ELECTRONIC SUPPORTING INFORMATION

for

Reductive disproportionation of carbon dioxide by an organosamarium(II) complex: Unprecedented f-element reactivity giving a bimetallic carbonate complex

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Synthesis of **1**. To a stirred toluene solution (80 mL) of the samarium(II) precursor[9] (0.86 g, 1.00 mmol) an excess of dry carbon dioxide (over P_2O_5) was introduced to the reaction vessel. The colour of the solution changed from purple to light orange and a pale yellow solid formed over 30 mins. The solution was filtered, toluene was removed *in vacuo* and the orange product extracted into a warmed thf solution. Filtration and concentrated *in vacuo* gave a crystalline orange product on standing overnight (0.40 g, 54 %). Found: C, 62.05; H, 7.5; N, 7.7%. Calc. for $C_{77}H_{108}N_8O_3Sm_2$: C, 61.9; H, 7.3; N, 7.5. δ_H(300 MHz, C_6D_6, , 298 K): -0.51 (24 H, m, CH_3), 1.09 (12H, s, NCH_3), 1.22 (8H, m, CH_2), 2.13 (8H, m, CH_2), 2.26 (8H, m, CH_2), 2.43 (8H, s, =CH, pyrMe), 3.57 (24H, m, CH_3), 6.14 (8H, m, CH_2), 6.79 (8H, s, =CH, pyr). δ_C(75.4 MHz, C_6D_6, , 298 K): 7.5, 10.4 (CH_3), 21.0, 33.9 (CH_2), 31.6 (CH_3), 47.3 (C), 97.0 (=CH, pyrMe), 101.3 (=CH, pyr), 133.8 (=CR, pyrMe), 154.6 (=CR, pyr), 190.8 (C, CO_3).

Details of GC-MS CO detection. A headspace sample from the reaction vessel was drawn into a fixed needle 1 mL hypodermic insulin syringe (Terumo Medical Corporation, Maryland, USA) and the needle was immediately sealed with a silicone rubber GC septum. A 200 µL aliquot of this sample was analysed by combined GC-MS using a HP5890 GC coupled to a Kratos ISQ high resolution magnetic sector mass spectrometer. The mass spectrometer was fitted with an electron ionisation source operating at 70 eV and a full accelerating voltage of 5.3 kV was used. Data was collected using the selected ion monitoring mode with accelerating voltage switching, at a resolution of 8,000 (10 % valley definition), and collecting full ion profiles over a 500 ppm voltage sweep about the monitored m/z values. Ions monitored within a full cycle time of 0.3 s were 28.0061 for N_2, 27.9949 for CO and 31.9898 for O_2, with 28.0061 also being used as a lock mass. A J&W 30 m x 0.53 mm internal diameter PLOT column was used with helium as carrier gas at a head pressure of 7 psi and an oven temperature of 60 °C, and the sample was injected with a 50:1 split ratio. Using standard gases, these conditions easily separated CO_2 from a mixed chromatographic peak containing N_2, O_2 and CO. While there was only a fractional offset observed in the retention times for N_2 and CO under these conditions, these two gases were fully resolved by their mass/charge ratio. An intense chromatographic peak was observed at the correct retention time in the CO channel from the reaction vessel headspace sample, and the centroid of this ion was measured as 27.9948, giving unequivocal confirmation of the presence of CO. A second peak in the CO channel 8 seconds after the retention time of CO and of similar intensity was due to the CO^+ fragment ion derived from CO_2. N_2 and O_2 were also detected in the reaction headspace, with the latter giving a significantly less intense signal than CO and the former giving a stronger signal than CO.