SUPPLEMENTARY DATA

The structures of $[Me_2P(H)(CH_2)_2P(H)Me_2][GeCl_3]_2$ and $[Me_2P(O)(CH_2)_2P(O)Me_2H][GeCl_3]$ are shown in Figs. S1 and S2 and corresponding bond lengths and angles are in Tables S1 and S2. The bond lengths in the approximately pyramidal $[GeCl_3]^-$ lie in the range 2.283(4)–2.324(3) Å with Cl–Ge–Cl *ca.* 95°. These values agree well with the twenty-five reported $[GeCl_3]^-$ anions in the Cambridge structural database where the Cl–Ge–Cl angle ranges from 92–98° with a mean of 95.5°; there is for the second compound (S2) a Ge···Ge distance of 3.197(1) Å with the two Ge atoms related by a centre of symmetry. The dimensions of the cations are unexceptional, however the structures confirm the identities of two of the final products resulting from reaction of $Me_2P(CH_2)_2PMe_2$ and $GeCl_4$ in CH_2Cl_2 solution.

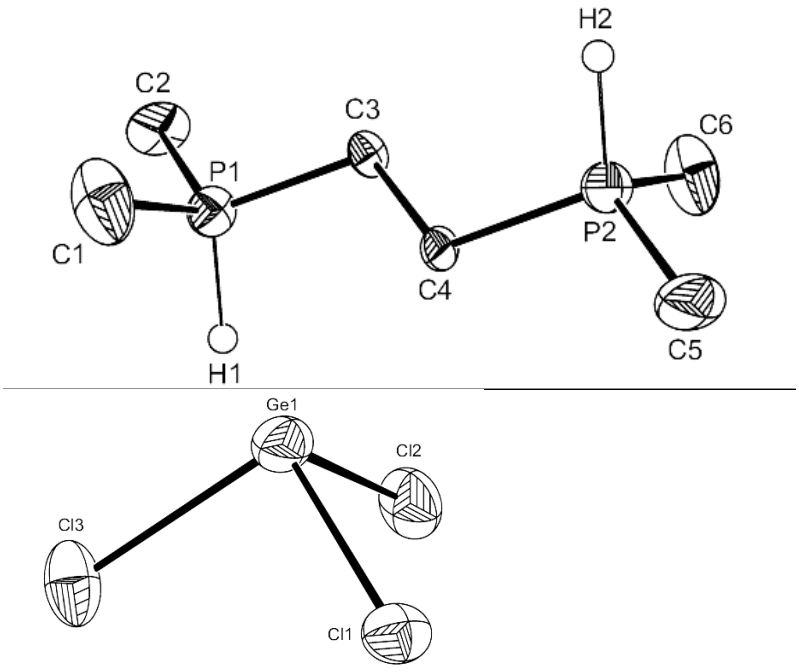

Fig. S1 Structure of one of the two cations and one of the four anions of $[Me_2P(H)(CH_2)_2P(H)Me_2][GeCl_3]_2$ with the atom numbering scheme adopted. Carbon H-atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. The cation H atoms bonded to P were not convincingly located in

later difference electron-density maps and were introduced in calculated positions. The other cation and anions are very similar.

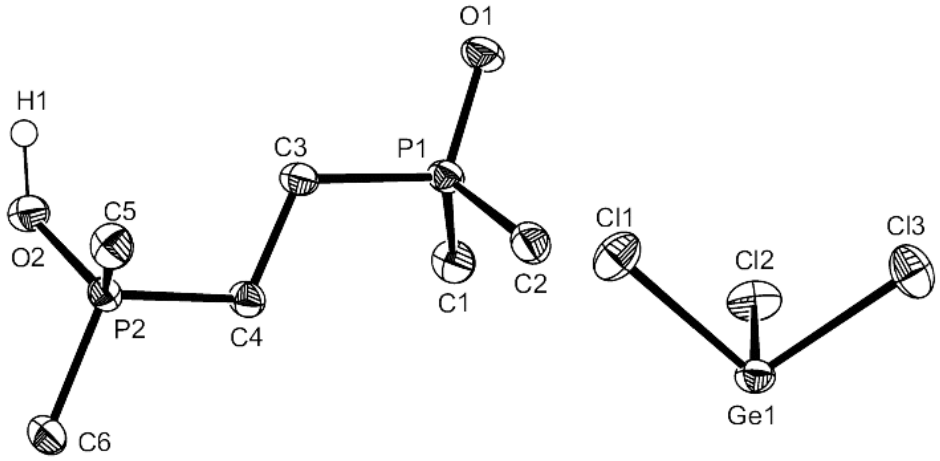

Fig. S2 Structure of $[Me_2P(O)(CH_2)_2P(O)Me_2H][GeCl_3]$ with the atom numbering scheme adopted. Carbon H-atoms are omitted for clarity and displacement ellipsoids are shown at the 50% probability level. H1 was identified in later electron-density maps but not refined. H1 is involved in H-bonding O2–H1···O1' where O1' is from an adjacent molecule. Note that P2–O2 is only a little longer than P1–O1 (see Table).

Table S1 Selected bond lengths (Å) and angles (°) for $[Me_2P(H)(CH_2)_2P(H)Me_2][GeCl_3]_2$

Ge1–Cl1	2.300(3)	Ge3–Cl7	2.318(3)
Ge1–Cl2	2.332(4)	Ge3–Cl8	2.310(3)
Ge1–Cl3	2.308(3)	Ge3–Cl9	2.324(3)
Ge2–Cl4	2.300(3)	Ge4–Cl10	2.299(4)
Ge2–Cl5	2.303(4)	Ge4–Cl11	2.311(4)
Ge2–Cl6	2.283(4)	Ge4–Cl12	2.285(3)
P–C(Me)	1.759(11)–1.816(10)		
Cl–Ge1–Cl	93.24(13)–95.08(12)	Cl–Ge3–Cl	93.78(12)–95.34(13)
Cl–Ge2–Cl	95.75(13)–96.10(14)	Cl–Ge4–Cl	94.71(13)– 96.10(13)

Table S2 Selected bond lengths (Å) and angles (°) for $[Me_2P(O)(CH_2)_2P(O)Me_2H][GeCl_3]$

Ge1–Cl1	2.3000(8)	Ge1–Cl2	2.3087(8)
Ge1–Cl3	2.3059(7)	P1–O1	1.5147(17)
P2–O2	1.5409(17)	P–C(Me)	1.773(2)–1.800(2)
Cl1–Ge1–Cl2	96.76(3)	Cl1–Ge1–Cl3	96.66(3)
Cl2–Ge1–Cl3	95.00(3)		