X-ray Crystallography for ESI.

The ESI crystal data table gives some of the numerical crystal data and information about the crystals, data collections and refinements. Full numerical data are given in the cif files. This section provides additional details for each individual structure. In general, all structures were refined with all non-H atoms anisotropic and H atoms included in a riding model with $U(H) = 1.2\ U_{eq}$ of the carrier atom for aromatic CH and CH_2, $1.5\ U_{eq}$ for methyl H and OH. Refinements were on F^2 using all data.

Data for compound **1** were collected using a conventional sealed tube source on a Bruker Smart 1000 CCD diffractometer. Higher symmetry could not be found despite cell lengths b and c being similar in length and α and β having similar angles. Full data sets were collected on three separate crystals on three different instruments with the same outcome. The ^{t}Bu group at C(40) had the three methyl groups disordered over two sets of positions which were modelled with restraints on geometry and displacement parameters. Major occupancy was 60.0(11)%.

Data for compound **2** were collected by the UK EPSRC National Crystallography Service at Southampton using a Bruker-Nonius Kappa CCD diffractometer with a rotating anode source and 10 cm confocal mirrors. The crystals were very small and thin with the structure exhibiting disorder. The final result clearly reveals the connectivity, but the geometrical data should be used with caution due to the fairly poor overall result. Atom O(2) was disordered over 2 positions, with 84.7(9)% occupancy on C(25) and 15.3(9)% on C(29). O(5) was similarly disordered with 76.8(10)% on C(78) and 23.2(10)% on C(82). ^{t}Bu groups at C(87) and C(101) had the methyl groups disordered over two sets of positions with major occupancies of 73.0(11) and 52.5(10)% respectively. The disorder was modelled with restraints as described above.

Note that whilst single crystals of **2** suitable for X-ray diffraction were grown from acetonitrile, the sample used for microanalysis was crystallised from dichloromethane.

Data for compounds **3-5** and **LH₃** were collected at the SRS, Daresbury Laboratory, Station 9.8 (16.2 SMX for **LH₃**) using Silicon 111 monochromated synchrotron radiation and Bruker Apex II CCD diffractometers. This source was required due to small crystal size or weak diffraction.

For **3** there is a short interaction between inversion related molecules; 2.838(2) Å separates O(4) from C(19) of an adjacent acetonitrile molecule at (1-x, 1-y, 1-z).

For compound **4** there are 2 vanadium complex molecules and one molecule of toluene in the asymmetric unit. In the complex containing V(2) one carbon atom in the propanol chain, C(41), is disordered over 2 positions which were modelled with restraints as described above with the major occupancy being 90.2(7)%.

For **5** the metric symmetry is close to orthorhombic, but the true symmetry is monoclinic with β close to 90°. This results in twinning via 180° rotation about *b*. Refinement of a batch scale factor for this twinning reduces the R factor from *ca*. 15% to 4%. There are 2 molecules in the asymmetric unit along with 2 molecules of MeCN. The MeCN H-bonds to the NH₂ group in each case, with the angles at H being about 10° different between the two.

Compound **LH₃** has methyl group disorder in both ^{i}Pr groups with major occupancies at C(7) and C(10) being 51.5(16) and 50(3)% respectively. On the C₆ ring containing C(39) the OH group is disordered over two alternative sites. At C(40) it is occupied 48.3(8)% while that at C(44) it is occupied 51.7(8)% of the time. Both ^{t}Bu groups on that ring are also disordered, with the methyl groups split over two sets of positions. The major occupancies at C(45) and C(49) are 70.0(16) and 53.3(9)% respectively. The various disordered parts of the molecule were modelled with restraints as described above.