

Electronic Supplemental Information (ESI) to accompany the manuscript

“Differences between the macroscopic and tracer level chemistry of rhenium and technetium: Contrasting cage isomerisation behaviour of Re(I) and Tc(I) carborane complexes”

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Experimental

Materials and Methods

Caution! The radiometals ^{99m}Tc ($t_{1/2} = 6.0$ h; $E_{\gamma} = 140$ keV) and $^{186/188}\text{Re}$ (^{186}Re , $t_{1/2} = 3.7$ d, $E_{\beta} = 1.07$ MeV; ^{188}Re , $t_{1/2} = 16.9$ h; $E_{\beta} = 2.12$ MeV) must only be used in a licensed facility with adequate shielding. Sodium pertechnetate $[\text{Na}][^{99m}\text{TcO}_4]$ was obtained from a commercial $^{99}\text{Mo}/^{99m}\text{Tc}$ generator (Lantheus Medical Imaging Inc.) while $[\text{ReO}_4]^{-}$ (> 350 GBq/mg) was provided by the McMaster Nuclear Reactor; conversion to $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^{+}$ ($\text{M} = ^{99m}\text{Tc}$, $^{186/188}\text{Re}$) was accomplished according to the literature procedures.¹ All radiochemical experiments were carried out under an inert (argon) atmosphere. The *nido*-carborane ligands and non-radioactive *closo*-rhenacarboranes, used as HPLC standards for the identification of the analogous ^{99m}Tc -carboranes, were prepared as described previously.² Aqueous tetraethylammonium phosphate (TEAP, pH 2.5), employed as an HPLC mobile phase, was prepared by combining concentrated phosphoric acid (85%, 5.5 mL, 80 mmol) and triethylamine (7.0 mL, 5.1 g, 50 mmol) in water (1.0 L).

In a typical ^{99m}Tc radiolabelling experiment, a stock solution of the *nido*-carborane (**1a-1c**, 3 - 12 mM) in deoxygenated $\text{EtOH}_{(\text{aq})}$ (10 % v/v) was distributed into several Emry vials. A saline solution of $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^{+}$ (0.1-1.0 mL, 50-150 MBq) was added to each vial of ligand solution (final concentration 2-10 mM) and the reaction mixture was heated using the specified conditions (5 min at 100, 120, 140, 160, 180 and 200 °C; additional experiments with **1a** were also conducted at lower temperatures).

Experiments with $^{186/188}\text{Re}$ were conducted in a similar manner, combining aliquots of a stock solution of $[\text{Na}][\text{nido-C}_2\text{B}_9\text{H}_{12}]$ (**1a**, 0.5 mL, 20-22 mM) with $[\text{Re}(\text{CO})_3(\text{H}_2\text{O})_3]^{+}$ (0.3-0.4 mL, 1.5-4.5 MBq) at pH 7.4 and diluting with $\text{EtOH}_{(\text{aq})}$ (10 % v/v) to a final ligand concentration of 7.8-8.8 mM. Reactions were heated for 5 min at 100, 120, 140, 160, 180 and 200 °C and analysed by radio-HPLC. Where applicable, reaction mixtures were purified using a C-18 solid phase extraction cartridge (1.6 mL, Waters) pre-treated by flushing with H_2O (10 mL), MeOH (10 mL) and again with H_2O (10 mL).

Instrumentation

Microwave-assisted reactions were conducted utilizing a Biotage Initiator 8 microwave reactor. Radioactivity was measured using a Capintec CRC-15W dose calibrator. High Performance Liquid Chromatography (HPLC) data were obtained using a Varian Pro Star 330 PDA detector operating at $\lambda = 254$ nm with a model 230 solvent delivery system and an in-line β -RAM Radio-HPLC detector (IN/US Systems, Model 3). A Nucleosil C-18 HPLC column (4.6 mm x 25 mm) operating at a flow-rate of 1.0 mL/min with a sample volume of 100 μ L was used for all analyses. The following solvent gradients were employed: **Method A** (Solvent A = TEAP, Solvent B = MeOH) 0-3 min, 100% A; 3-6 min, 0% B to 25% B; 6-9 min, 25% B to 33% B; 9-20 min, 33% B to 100% B; 20-22 min, 100% B; 22-25 min, 100% B to 100% A; 25-30 min, 100% A; : **Method B** (Solvent A = TEAP, Solvent B = MeOH) 0-15 min, 70-90% B.

References

1. P.W. Causey, T.R. Besanger, P.S. Schaffer and J.F. Valliant, *Inorg. Chem.*, 2008, **47**, 8213.
2. A.F. Armstrong and J.F. Valliant, *Inorg. Chem.*, 2007, **46**, 2148.