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 °C; IR (Nujol): $\tilde{v} = 1775$ cm^{-1} (Al–H); elemental analysis calcd for $C_{60}H_{94}Al_4Li_4$-N_6O_6 (%): C 63.72, H 8.32, N 7.43; found: C 63.45, H 7.55, N 8.70; ^{1}HNMR (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; Al*H*), 2.88 (q, 4H; OCH$_2$), 0.60 (t, 6H; CH$_3$); ^{13}CNMR (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$_3$); ^{7}Li 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$_2$O, [D$_8$]toluene, 193 K): $\delta = 6.75$, δ 6.58; ^{27}Al NMR (C_6D_6, 298 K, 52.12 MHz, referenced to AlCl$_3$ in D$_2$O): $\delta = 131.30$, 69.91.

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New Fused Bicyclic Cyclotrigermanes from Cycloaddition Reactions of Cyclotrigermene**
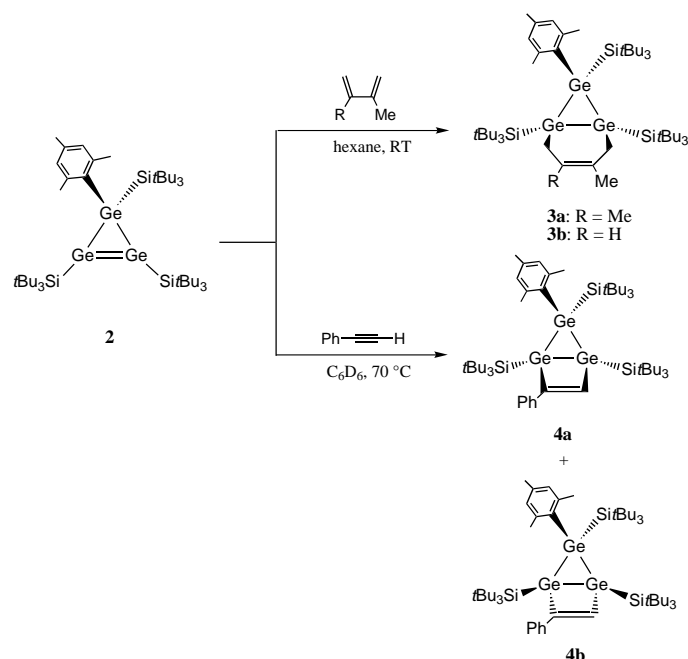
Norihisa Fukaya, Masaaki Ichinohe, and Akira Sekiguchi*

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, cyclotrigermane derivatives incorporating a bicyclic system are completely unknown for synthetic reasons.[3, 4] Most of the cyclotrigermane derivatives were synthesized by the simple reductive coupling reaction of the corresponding diorganodihalogermane with the appropriate reducing agents.[1, 2] Recently, we succeeded in synthesizing a variety of cyclotrigermene analogues of cyclopropene by reaction of the cyclotrigermenium 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 cyclotrigermane 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 (tBu$_3$Si)$_4$Ge$_3$ (**1a**)[6] and tetrakis(tri-*tert*-butylgermyl)cyclotrigermene (tBu$_3$Ge)$_4$Ge$_3$ (**1b**)[6] by reaction of GeCl$_2$(dioxane) with tBu$_3$SiNa or tBu$_3$GeLi, we presumed that the cyclotrigermenes should be suitable as precursors of

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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.

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

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
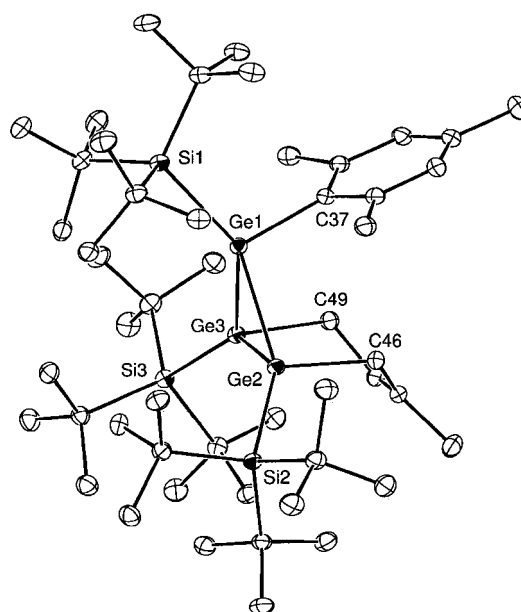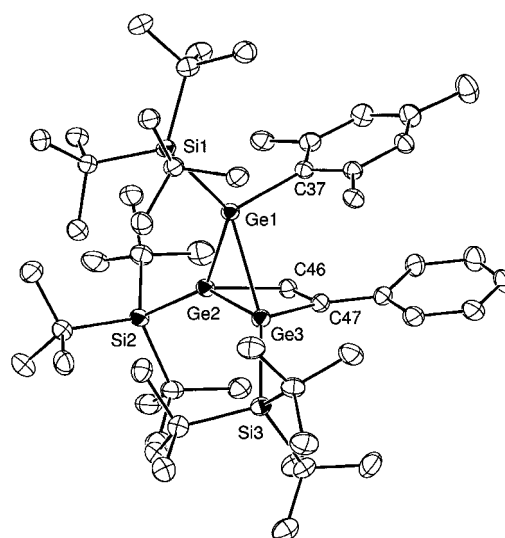

Figure 2. Structure of **4a** (ORTEP plot; hydrogen atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Ge1–Ge2 2.5958(5), Ge1–Ge3 2.5592(4), Ge2–Ge3 2.4857(4), Ge1–Si1 2.5248(9), Ge2–Si2 2.4780(9), Ge3–Si3 2.4797(9), Ge1–C37 2.032(3), Ge2–C46 1.963(3), Ge3–C47 2.021(3), C46–C47 1.357(4); 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*Bu$_3$Si 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 cyclotrigermane **3a** at 70 °C in dry C$_6$D$_6$ 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.
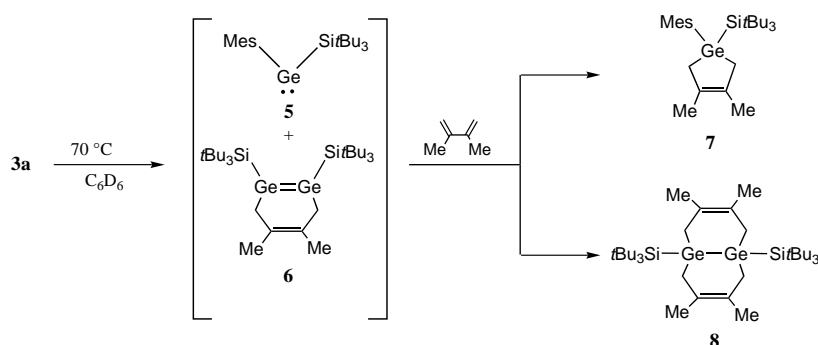
Scheme 2. Thermolysis of **3a** and trapping of the thermolysis products.

The present [2+4] and [2+2] cycloaddition reactions of cyclotrigermenes cleanly afford fused bicyclic cyclotrigermane 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); ^{1}H NMR ([D$_6$]benzene, TMS): δ = 1.30 (s, 27 H), 1.37 (s, 54 H), 1.70 (s, 6 H), 1.90 (s, 3 H), 2.60 (s, 2 H), 2.64 (s, 2 H), 2.80 (s, 6 H), 6.78(s, 2 H); ^{13}C{^{1}H} NMR ([D$_6$]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; ^{29}Si{^{1}H} NMR ([D$_6$]benzene, TMS): δ = 45.9, 49.4; UV/Vis (*n*-hexane): λ$_{max}$ (ε) = 277 (18950), 388 nm (1740); elemental analysis calcd for C$_{51}$H$_{102}$Ge$_3$Si$_3$ (%): 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); ^{1}H NMR ([D$_6$]benzene, TMS): δ = 1.30 (s, 27 H), 1.35 (s, 27 H), 1.37 (s, 27 H), 1.84 (s, 3 H), 1.97 (s, 3 H), 2.57 – 2.61 (m, 2 H), 2.70 – 2.73 (m, 1 H), 2.79 (s, 3 H), 2.80 (s, 3 H), 2.95 – 3.00 (m, 1 H), 5.51 – 5.53 (m, 1 H), 6.78 (s, 2 H); ^{13}C{^{1}H} NMR ([D$_6$]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; ^{29}Si{^{1}H} NMR ([D$_6$]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 C$_{50}$H$_{100}$Ge$_3$Si$_3$ (%): 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; ^{1}H NMR ([D$_6$]benzene, TMS): δ = 1.30 (s, 27 H), 1.37 (s, 27 H), 1.40 (s, 27 H), 1.89 (s, 3 H), 2.67 (s, 3 H), 3.11 (s, 3 H), 6.59 (s, 1 H), 6.61 (s, 1 H), 6.82 – 6.99 (m, 5 H), 7.24 (s, 1 H); ^{13}C{^{1}H} NMR ([D$_6$]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; ^{29}Si{^{1}H} NMR ([D$_6$]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; ^{1}H NMR ([D$_6$]benzene, TMS): δ = 1.19 (s, 27 H), 1.27 (s, 27 H), 1.38 (s, 27 H), 2.11 (s, 3 H), 2.99 (s, 3 H), 3.18 (s, 3 H), 6.81 (s, 2 H), 7.06 (t, J = 7.8 Hz, 1 H), 7.22 (t, J = 7.8 Hz, 2 H), 7.45 (d, J = 7.8 Hz, 2 H), 7.52 (s, 1 H); ^{13}C{^{1}H} NMR ([D$_6$]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 (2 C), 145.7, 153.0, 167.4; ^{29}Si{^{1}H} NMR ([D$_6$]benzene, TMS): δ = 39.6, 45.5, 49.4; UV/Vis (*n*-hexane): λ$_{max}$ (ε) = 240 (41200), 302 (20900), 400 nm (2500).

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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 Mo$_{Kα}$ 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**·C$_7$H$_8$: C$_{57}$H$_{108}$Ge$_3$Si$_3$, M_r = 1095.47, monoclinic, space group $P2_1/n$, a = 15.2160(3), b = 13.6410(3), c = 29.2430(5) Å, $β$ = 99.810(1)°, V = 5981.0(2) Å^3, Z = 4, $ρ_{calcd}$ =

1.217 gcm^{-3}. The final R factor was 0.0461 ($Rw = 0.1328$) for 12902 reflections with $I > 2\sigma(I)$. Crystal data for **4a**·0.5C$_6$H$_{14}$: C$_{56}$H$_{105}$Ge$_3$Si$_3$, $M_r = 1080.47$, triclinic, space group = $P\bar{1}$, $a = 13.7810(7)$, $b = 14.485(1)$, $c = 15.339(1)$ Å, $\alpha = 100.917(3)$, $\beta = 91.953(4)$, $\gamma = 95.408(4)°$, $V = 2988.9(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.201$ gcm^{-3}. The final R factor was 0.0496 ($Rw = 0.1408$) for 10780 reflections with $I > 2\sigma(I)$. 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 [PW$_9$O$_{28}$Br$_6$]$^{3-}$: 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 [PW$_{11}$O$_{39}$]$^{7-}$, [SiW$_{11}$O$_{39}$]$^{8-}$, [SiW$_{10}$O$_{36}$]$^{8-}$, [PW$_9$O$_{34}$]$^{9-}$, and [SiW$_9$O$_{34}$]$^{10-}$, 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 fluoropolyoxoanions 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 [PW$_9$O$_{34}$]$^{9-}$ and [NaPW$_{11}$O$_{39}$]$^{6-}$

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

The bromoanion [PW$_9$O$_{28}$Br$_6$]$^{3-}$ (**1**) was initially obtained as one of the products from the reaction between (nBu$_4$N)$_6$-[NaPW$_{11}$O$_{39}$][5] and C$_2$O$_2$Br$_2$ in an attempt to attach oxalate groups to the surface of the PW$_{11}$ Keggin fragment. The acetonitrile solvate of (nBu$_4$N)$_3$-**1** crystallized as yellow crystals along with colorless crystals of (nBu$_4$N)$_2$[W$_2$O$_4$-Br$_4$(μ-C$_2$O$_4$)] and both compounds were structurally characterized by single-crystal X-ray diffraction.[6] The bromoanion **1** has the β,A-PW$_9$ structure (Figure 1), and is formally
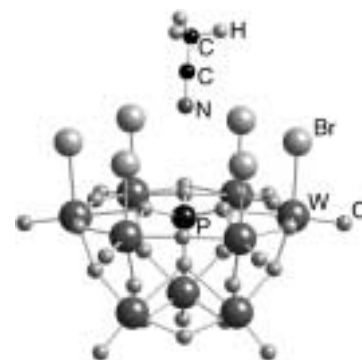

Figure 1. Structure of **1** showing also the position of the acetonitrile solvate molecule. Selected bond lengths [Å] and angles [°] (mean values within W$_6$ ring, values in parentheses are ranges of esds for individual measurements): W-Br 2.500(2–3), W-O$_{term}$ 1.698(10–13), W-O(P) 2.399(10–11), 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 W$_6$ and W$_3$ rings: (Br)W-O(W) 1.875(11–13), (BrW)O-W 1.928(11–14), W-O-W 147.8(6).

derived from the triply vacant lacunary Keggin anion β, A-[PW$_9$O$_{34}$]$^{9-}$ 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 [W$_2$O$_4$Br$_4$(μ-C$_2$O$_4$)]$^{2-}$ (**2**) is analogous to that of the molybdenum chloro analogue [Mo$_2$O$_4$Cl$_4$(μ-C$_2$O$_4$)]$^{2-}$[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-[PW$_9$O$_{28}$X$_6$] structures have previously been reported, W–O bond lengths in **1** are similar to those in α,A-[PW$_9$O$_{34}${Si(tBu)OH}$_3$]$^{3-}$[8] and in [(PhSnOH)$_3$(β,A-PW$_9$O$_{34}$)$_2$]$^{12-}$.[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 $\cdots$ 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 [NaPW$_{11}$O$_{39}$]$^{6-}$ and C$_2$O$_2$Br$_2$ is consistent with a degradation process in which initial electrophilic attack at the basic oxide surface is followed by excision of two WO$_2$Br$_2$ 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 (nBu$_4$N)$_3$-**1** are at higher wavenumbers than those for Na$_8$H[PW$_9$O$_{34}$], as previously observed for α,A-[PW$_9$O$_{34}$(RPO)$_2$]$^{5-}$ ions.[10] A band at 928 cm^{-1} is low for terminal W=O, and may reflect stronger bonding in the