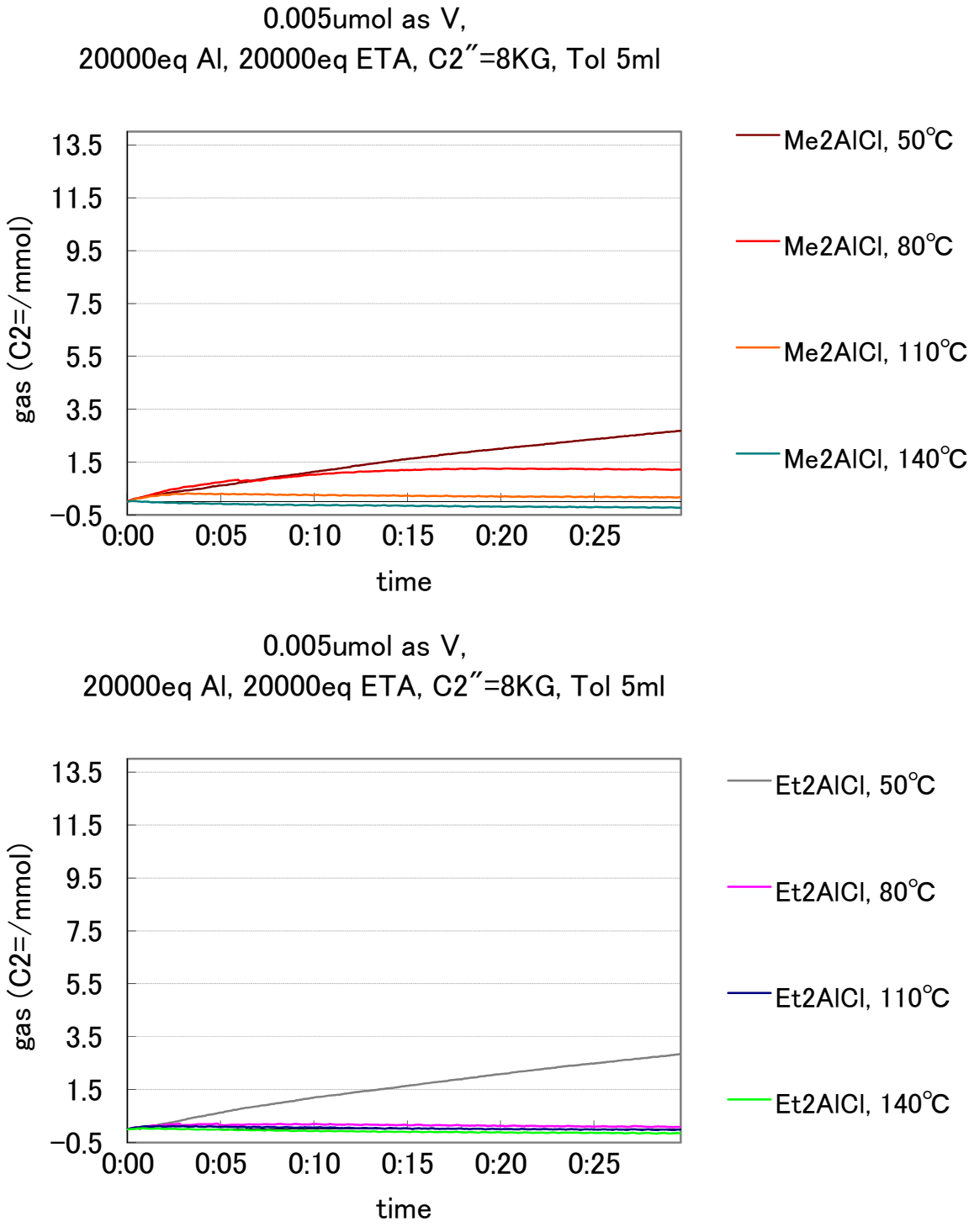
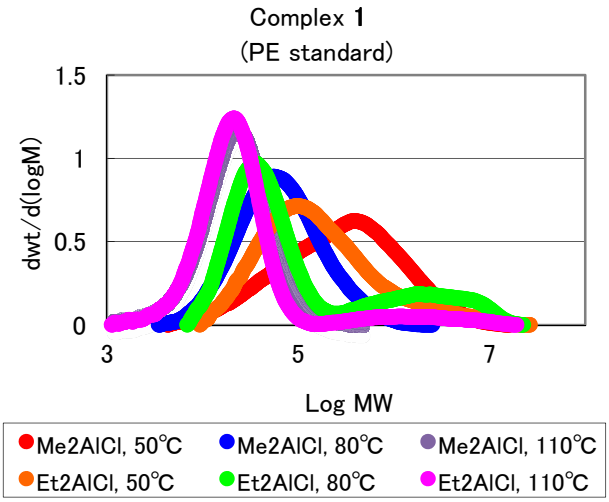


Figure S4. Ethylene uptake for **5** *versus* temp. Top using DMAC and bottom DEAC as co-catalyst.



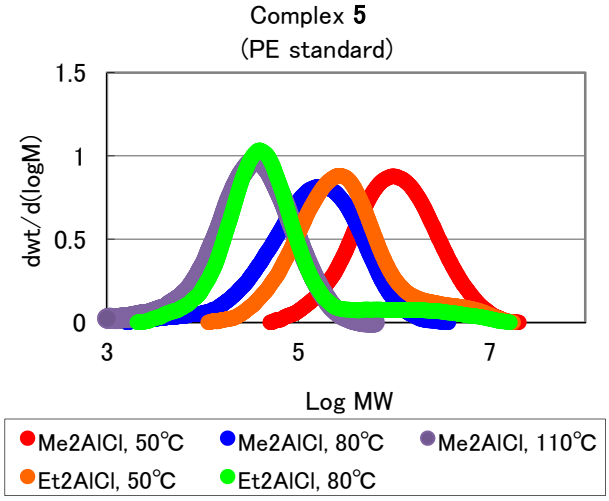


Figure S5: GPC traces for **1** and **5** (Table 7).

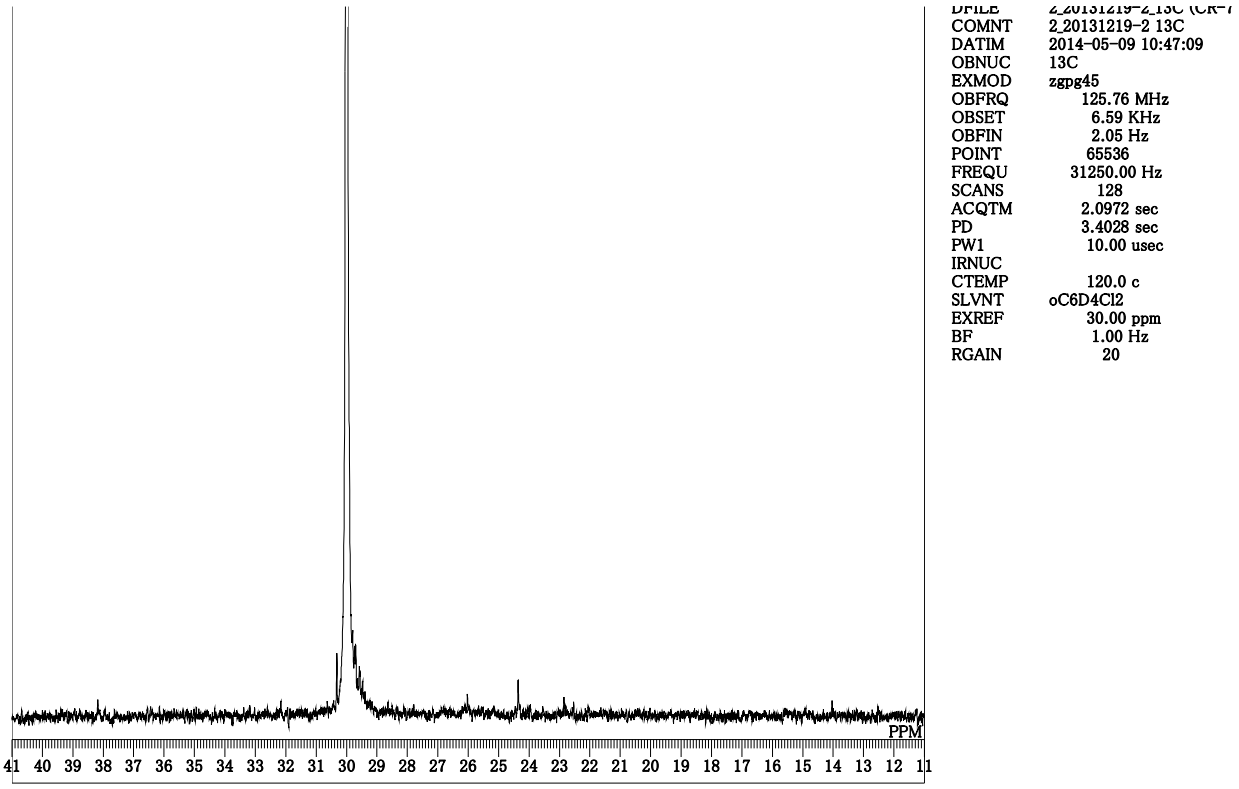


Figure S6: ^{13}C NMR of polyethylene using **1** (run 10,Table 7).

Table S1. PPR-Ethylene Polymerization Results for **S1** with EADC or TIBA[a]

Run	Pre-catalyst[b]	Co-Catalyst	Metal Content[c]	Ethylene Uptake[d]	ETA: M Ratio
1	**S1** (0.3)	TIBA	0.014	3.5	1440
2	**S1** (0.8)	TIBA	0.038	3.8	1440
3	**S1** (0.3)	EADC	0.014	4.4	1440
4	**S1** (0.3)[e]	EADC	0.014	5.1	1440

[a] **Conditions**: 6.69 bar ethylene, 1 h reaction time, Al/V (Molar ratio) 4000; [b](mg). [c] µmol [d] psi [e] ETA was pre-mixed prior to addition of ethylene

Table S2 PPR - Ethylene/1-hexene Co-Polymerization Results with EADC or TIBA[a]

Run	Pre-Catalyst (mg)	Co-Catalyst	Metal Content[b]	Yield[c]	Activity[d]	Ethylene Uptake[e]
1	**S1** (0.4)	TIBA	0.019	0.006	0.16	5.2
2	**S1** (0.8)	TIBA	0.047	0.022	0.23	12.5
3	**S1** (1.0)	TIBA	0.038	0.008	0.11	6.6
4	**S1** (0.4)	EADC	0.019	0.001	0.04	7.2
5	**S1** (0.8)	EADC	0.047	0.027	0.29	17.9
6	**S1** (1.0)	EADC	0.038	0.023	0.30	14.3

[a] **Conditions**: 6.69 bar ethylene, 1h reaction time, Al/V (Molar ratio) 4000, 80°C.; [b] µmol. [c] grams of polymer. [d] Kg/mmolV.h.bar. [e] psi. PPR = Parallel Pressure Reactor.