Supporting Information

Electronic Control of the Bergman Cycloaromatization: Synthesis and Chemistry of Chloroenediynes

Graham B. Jones* and Gary W. Plourde II

Preparation of enediyne **15** and its cobalt carbonyl complex. 1,1,10-trichloro-2,8-decadiyne (238 mg, 1.0 mmol) and HMPA (1.74 mL, 1.79 g, 10 mmol) were dissolved in THF (25 mL) in a 100 mL round bottom flask, and the resulting solution cooled to -45°C. A solution of lithium hexamethyldisilylazide (2.2 mL, 2.2 mmol) in THF (18 ml) was added dropwise *via* mechanical syringe pump over a period of 5.0 h. The solution was poured, *without warming*, into a slurry of saturated NH_4Cl (60 mL) and crushed ice (20 g). The organic material was extracted into Et_2O (4 x 20 mL) and the combined extracts treated with cold HCl (10 %, 2 x 20 mL), water (1 x 20 mL), saturated $NaHCO_3$, (1 x 20 mL), and brine (1 x 10 mL). The organic extracts were dried briefly over Na_2SO_4, filtered through a plug of silica gel, concentrated *in vacuo*, then eluted (pentane) through a short column of silica gel to afford **15** (99 mg, 60%) as a faintly colored oil. ^{1}H NMR: δ 5.87 (s, 1H), 2.40 (m, 4H), 1.93 (m, 4H); ^{13}C NMR: δ 125.0, 119.3, 104.2, 104.1, 81.7, 80.3, 28.7, 28.4, 21.7, 21.3; MS (EI) *m/z* 166 (M+1), 131, 115, 103, 91, 77, 64, 51. Complexation with dicobalt octacarbonyl using standard conditions,[10] gave **10**, X=CH_2 (95%) isolated as a maroon solid m.p. 100 (dec.); ^{1}H NMR: δ 6.78 (s, 1H), 3.28 (m, 2H), 3.17 (m, 2H), 1.87 (m, 4H); ^{13}C NMR: δ 199.0, 132.3, 126.8, 101.3, 95.2, 84.2, 81.9, 34.1, 32.2, 29.7, 28.1; $C_{22}H_9O_{12}ClCo_4$ requires: C, 35.88, H, 1.23, O, 26.07, Cl, 4.81; Found, C, 35.95, H, 1.30, O, 25.92, Cl, 4.95.