

reaction mixture was stirred for 1 h before it was allowed to warm to ambient temperature. After the mixture had been stirred for a further 24 h, a cloudy yellow/brown solution was produced. The mixture was filtered through Celite, cooled to -20°C , and left to stand for 12 h, resulting in the precipitation of small, colorless crystals of **1**. Yield 60.5%; m.p. $> 300^{\circ}\text{C}$; IR (Nujol): $\tilde{\nu} = 1775\text{ cm}^{-1}$ (Al–H); elemental analysis calcd for $\text{C}_{60}\text{H}_{94}\text{Al}_4\text{Li}_4\text{N}_6\text{O}_6$ (%): C 63.72, H 8.32, N 7.43; found: C 63.45, H 7.55, N 8.70; ^1H NMR (variable-temperature studies showed only one set of resonances (with broadening) in the range 300–193 K; 400.13 MHz, C_6D_6 , 300 K): $\delta = 7.76$ (d, 2H; *o*-H, Ph), 7.16 (t, 2H; *m*-H, Ph), 6.74 (t, 1H; *p*-H, Ph), 5.40 (v br., 1H; AlH), 2.88 (q, 4H; OCH_2), 0.60 (t, 6H; CH_3); ^{13}C NMR (100.62 MHz, C_6D_6 , 300 K): $\delta = 156.70$ (*i*-C; Ph), 129.21 (*m*-C; Ph), 124.88 (*o*-C; Ph), 117.58 (*p*-C; Ph), 65.33 (OCH_2), 13.66 (CH_3); ^7Li NMR (variable-temperature studies showed only a single resonance in the range 300–213 K but the appearance of a second resonance at 193 K; 155.51 MHz, referenced to LiCl in D_2O , $[\text{D}_8]\text{toluene}$, 193 K): $\delta = 6.75$, $\delta = 6.58$; ^{27}Al NMR (C_6D_6 , 298 K, 52.12 MHz, referenced to AlCl_3 in D_2O): $\delta = 131.30$, 69.91.

Received: April 25, 2000 [Z15042]

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Crystallographic Data Centre as supplementary publication no. CCDC-142922. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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New Fused Bicyclic Cyclotrigermanes from Cycloaddition Reactions of Cyclotrigermene**

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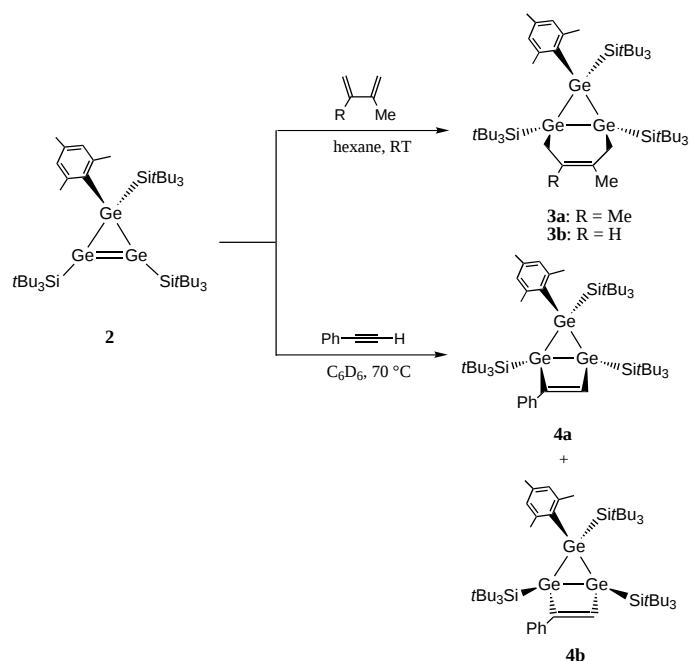
The chemistry of three- and four-membered ring systems consisting of Group 14 elements heavier than carbon is a subject of considerable interest.^[1] The thermal and photochemical conversion of cyclotrigermanes into digermenes and germylenes is well established and has been used for the synthesis of a variety of novel germanium compounds.^[2] However, cyclotrigermene derivatives incorporating a bicyclic system are completely unknown for synthetic reasons.^[3, 4] Most of the cyclotrigermene derivatives were synthesized by the simple reductive coupling reaction of the corresponding diorganodihalogermene with the appropriate reducing agents.^[1, 2] Recently, we succeeded in synthesizing a variety of cyclotrigermene analogues of cyclopropene by reaction of the cyclotrigermanium ion with nucleophiles.^[5] The reactivity of the cyclotrigermenes is of special interest, since cycloaddition to the endocyclic Ge=Ge bond could provide access to new bicyclic compounds. We now report the synthesis of the first bicyclic cyclotrigermene derivatives by the reaction of a mesityl-substituted cyclotrigermene with isoprene, 2,3-dimethyl-1,3-butadiene, and phenylacetylene.

After the successful synthesis of tetrakis(tri-*tert*-butylsilyl)-cyclotrigermene ($t\text{Bu}_3\text{Si}$)₄Ge₃ (**1a**)^[6] and tetrakis(tri-*tert*-butylgermyl)cyclotrigermene ($t\text{Bu}_3\text{Ge}$)₄Ge₃ (**1b**)^[6] by reaction of GeCl₂(dioxane) with $t\text{Bu}_3\text{SiNa}$ or $t\text{Bu}_3\text{GeLi}$, we presumed that the cyclotrigermenes should be suitable as precursors of

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[**] This work was supported by a Grant-in-Aid for Scientific Research (Nos. 10304051, 12020209, 12042213) from the Ministry of Education, Science and Culture of Japan, and TARA (Tsukuba Advanced Research Alliance) Fund.

bicyclic cyclotrigermanes. Nevertheless, all attempted reactions of **1a,b** with various dienes or acetylenes failed due to the steric overcrowding of **1a,b**. However, we found that 1,2,3-tris(tri-*tert*-butylsilyl)-3-mesitylcyclotrigermene (**2**)^[5] shows relatively high reactivity at the Ge=Ge bond due to the decrease in steric crowding on replacing one *t*Bu₃Si group at the saturated germanium atom with a mesityl group. The reaction of **2** with 2,3-dimethyl-1,3-butadiene in hexane at room temperature produced the Diels–Alder adduct **3a** as a yellow, air-stable crystalline compound in 63 % yield (Scheme 1). The reaction of **2** with isoprene gave **3b** in 78 % yield. These [2+4] cycloadducts were isolated by chromatography on silica gel without any decomposition. The NMR spectral data and X-ray crystal structure suggest the formation of just one of the two possible stereoisomers.



Scheme 1. Synthesis of **3** and **4**.

The molecular structure of **3b** was determined by X-ray diffraction (Figure 1).^[7] It reveals that isoprene attacked the Ge=Ge bond from the mesityl side of the three-membered ring to give only one stereoisomer. The difference in the steric bulk of the substituents on the sp³ Ge atom of **2** (Mes < *t*Bu₃Si) apparently can control the facial selectivity in the [2+4] cycloaddition. The three *t*Bu₃Si groups in **3b** are arranged in the same direction relative to the three-membered cyclotrigermane skeleton. Due to the large steric bulk of the *t*Bu₃Si group, the three *t*Bu₃Si groups occupy the less hindered pseudoequatorial positions, whereas the mesityl group and the CH₂C(Me)=CHCH₂ moiety occupy the pseudoaxial positions, as determined by the angles between the three-membered ring plane and the Ge–R bond (R = *t*Bu₃Si, CH₂C(Me)=CHCH₂, and Mes): 29.6° for *t*Bu₃Si, 100.8° for CH₂C(Me)=CHCH₂, and 106.6° for Mes. The Ge1–Ge2 (2.5938(3) Å) and Ge1–Ge3 (2.6068(3) Å) bond lengths lie in the upper range of known values for cyclotrigermanes

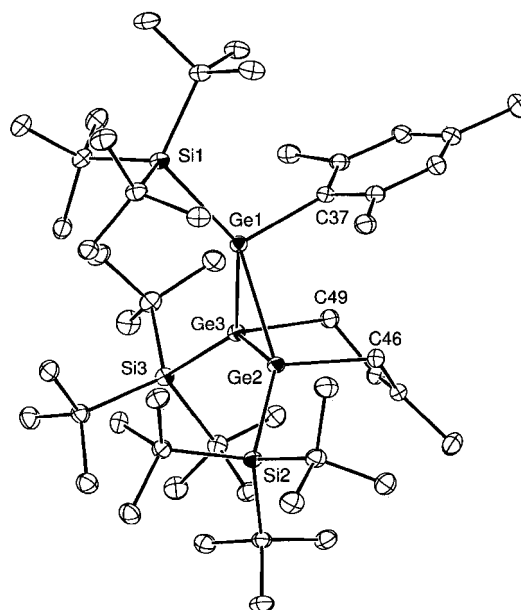


Figure 1. Structure of **3b** (ORTEP plot; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.5938(3), Ge1–Ge3 2.6068(3), Ge2–Ge3 2.4705(3), Ge1–Si1 2.5529(7), Ge2–Si2 2.4873(6), Ge3–Si3 2.5314(7), Ge1–C37 2.029(2), Ge2–C46 2.048(2), Ge3–C49 2.050(2); Ge2–Ge1–Ge3 56.724(9), Ge3–Ge2–Ge1 61.903(9), Ge2–Ge3–Ge1 61.374(9).

(typically 2.460–2.590 Å).^[1, 2] In contrast, the Ge2–Ge3 bond is appreciably shorter (2.4705(3) Å), probably due to the effect of the fused ring system.

The [2+2] cycloaddition of **2** with phenylacetylene at 70 °C smoothly proceeded to give the more strained molecule **4** (Scheme 1), which was isolated as orange crystals of the two isomers **4a** (57 %) and **4b** (22 % yield).

The molecular structure of the favored isomer **4a** was determined by X-ray crystallography (Figure 2).^[7] The three

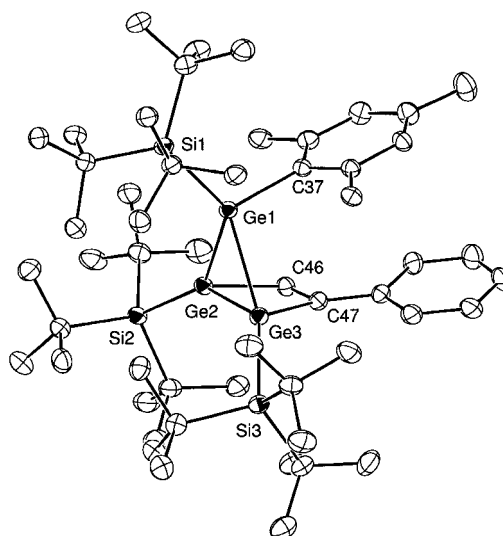
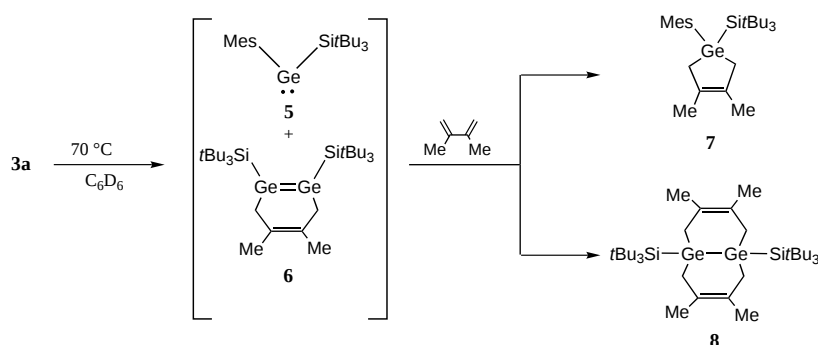


Figure 2. Structure of **4a** (ORTEP plot; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.5958(5), Ge1–Ge3 2.5592(4), Ge2–Ge3 2.4857(4), Ge1–Si1 2.5248(9), Ge2–Si2 2.4780(9), Ge3–Si3 2.4797(9), Ge1–C37 2.032(3), Ge2–C46 1.963(3), Ge3–C47 2.021(3), C46–C47 1.357(4); Ge3–Ge1–Ge2 57.65(1), Ge3–Ge2–Ge1 60.44(1), Ge2–Ge3–Ge1 61.91(1), C46–Ge2–Ge3 73.36(9), C47–Ge3–Ge2 73.66(9), C47–C46–Ge2 109.1(2), C46–C47–Ge3 103.8(2).

*t*Bu₃Si groups are situated in *cis,cis* positions, as in **3b**, and the bicyclo[2.1.0] skeleton is highly folded to relieve steric repulsion, as shown by the dihedral angle between the planes of the three- and four-membered rings (97.4°).

It is noteworthy that **3** is a good precursor of germylene and digermene under mild conditions. Thermolysis of cyclotrimer-germane **3a** at 70 °C in dry C₆D₆ for 3 h in the presence of an excess of 2,3-dimethyl-1,3-butadiene cleanly yielded germacyclopent-3-ene **7** (80%) and digermabicyclo[4.4.0]deca-3,8-diene **8** (86%), clear evidence for the trapping of the germylene **5** and the digermene **6**, respectively (Scheme 2). However, heating of **3** in the solid state at 180 °C in vacuo led to the quantitative formation of **2** by retro-Diels–Alder reaction.



Scheme 2. Thermolysis of **3a** and trapping of the thermolysis products.

The present [2+4] and [2+2] cycloaddition reactions of cyclotrimer-germanes cleanly afford fused bicyclic cyclotrimer-germane derivatives and thus provide a new route to small ring systems of Group 14 elements heavier than carbon.

Experimental Section

3a: Orange crystals of **2** (60 mg, 0.064 mmol) were placed in a reaction vessel with a magnetic stirrer. Dry, degassed hexane (1.5 mL) and 2,3-dimethyl-1,3-butadiene (70 mg, 0.85 mmol) were introduced by vacuum transfer, and the mixture was stirred for 6 h at room temperature. The solvent and excess 2,3-dimethyl-1,3-butadiene were removed in vacuo, and the resulting residue was separated by column chromatography on silica gel with hexane as eluent to give **3a** (41 mg, 63%) as yellow crystals; m.p. 123–126 °C (decomp); ¹H NMR ([D₆]benzene, TMS): δ = 1.30 (s, 27H), 1.37 (s, 54H), 1.70 (s, 6H), 1.90 (s, 3H), 2.60 (s, 2H), 2.64 (s, 2H), 2.80 (s, 6H), 6.78 (s, 2H); ¹³C{¹H} NMR ([D₆]benzene, TMS): δ = 14.3, 23.0, 25.6, 26.8, 28.4, 29.9, 32.9, 33.5, 126.6, 128.8, 129.1, 137.0, 144.8; ²⁹Si{¹H} NMR ([D₆]benzene, TMS): δ = 45.9, 49.4; UV/Vis (*n*-hexane): λ_{max} (ε) = 277 (18950), 388 nm (1740); elemental analysis calcd for C₅₁H₁₀₂Ge₃Si₃ (%): C 60.21, H 10.10; found: C 60.14, H 10.17.

3b: Compound **3b** was prepared in 78% yield as yellow crystals; m.p. 130–132 °C (decomp); ¹H NMR ([D₆]benzene, TMS): δ = 1.30 (s, 27H), 1.35 (s, 27H), 1.37 (s, 27H), 1.84 (s, 3H), 1.97 (s, 3H), 2.57–2.61 (m, 2H), 2.70–2.73 (m, 1H), 2.79 (s, 3H), 2.80 (s, 3H), 2.95–3.00 (m, 1H), 5.51–5.53 (m, 1H), 6.78 (s, 2H); ¹³C{¹H} NMR ([D₆]benzene, TMS): δ = 20.9, 22.7, 25.6, 25.8, 26.8, 26.9, 27.0, 28.0, 28.6, 32.8, 32.9, 33.4, 123.3, 129.0, 129.1, 132.0, 137.0, 143.7, 144.5, 144.8; ²⁹Si{¹H} NMR ([D₆]benzene, TMS): δ = 45.3, 45.4, 47.9; UV/Vis (*n*-hexane): λ_{max} (ε) = 277 (16860), 388 nm (1520); elemental analysis calcd for C₅₀H₁₀₀Ge₃Si₃ (%): C 59.85, H 10.04; found: C 59.74, H 10.06.

4a and **4b**: Orange crystals of **2** (60 mg, 0.064 mmol) were placed in a reaction tube. Dry, degassed benzene (0.5 mL) and phenylacetylene (90 mg, 0.88 mmol) were introduced by vacuum transfer, and the mixture was heated for 6 h at 70 °C. The solvent and the excess phenylacetylene

were removed in vacuo, and the resulting residue was separated by column chromatography on silica gel with hexane as eluent to give **4a** (57 mg, 57%) and **4b** (22 mg, 22%). **4a**: orange crystals; m.p. 178–180 °C; ¹H NMR ([D₆]benzene, TMS): δ = 1.30 (s, 27H), 1.37 (s, 27H), 1.40 (s, 27H), 1.89 (s, 3H), 2.67 (s, 3H), 3.11 (s, 3H), 6.59 (s, 1H), 6.61 (s, 1H), 6.82–6.99 (m, 5H), 7.24 (s, 1H); ¹³C{¹H} NMR ([D₆]benzene, TMS): δ = 20.9, 25.5, 26.0, 26.4, 29.3, 30.8, 32.3, 32.7, 33.2, 125.7, 126.1, 127.3, 128.5, 128.7, 129.8, 130.0, 136.1, 143.1, 143.5, 144.7, 145.5, 155.9, 170.8; ²⁹Si{¹H} NMR ([D₆]benzene, TMS): δ = 38.5, 44.7, 50.0; UV/Vis (*n*-hexane): λ_{max} (ε) = 250 (46700), 303 (21930), 410 nm (2410); **4b**: orange crystals; m.p. 90–93 °C; ¹H NMR ([D₆]benzene, TMS): δ = 1.19 (s, 27H), 1.27 (s, 27H), 1.38 (s, 27H), 2.11 (s, 3H), 2.99 (s, 3H), 3.18 (s, 3H), 6.81 (s, 2H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 7.8 Hz, 2H), 7.52 (s, 1H); ¹³C{¹H} NMR ([D₆]benzene, TMS): δ = 21.2, 25.8, 26.0, 26.5, 30.3, 31.0, 32.3, 32.4, 33.6, 126.5, 127.2, 128.0, 128.1, 129.1, 137.3, 140.7, 143.6 (2C), 145.7, 153.0, 167.4; ²⁹Si{¹H} NMR ([D₆]benzene, TMS): δ = 39.6, 45.5, 49.4; UV/Vis (*n*-hexane): λ_{max} (ε) = 240 (41200), 302 (20900), 400 nm (2500).

Received: May 16, 2000 [Z15130]

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- [7] Diffraction data were collected at 120 K for **3b** and 150 K for **4a** on a Mac Science DIP2030 Image Plate Diffractometer with a rotating anode (50 kV, 90 mA) and graphite-monochromated MoK_α radiation (λ = 0.71070 Å). The structures were solved by direct methods and refined by full-matrix least-squares method with the SHELXL-97 program. Crystal data for **3b**·C₇H₈: C₅₇H₁₀₈Ge₃Si₃, *M*_r = 1095.47, monoclinic, space group *P*2₁/*n*, *a* = 15.2160(3), *b* = 13.6410(3), *c* = 29.2430(5) Å, β = 99.810(1)°, *V* = 5981.0(2) Å³, *Z* = 4, ρ_{calcd} =

1.217 g cm⁻³. The final *R* factor was 0.0461 (*R*_w = 0.1328) for 12902 reflections with *I* > 2σ(*I*). Crystal data for **4a** · 0.5 C₆H₁₄: C₅₆H₁₀₈Ge₃Si₃, *M*_r = 1080.47, triclinic, space group = *P* $\bar{1}$, *a* = 13.7810(7), *b* = 14.485(1), *c* = 15.339(1) Å, α = 100.917(3), β = 91.953(4), γ = 95.408(4)°, *V* = 2988.9(3) Å³, *Z* = 2, ρ_{calcd} = 1.201 g cm⁻³. The final *R* factor was 0.0496 (*R*_w = 0.1408) for 10780 reflections with *I* > 2σ(*I*). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-144512 and CCDC-144513. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Direct Bromination of Keggin Fragments To Give [PW₉O₂₈Br₆]³⁻: A Polyoxotungstate with a Hexabrominated Face*

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The design and synthesis of polyoxometalates with specific structures and properties requires synthetic methodologies that enable framework morphology and surface functionality to be manipulated in a rational fashion and, although some progress has been made in recent years, there is still enormous scope for new, systematic chemistry in this area. Since the initial work by Knoth,^[1] a particularly fruitful approach has been the attachment of organometal or organometalloid groups to lacunary species such as the tungstate Keggin fragments [PW₁₁O₃₉]⁷⁻, [SiW₁₁O₃₉]⁸⁻, [SiW₁₀O₃₆]⁸⁻, [PW₉O₃₄]⁹⁻, and [SiW₉O₃₄]¹⁰⁻, and derivatives resulting from this strategy have been reviewed recently.^[2] However, reactions involving the metathesis of labile halides, a ubiquitous method for ligand manipulation in synthetic organometallic and metal-organic chemistry, are not generally available for the surface functionalization of polyoxometalates because of the paucity of suitable halogenated derivatives. Although several fluoropolyxoanions have been characterized,^[2] and polyoxometalates containing heterometal–halide bonds have been prepared from reactions between lacunary anions and heterometal halides,^[3] previously reported attempts to halogenate a polyoxometalate surface to produce reactive M–X sites resulted instead in degradation of the polyoxometalate framework and the production of low-nuclearity oxohalide complexes.^[4] Herein we report the first successful halogenation of Keggin derivatives [PW₉O₃₄]⁹⁻ and [NaPW₁₁O₃₉]⁶⁻

and the structure of the resulting unique polyoxometalate with multiple terminal halide ligands.

The bromoanion [PW₉O₂₈Br₆]³⁻ (**1**) was initially obtained as one of the products from the reaction between (nBu₄N)₆[NaPW₁₁O₃₉]^[5] and C₂O₂Br₂ in an attempt to attach oxalate groups to the surface of the PW₁₁ Keggin fragment. The acetonitrile solvate of (nBu₄N)₃-**1** crystallized as yellow crystals along with colorless crystals of (nBu₄N)₂[W₂O₄Br₄(μ-C₂O₄)] and both compounds were structurally characterized by single-crystal X-ray diffraction.^[6] The bromoanion **1** has the β, A-PW₉ structure (Figure 1), and is formally

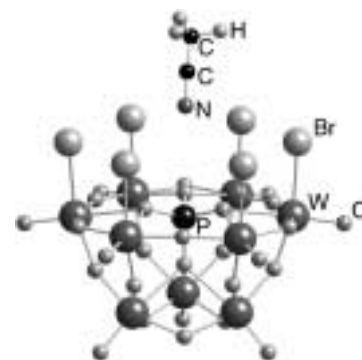


Figure 1. Structure of **1** showing also the position of the acetonitrile solvate molecule. Selected bond lengths [Å] and angles [°] (mean values within W₆ ring, values in parentheses are ranges of esds for individual measurements): W–Br 2.500(2–3), W–O_{term} 1.698(10–13), W–O(P) 2.399(10–11), W–O(W) (edge-sharing) 1.902(11–12), W–O(W) (corner-sharing) 1.881(10–12), W–O–W (edge-sharing) 125.3(5–6), W–O–W (corner-sharing) 159.9(6–7). Mean values between W₆ and W₃ rings: (Br)W–O(W) 1.875(11–13), (Br)W–O–W 1.928(11–14), W–O–W 147.8(6).

derived from the triply vacant lacunary Keggin anion β, A-[PW₉O₃₄]⁹⁻ by replacement of six terminal oxo ligands with six bromo ligands, giving a molecular oxide with a fully brominated face. The structure of the dinuclear anion [W₂O₄Br₄(μ-C₂O₄)]²⁻ (**2**) is analogous to that of the molybdenum chloro analogue [Mo₂O₄Cl₄(μ-C₂O₄)]²⁻^[7] and will be reported separately.

The mean W–Br bond length of 2.50 Å in **1** is similar to that in **2** (2.52 Å) and, although no discrete β, A-[PW₉O₂₈X₆] structures have previously been reported, W–O bond lengths in **1** are similar to those in α, A-[PW₉O₃₄{Si(*t*Bu)OH}₃]³⁻^[8] and in [(PhSnOH)₃(β, A-PW₉O₃₄)₂]¹²⁻.^[9]

Another feature of this crystal structure also shown in Figure 1 is the acetonitrile solvate molecule situated with the N atom 1.19 Å above the mean plane of the six bromo ligands, with N...Br distances of 3.773–4.053 Å. Partial occupancy of a second acetonitrile molecule position is correlated with disorder in some cation alkyl chains. The formation of **1** from [NaPW₁₁O₃₉]⁶⁻ and C₂O₂Br₂ is consistent with a degradation process in which initial electrophilic attack at the basic oxide surface is followed by excision of two WO₂Br₂ fragments as the oxalato-bridged dinuclear complex **2**.

Bands for ν(P–O), ν(W=O), and ν(W–O–W) in the IR spectrum of (nBu₄N)₃-**1** are at higher wavenumbers than those for Na₈H[PW₉O₃₄], as previously observed for α, A-[PW₉O₃₄(RPO)₂]⁵⁻ ions.^[10] A band at 928 cm⁻¹ is low for terminal W=O, and may reflect stronger bonding in the

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[**] This work was supported by the UK Engineering and Physical Sciences Research Council.