

Synthesis of the Germanium(I) Compounds $[\text{Ge}_2\text{Hal}_4]^{2-}$ and Their Reductive Condensation to Octahedral $[\text{Ge}_6]^{2-}$ Clusters in an Organometallic Environment

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Dedicated to Professor Jürgen Felsche on the occasion of his 60th birthday

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GeI_2 reacts with $[\text{M}_2(\text{CO})_{10}]^{2-}$ ($\text{M} = \text{Cr}, \text{W}$) leading to reductive coupling of two GeI_2 units to produce the $[\text{Ge}_2\text{I}_4]^{2-}$ ligands of $[\{(\text{OC})_5\text{M}\}_2\text{Ge}-\text{GeI}_2\{\text{M}(\text{CO})_5\}]^{2-}$ (**1a** and **2a**). The $[\text{Ph}_4\text{P}]$ salts of these anions have been characterised by X-ray structure analyses as have the $[\text{Ph}_4\text{P}]$ salts of $[\{(\text{OC})_5\text{M}\}_2\text{Cl}_2\text{Ge}-\text{GeCl}_2\{\text{M}(\text{CO})_5\}]^{2-}$ (**1b** and **2b**) obtained from the iodo derivatives **1a** and **2a** by halide metathesis with $[\text{Ph}_4\text{P}]\text{Cl}$. Treatment of GeI_2 with $[\text{W}_2(\text{CO})_{10}]^{2-}$ in the pres-

ence of 2,2'-bipyridine leads to $[\{(\text{OC})_5\text{W}\}_2\text{Ge}-\text{Ge}(\text{bipy})\{\text{W}(\text{CO})_5\}]$ (**3**). The digermanium ligands in **1–3** contain germanium in the unconventional formal oxidation state +I. Reductive condensation of $[\{(\text{OC})_5\text{Cr}\}_2\text{Ge}-\text{GeI}_2\{\text{Cr}(\text{CO})_5\}]^{2-}$ (**1a**) by addition of $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ leads to the octahedral cluster $[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]^{2-}$ (**4**) in a yield of 40%. The sequence of reactions as reported describes the first systematic approach to the synthesis of $[\text{E}_6]^{2-}$ clusters.

Introduction

It has recently been shown that mononuclear Sn^{II} or Ge^{II} species may be transformed by group-16 carbonylmetallates to produce the octahedral $[\text{E}_6]^{2-}$ clusters ($\text{E} = \text{Ge}, \text{Sn}$) at the core of the well-characterised compounds $[\{(\text{OC})_5\text{Cr}\}_6\text{E}_6]^{2-}$.^[1] By statistical reasoning, the selective formation of such six-atom aggregates $[\text{E}_6]^{2-}$ from six individual constituents – each of which contains only one single element E – is a highly improbable process. Thermodynamic and kinetic control along the reaction pathway must play an important role if, as observed, six mononuclear entities aggregate to form an octahedral species. Because of the high number of oligonuclear intermediates that necessarily line out the pathway of such a process, these thermodynamic and kinetic factors are difficult to control. An extended series of experiments is needed to find the proper conditions for such selective aggregation procedures.

The number of potential steps involved in this type of reaction might be considerably reduced if oligonuclear precursors could be used in the condensation process. With this in mind we have tried to prepare dinuclear precursors that, when appropriately functionalised, would allow better control of the condensation process and a suitable procedure has in fact been developed in the case of germanium.

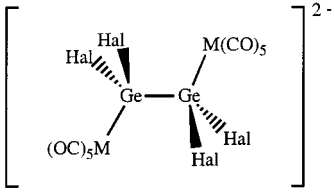
With germanium as the main-group centre it is known that dinuclear species Ge_2R_6 are intrinsically stable entities.^[2] Such organically substituted digermanes do, however, lack the reactive functionalisation necessary to produce di-element E_2 building blocks for the formation of E_6 clusters.

Ge_2H_6 might be a potential candidate as it is known that $\text{Ge}-\text{H}$ bonds may be broken in the presence of organometallic entities,^[3] although Ge_2H_6 is not easy to handle and is thus perhaps not the best choice.^[4] Moreover, the established procedures for the syntheses of $[\{(\text{OC})_5\text{M}\}_6\text{E}_6]^{2-}$ clusters all start from mononuclear EHal_2 compounds with the anionic pentacarbonylmethyl entities $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ ^[5] or $[\text{Cr}(\text{CO})_5]^{2-}$ ^[6] acting as halide abstractors and reducing agents at the same time.^[1] The ideal precursors in this respect would therefore be the compounds Ge_2Cl_2 or Ge_2Cl_6 ; the former compound is still unknown while the latter has been characterised as a rather unstable species.^[7] Since these precursors are not available or not suitable as such, one might try to produce them in an organometallically protected form. Since base-stabilised germylene compounds $[(\text{OC})_5\text{M}-\text{GeHal}_2\text{base}]$ ($\text{M} = \text{Cr}, \text{W}$) are known,^[8] a conceptual approach would consist of the reductive coupling of two such entities to give $[\{(\text{OC})_5\text{M}\}_2\text{Hal}_2\text{Ge}-\text{GeHal}_2\{\text{M}(\text{CO})_5\}]^{2-}$. This approach receives some additional credit from the observation that PhPCl_2 as well as PCl_3 undergo reductive coupling with $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ to produce the corresponding diphosphane coordination compounds $[\{(\text{OC})_5\text{Cr}\}_2\text{Cl}(\text{R})\text{P}-\text{P}(\text{R})\text{Cl}\{\text{Cr}(\text{CO})_5\}]$ ($\text{R} = \text{Ph}, ^{[9]}\text{Cl}^{[10]}$).

Compounds Containing a $[\text{Ge}_2\text{Hal}_4]^{2-}$ Ligand

It is shown in this paper that GeI_2 may be reductively coupled by its reaction with $[\text{M}_2(\text{CO})_{10}]^{2-}$ ($\text{M} = \text{Cr}, \text{W}$) to produce $[\{(\text{OC})_5\text{M}\}_2\text{Ge}-\text{GeI}_2\{\text{M}(\text{CO})_5\}]^{2-}$ (**1a** and **2a**, Table 1). Halide exchange by $[\text{Ph}_4\text{P}]\text{Cl}$ leads to the corresponding tetrachlorodigermanate compounds **1b** and **2b** (Table 1).

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Table 1. Complexes of type **1** and **2**


	halide	metal	cation
1a	I	Cr	[Na ⁺]
1a	I	Cr	[Ph ₄ P ⁺]
1b	Cl	Cr	[Ph ₄ P ⁺]
2a	I	W	[Na ⁺]
2a	I	W	[Ph ₄ P ⁺]
2a	I	W	[<i>n</i> Bu ₄ N ⁺]
2b	Cl	W	[Ph ₄ P ⁺]

These compounds contain the unconventional and hitherto unknown [Ge₂Hal₄]²⁻ ligands with the formal oxidation state of Ge corresponding to +I. In assigning this oxidation state the Cr(CO)₅ entities are seen as neutral sixteen-electron Lewis acids with chromium in an oxidation state of zero.

In agreement with the conceptual model, it is further found that Na₂[{(OC)₅Cr}I₂Ge–GeI₂{Cr(CO)₅}] ([Na⁺]₂·**1a**) undergoes transformation to the octahedral cluster anion [{(OC)₅Cr}₆Ge₆]²⁻ (**4**) by reaction with [Cr₂(CO)₁₀]²⁻ in an overall yield of 40%.

Syntheses and Structures

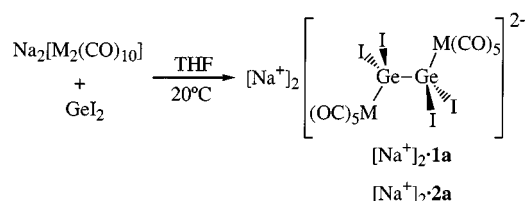
When a THF solution of Na₂[Cr₂(CO)₁₀] is treated with an equimolar amount of GeI₂, the solution immediately changes colour from orange to red. Chromatography gives

Table 2. $\tilde{\nu}_{\text{CO}}$ -IR spectroscopic data for the compounds **1–2**

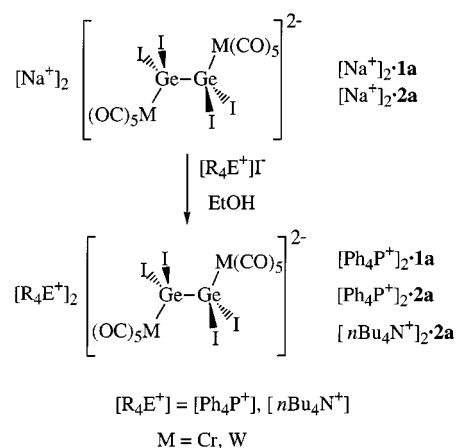
$\tilde{\nu}_{\text{CO}}$ -IR [cm ⁻¹]					
[Na ⁺] ₂ · 1a ^[a]	-	2037s	1970sh	1935vs,br	-
[Ph ₄ P ⁺] ₂ · 1a ^[b]	-	2034s	1967sh	1933vs	1890s
[Ph ₄ P ⁺] ₂ · 1a ^[c]	-	2032s	-	1924vs	1892sh
[Ph ₄ P ⁺] ₂ · 1b ^[b]	-	2030s	1950sh	1930vs	1889vs
[Ph ₄ P ⁺] ₂ · 1b ^[c]	-	2028s	-	1926vs,br	-
[Na ⁺] ₂ · 2a ^[d]	-	2049s	1967sh	1935vs	1884vs
[Na ⁺] ₂ · 2a ^[a]	-	2052s	-	1934vs,br	1909sh
[Ph ₄ P ⁺] ₂ · 2a ^[b]	-	2049s	1968sh	1930vs	1885s
[Ph ₄ P ⁺] ₂ · 2a ^[c]	-	2047s	1963sh	1920vs,br	1889s
[<i>n</i> Bu ₄ N ⁺] ₂ · 2a ^[b]	-	2049s	1967sh	1932vs	1885s
[<i>n</i> Bu ₄ N ⁺] ₂ · 2a ^[d]	2057w	2049s	1967sh	1934vs	1889s
[<i>n</i> Bu ₄ N ⁺] ₂ · 2a ^[c]	-	2049s	1969sh	1929vs	1879s
[Ph ₄ P ⁺] ₂ · 2b ^[b]	2055w	2046s	1963sh	1929vs	1883vs
3 ^[d]	2058m	2039s	1958sh	1927vs	-

[a] EtOH. – [b] DMA. – [c] CsI. – [d] THF.

Na₂[{(OC)₅Cr}I₂Ge–GeI₂{Cr(CO)₅}] ([Na⁺]₂·**1a**) as a red oil (Scheme 1).

Scheme 1. Reaction of Na₂[M₂(CO)₁₀] (M = Cr, W) with GeI₂

The compound [Ph₄P⁺]₂·**1a** is obtained as a crystalline derivative upon metathesis with [Ph₄P]I in ethanol (Scheme 2).



Scheme 2. Salt metathesis reaction

The anionic constituent of the sodium salt [Na⁺]₂·**1a** is the same as that of the phosphonium salt [Ph₄P⁺]₂·**1a**, as evidenced by the $\tilde{\nu}_{\text{CO}}$ -IR spectra of these compounds (Table 2). The properties of **1a** were therefore fully characterised with [Ph₄P⁺]₂·**1a** as the example studied (Tables 5 and 6).

The constitution of **1a**, as given, is in agreement with the spectroscopic data as well as with the microanalytical data. Proof of the constitution of **1a** comes from the X-ray analysis of [Ph₄P⁺]₂·**1a** (Figure 1, Tables 3 and 7).

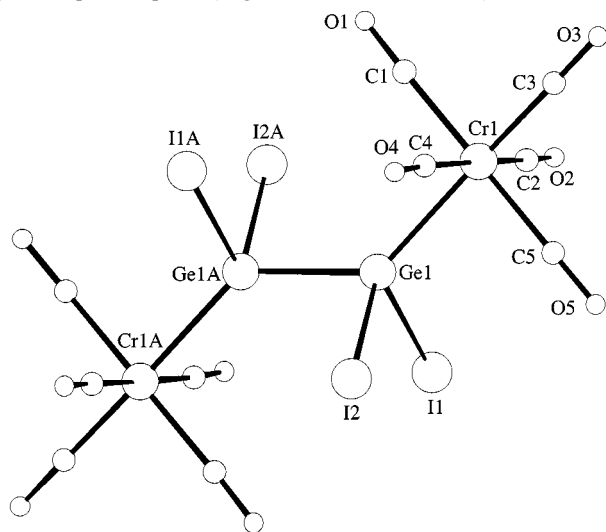


Figure 1. Structure of compound [Ph₄P⁺]₂·**1a**

The anion has crystallographically imposed inversion symmetry (Table 7). The Ge–Ge bond length is 244.8 pm (Table 3) and is thus well within the range of Ge–Ge distances reported for Ge₂R₆ compounds and their derivatives.^[2] The Ge–Cr distances (Table 3) compare favourably with the corresponding distances reported for [{(OC)₅Cr}GeR₂(Donor)],^[11] as well as with those observed for the mononuclear chelate compounds [{(OC)₅Cr}₂–

Ge(bipy)] and [{(OC)₅Cr}₂Ge(phen)] (bipy = 2,2′-bipyridine; phen = 1,10-phenanthroline).^[12]

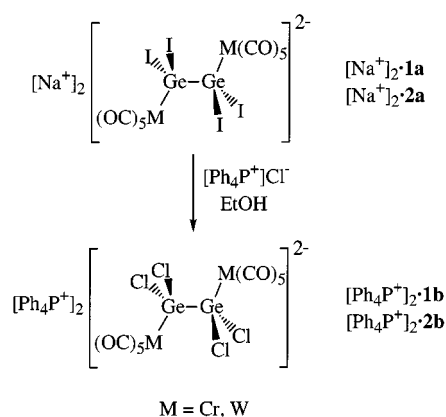
The mean Ge–I bond length of 264.5 pm (Table 3) is similar to that observed for [{Cp′(CO)₂Mn}GeI₃][–] (261.6 pm).^[13] Corresponding to the inversion symmetry of the molecule, the bonds radiating from the two Ge atoms are in a perfectly staggered arrangement. The pentacarbonylchromium entities are in their conventional idealised octahedral geometry with an overall slight umbrella effect for the equatorial carbonyl groups (Table 3). The CO group C1–O1 – equivalent to C1A–O1A by symmetry – is found to bend in an obverse sense (Table 3). These latter two groups are in close proximity to the GeI₂ entity in the symmetry-related part of the molecule.

The halide functionalities in **1a** are substitutionally labile: treatment of the sodium salt of **1a** (vide supra) with [Ph₄P]Cl results in an exchange of the iodine substituents of **1a** versus chlorine substituents to give **1b** (Scheme 3). Complex **1b** is obtained as a yellow microcrystalline material. The $\tilde{\nu}_{\text{CO}}$ -IR pattern observed for **1b** is very similar to that shown by **1a** (Table 2). Elemental analysis indicates that halide exchange is not complete under the experimental conditions and the presence of 5 to 10% of unexchanged iodine substituents is inferred from these data (Table 5).

X-ray analysis of [Ph₄P⁺]₂·**1b** substantiates this hypothesis. Crystals of [Ph₄P⁺]₂·**1b** are isotypic with those of [Ph₄P⁺]₂·**1a** (Table 7). The volume of the cell is reduced by about 4% upon substitution of iodine (**1a**) with chlorine (**1b**). The two anions **1a** and **1b** are isostructural in a qualitative sense. The Ge–Ge bond length of 245.5 pm in **1b** (Table 3) is almost equal to that observed for **1a** (244.8 pm,

Table 3. Selected bond lengths [pm], angles [°], and torsion angles [°] for the compounds **1–2**

	[Ph ₄ P ⁺] ₂ · 1a (M = Cr, Hal = I)	[Ph ₄ P ⁺] ₂ · 1b (M = Cr, Hal = Cl)	[Ph ₄ P ⁺] ₂ · 2a (M = W, Hal = I)	[Ph ₄ P ⁺] ₂ · 2b (M = W, Hal = Cl)
Ge1–Ge1A	244.8 (1)	245.5 (1)	245.6 (2)	245.0 (2)
Ge1–M1	246.8 (1)	244.0 (1)	260.6 (1)	258.4 (1)
Ge1–Hal1	264.8 (1)	226.6 (1)	262.8 (1)	225.9 (2)
Ge1–Hal2	264.1 (1)	234.7 (1)	266.2 (1)	238.7 (2)
Hal1–Ge1–Hal2	98.9 (1)	98.3 (1)	97.5 (1)	98.4 (1)
Hal1–Ge1–M1	115.1 (1)	114.9 (1)	115.6 (1)	116.2 (1)
Hal2–Ge1–M1	114.6 (1)	111.7 (1)	110.7 (1)	110.9 (1)
M1–Ge1–Ge1A	132.1 (1)	132.3 (1)	134.8 (1)	130.6 (1)
Hal1–Ge1–Ge1A	95.0 (1)	95.8 (1)	94.4 (1)	96.1 (1)
Hal2–Ge1–Ge1A	94.9 (1)	98.0 (1)	96.8 (1)	99.2 (1)
C1–M1–Ge1	92.8 (2)	90.4 (2)	92.4 (3)	89.4 (3)
C2–M1–Ge1	87.4 (2)	89.2 (2)	89.4 (3)	89.3 (3)
C3–M1–Ge1	178.1 (2)	174.9 (2)	174.4 (3)	174.7 (3)
C4–M1–Ge1	87.9 (2)	87.7 (2)	87.8 (3)	87.0 (3)
C5–M1–Ge1	86.2 (2)	83.5 (2)	86.3 (3)	86.1 (5)
Hal2–Ge1–Ge1A–Hal1A	81	81	81	80
M1A–Ge1A–Ge1–Hal1	49	48	47	47
M1–Ge1–Ge1A–Hal2A	50	51	52	52
C5–M1–Ge1–Hal1	–61	–59	–55	–59
C5–M1–Ge1–Hal2	52	52	54	52



Scheme 3. Salt metathesis reaction combined with an exchange of the iodine versus chlorine substituents

Table 3). The observed discrepancy of the Ge–Cl distances (Table 3), however, as well as the region of residual electron density of $1.6 \text{ electrons} \cdot 10^{-6} \text{ pm}^{-3}$ in the neighbourhood of the chlorine substituent Cl2 with the Ge1–Cl2 bond that is apparently too long (Table 3), have to be interpreted in terms of a partial occupancy of the chlorine position by an iodine substituent. Values of individual parameters will therefore be subject to errors and hence do not warrant a detailed discussion. The overall structure of **1b** is nevertheless unequivocally clear from the X-ray analysis.

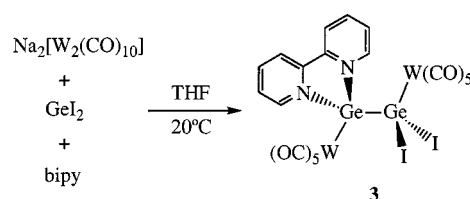
The mass-spectrometric analyses of $[\text{Ph}_4\text{P}^+]_2 \cdot \mathbf{1a}$ and $[\text{Ph}_4\text{P}^+]_2 \cdot \mathbf{1b}$ show fragmentation patterns which that are in accordance with their assigned constitution (Table 5).

The synthetic strategy leading to the pentacarbonylchromium derivatives **1a** and **1b** works equally well for the pentacarbonyltungsten derivatives **2a** and **2b** (Schemes 1, 2, and 3; Table 1). The anions **2a** and **2b** are isolated as their respective $[\text{Ph}_4\text{P}^+]$ or $[n\text{Bu}_4\text{N}^+]$ salts. Single crystals suitable for X-ray analysis could be obtained for their $[\text{Ph}_4\text{P}^+]$ salts (Tables 3 and 7). As seen from Table 7, the phosphonium salts of **1a**, **1b**, and **2b** form a set of isotypic crystals. The corresponding salt of **2a** also crystallises in a triclinic space group. The cell parameters (Table 7) are, however, numerically quite different from those characterising the above isotypic series. The unit cell observed for $[\text{Ph}_4\text{P}^+]_2 \cdot \mathbf{2a}$ cannot be transformed to a unit cell showing distances and angles that would be in close numerical agreement with those for the isotypic series of the phosphonium salts **1a**, **1b**, and **2b**. Transformation of the cell data of the phosphonium salt of **2a** by $\{00-1, 100, 0-10\}$ leads to a cell with dimensions (12.76, 12.06, 12.26 [Å]; 69.00, 90.39, 69.09 [°]). On using this transformed unit cell for comparison, the centres of the molecules are seen to have rather similar coordinates in all four salts. In the salt of **2a** the anionic part is, however, at a different rotational position as compared to the orientations of the anions in **1a**, **1b**, and **2b** with respect to the unit cells. By comparing the volumes of the cells (Table 7) it is clear that within the series of phosphonium salts the packing is least efficient in **2a**. This may explain the observation that crystals of $[\text{Ph}_4\text{P}^+]_2 \cdot \mathbf{2a}$ crack when cooled down to 200 K. A phase transition to the more closely packed pat-

tern is in accord with this finding. Nevertheless, the structures of all four compounds (**1a**, **1b**, **2a**, and **2b**) are qualitatively identical with that shown in Figure 1, which illustrates the general arrangement with the structure of **1a** shown as the specific example. In a quantitative respect, the essential difference between the pairs of structures **1a/2a** and **1b/2b** results from the replacement of the $\text{Cr}(\text{CO})_5$ groups in compounds **1** by $\text{W}(\text{CO})_5$ groups in compounds **2** (Tables 1, 3, and 7). The torsion angles within the molecules are not affected to a great extent by this replacement and, in particular, the Ge–Ge bond lengths are almost identical in all four compounds within the limits of error, with an average value of 245.2 pm (Table 3). As already observed for **1b**, some of the chlorine positions in **2b** are affected by an incomplete substitution of iodine versus chlorine, with the numerical values of the distances for Ge1–Hal2 in compounds **1b** and **2b** being too large. The remaining distances and angles (Table 3) agree favourably within the set of compounds **1** and **2**. The W–Ge distances observed for **2** are also within the range of W–Ge single bond lengths known to date.^[14]

$[\text{Hal}_2\text{Ge}-\text{Ge}(\text{bipy})]$ as a Ligand

It has been observed that formation of the cluster $[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]^{2-}$ from $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ and GeI_2 is promoted by the presence of bipy (2,2'-bipyridine)^[1a] and so the reactions leading to **1** and **2** were repeated in the presence of bipy. It was hoped that some bipy derivative could be detected that would help to explain the role of the bipy ligand in cluster formation.^[1a] However, treatment of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ in THF solution with equimolar amounts of GeI_2 and bipy did not produce any new insight into the process. The only products isolated were $[\{(\text{OC})_5\text{Cr}\}_2\text{Ge}(\text{bipy})]$ and $[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]^{2-}$, both of which have already been reported.^[1a,12] However, the use of $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$ as the starting material, under otherwise identical conditions, gave the digermanium compound **3** (Scheme 4).



Scheme 4. Reaction of $\text{Na}_2[\text{W}_2(\text{CO})_{10}]$ with GeI_2 and 2,2'-bipyridine

Compound **3** was purified by column chromatography and the side products $[(\text{OC})_4\text{W}(\text{bipy})]$ and $\text{W}(\text{CO})_6$ were separated by this procedure.^[17] Compound **3** was eluted with THF as a broad red band. Some additional red material was obtained by elution with ethanol and this, by analogy, is thought to contain $[\{(\text{OC})_5\text{W}\}_6\text{Ge}_6]^{2-}$. Compound **3** was obtained as a red oil by evaporation of the solvent from the combined THF fractions whose $\tilde{\nu}_{\text{CO}}$ -IR spectra showed only the bands due to **3** (Table 2) with no indication of by-products. Compound **3** could be obtained in a crystal-

line form from its concentrated solutions by a vapour phase diffusion process (see Experimental Section). The red crystals are stable over several days when retained in the mother liquor in the dark. Handling of the crystals is nevertheless problematic since they are found to produce an amorphous material under the conditions of evaporation. It is not yet clear whether this disintegration is due to the reduced pressure – a possibility that is not highly probable since compound **3** is found to crystallise without inclusion of solvent – or whether the material is sensitive to daylight. When the amorphous material that remained after evaporation of the solvent was redissolved, red solutions were obtained and the ¹H-NMR spectra of these indicate the presence of a minimum of three different types of coordinated bipy ligands. By comparison with spectra of authentic samples it appears that one of these products is [(OC)₄W(bipy)];^[17] the identity of the two other compounds is as yet unknown. The only way to identify the nature of the primary product **3** is therefore by X-ray analysis. Single crystals of **3** were immediately transferred from the mother liquor into perfluorinated oil and then placed onto a diffractometer in as short a period of time as possible while keeping the temperature below –70 °C. This procedure ensured that the crystals survived without disintegration. The structure of **3**, as determined by crystal structure analysis, is depicted in Figure 2 (Table 4).

Crystals of **3** contain discrete molecular entities, the central part of which is the digermanium-derived constituent [I₂Ge–Ge(bipy)] (Figure 2). Each of the germanium centres is coordinated to a W(CO)₅ group. One of the germanium centres (Ge1) has two iodine substituents, while the other germanium is coordinated to the bipy ligand (Figure 2). The germanium centres are linked by a Ge–Ge bond, the

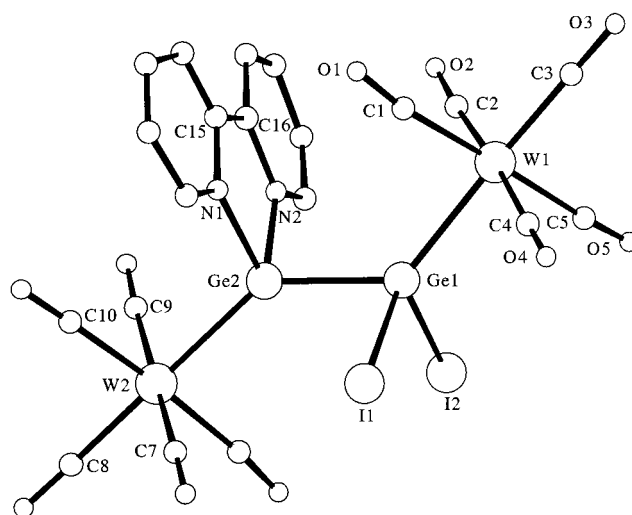


Figure 2. Structure of compound **3**

length of which (248.2 pm) is close to the Ge–Ge bond lengths observed for **1** and **2** (Tables 3 and 4).

The Ge–N and Ge–I bond lengths are also within the usual range,^[12,13] as are the Ge–W distances^[14] (compare Tables 3 and 4). The arrangement of the substituents around the Ge–Ge axis corresponds to that observed for **1** and **2**, with the bonds radiating from the two germanium centres being staggered with respect to one another (Table 4). Even though there is no crystallographically imposed molecular symmetry for **3**, the effective molecular symmetry is close to C_s (for torsion angles, see Table 4). In contrast to the structures of **1** and **2**, the rotation of the M(CO)₅ groups around their respective Ge–M axis is close to an eclipsed arrangement in **3** (Table 4, Figure 2); it ap-

Table 4. Selected bond lengths [pm], angles [°], and torsion angles [°] for the compound **3**

Ge1–Ge2	248.2 (3)	N1–Ge2–N2	80.2 (7)
Ge1–W1	259.0 (3)	N1–Ge2–W2	111.8 (5)
Ge1–I1	266.4 (4)	N2–Ge2–W2	111.6 (6)
Ge1–I2	262.0 (3)	C1–W1–Ge1	90.9 (8)
Ge2–W2	259.4 (3)	C2–W1–Ge1	87.3 (6)
Ge2–N1	202.8 (2)	C3–W1–Ge1	177.5 (7)
Ge2–N2	201.4 (2)	C4–W1–Ge1	89.4 (6)
		C5–W1–Ge1	86.8 (6)
W1–Ge1–Ge2–W2	180	I1–Ge1–I2	103.4 (1)
W2–Ge2–Ge1–I2	–48	I1–Ge1–W1	117.8 (1)
W2–Ge2–Ge1–I1	55	I2–Ge1–W1	117.3 (1)
N1–Ge2–Ge1–W1	–40	C6–W2–Ge2	92.4 (7)
N2–Ge2–Ge1–W1	41	C7–W2–Ge2	91.7 (6)
W2–Ge2–N1–C15	–110	C8–W2–Ge2	179.8 (9)
W2–Ge2–N2–C16	107	C9–W2–Ge2	85.7 (7)
C5–W1–Ge1–I1	–13	C10–W2–Ge2	90.8 (6)
C5–W1–Ge1–I2	111	I1–Ge1–Ge2	88.4 (1)
C10–W2–Ge2–N1	–3	I2–Ge1–Ge2	92.8 (1)
C10–W2–Ge2–N2	–91	W1–Ge1–Ge2	130.7 (1)
		W2–Ge2–Ge1	138.7 (1)
		Ge2–N1–C15	115.5 (2)
		Ge2–N2–C16	116.7 (2)

proximates a staggered orientation in the structures **1** and **2** (Table 3, Figure 1).

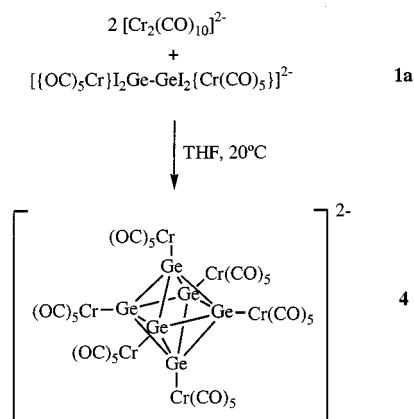
Compound **3** contains the digermanium species $[\text{I}_2\text{Ge}-\text{Ge}(\text{bipy})]$, which is unknown in the free state and stabilised in **3** by protection with bulky $\text{W}(\text{CO})_5$ groups. This digermanium entity may be interpreted in terms of a Lewis base/Lewis acid interaction with the organometallically protected eight electron species $\text{L}_n\text{MGe}(\text{bipy})$ acting as the base and the equivalently protected six-electron species L_nMGeI_2 as the Lewis acid.^[15] This type of interpretation is appealing since the protected six electron species $[(\text{OC})_5\text{M}-\text{GeR}_2]$ ^[16] are known as such and also in their base-stabilised form.^[8] Lewis acid adducts of $[(\text{OC})_5\text{M}-\text{Ge}(\text{bipy})]$ are equally well known and are well characterised as having $[\text{M}(\text{CO})_5]$ as the Lewis acidic group.^[12] By whatever electron-counting approach the bonding situation in $[\text{I}_2\text{Ge}-\text{Ge}(\text{bipy})]$ is analysed, it is found that it is in a formal sense isoelectronic to the $[\text{Ge}_2\text{Hal}_4]^{2-}$ entities of **1** and **2**.

The unsymmetrical substitution of the Ge–Ge entity in **3** might form the basis of its reactivity. To date, however, no attempt to transform **3** into the cluster $[\{(\text{OC})_5\text{W}\}_6\text{Ge}_6]^{2-}$ has been successful and it may therefore be assumed that compounds of type **3** do not play a key role in the bipy-mediated^[1a] synthesis of $[\{(\text{OC})_5\text{W}\}_6\text{Ge}_6]^{2-}$.

A Straightforward Synthesis of the $[\text{Ge}_6]^{2-}$ Core

Even though **3** could not be transformed to produce a $[\text{Ge}_6]^{2-}$ cluster, an efficient synthesis of the $[\text{Ge}_6]^{2-}$ core has nevertheless been found by following a different strategy (Scheme 5). When THF solutions of $\text{Na}_2[\{(\text{OC})_5\text{Cr}\}_2\text{I}_2\text{Ge}-\text{GeI}_2\{\text{Cr}(\text{CO})_5\}]$ ($[\text{Na}^+]_2\cdot\textbf{1a}$) (vide supra) are treated with two equivalents of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ ^[5] dissolved in THF, a continuous change of the $\tilde{\nu}_{\text{CO}}$ -IR spectra of the reaction mixture is observed. While the long-wavelength region is obscured by the bands that are characteristic of $[\text{Cr}_2(\text{CO})_{10}]^{2-}$, in the short-wavelength range the bands characteristic of the reaction products are observed to evolve. The band pattern at $2053/2030\text{ cm}^{-1}$ indicates the formation of $[\text{Cr}_2(\text{CO})_{10}\text{H}]^-$.^[5,18] The assignment of this pattern to $[\text{Cr}_2(\text{CO})_{10}\text{H}]^-$ was corroborated by the independent synthesis of $[\text{Ph}_4\text{P}][\text{Cr}_2(\text{CO})_{10}\text{H}]$, which was characterised by single-crystal analysis and comparison with the known structure of this compound,^[18] by its proton-NMR signal in CD_2Cl_2 solution at $\delta = -19.4$ and its $\tilde{\nu}_{\text{CO}}$ -IR spectrum in THF solution.^[5,18] A band characteristic of the cluster $[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]^{2-}$ (**4**) (2043 cm^{-1})^[1a] was also found to increase in intensity during the reaction. After complete addition of the two equivalents of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ during a period of three hours, the band at 2043 cm^{-1} was found not to increase any further when an additional 0.3 equivalents of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ were added. These findings indicate that the formation of the compound that gives rise to the band at 2043 cm^{-1} requires two equivalents of $\text{Na}_2[\text{Cr}_2(\text{CO})_{10}]$ for completion. The red-brown solution was concentrated, filtered through Kieselgur, and chromatographed on silica gel. $\text{Na}_2[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6] \{[\text{Na}^+]_2\cdot\textbf{4}\}$ was obtained as a red ethanolic eluate from which **4** could be precipitated by

metathesis with $[\text{Ph}_4\text{P}]\text{Cl}$ in ethanol. The salt $[\text{Ph}_4\text{P}^+]_2\cdot\textbf{4}$ was obtained as a microcrystalline red-brown material in fair yields (40%). Crystals were obtained by layering a solution of $[\text{Ph}_4\text{P}^+]_2\cdot\textbf{4}$ in DMA (*N,N*-dimethylacetamide) with ethanol. The identity of **4** has been inferred by comparison of the unit-cell data obtained for $[\text{Ph}_4\text{P}^+]_2\cdot\textbf{4}$ by X-ray analysis with the authentic data.^[1a] X-ray analysis of these crystals proved that the sample is identical with authentic $[\text{Ph}_4\text{P}]_2[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]$.^[1a]



Scheme 5. Reaction of **1a** with $[\text{Cr}_2(\text{CO})_{10}]^{2-}$ to produce **4**

Conclusions

In the presence of $\text{M}(\text{CO})_5$ moieties ($\text{M} = \text{Cr}, \text{W}$) germanium(II) halides may be reductively coupled to produce $[\text{Ge}_2\text{Hal}_4]^{2-}$ ligands. In a formal sense these ligand entities contain germanium in its unconventional +I oxidation state and are formally isoelectronic to P_2R_4 ligands,^[9,10] which act as bridging entities in several well-characterised organometallic derivatives. In contrast to P_2R_4 , their anionic equivalents $[\text{Ge}_2\text{R}_4]^{2-}$ are not known but they are found to be stable in their $\text{M}(\text{CO})_5$ -protected form $[\{(\text{OC})_5\text{M}\}_2\text{Ge}-\text{GeI}_2\{\text{M}(\text{CO})_5\}]^{2-}$ (**1** and **2**).

In the presence of bipy, the organometallically protected ligands of the type $[\text{Hal}_2\text{Ge}-\text{Ge}(\text{bipy})]$ may be obtained under otherwise similar conditions. Here again the formal average oxidation state of germanium is +I and the ligands are not known in the free state but are stable under organometallic protection, as shown for $[\{(\text{OC})_5\text{W}\}_2\text{Ge}-\text{Ge}(\text{bipy})\{\text{W}(\text{CO})_5\}]$ (**3**).

Starting from the digermanium precursor $[\{(\text{OC})_5\text{Cr}\}_2\text{Hal}_2\text{Ge}-\text{GeHal}_2\{\text{Cr}(\text{CO})_5\}]^{2-}$ (**1**), a reductive condensation procedure produces $[\{(\text{OC})_5\text{Cr}\}_6\text{Ge}_6]^{2-}$ (**4**), which has a $[\text{Ge}_6]^{2-}$ core. This type of process is the first straightforward approach to the selective synthesis of the $[\text{Ge}_6]^{2-}$ core.

Experimental Section

General: All manipulations were carried out under argon by means of standard Schlenk techniques at 20°C unless mentioned otherwise. All solvents were dried by standard methods and distilled

under argon. The [D₆]DMSO and [D₆]acetone used for the NMR-spectroscopic measurements were degassed by three successive “freeze-pump-thaw” cycles and dried over 4-Å molecular sieves. Silica gel (Kieselgel z. A. 0.06–0.2 mm, J. T. Baker Chemicals B. V.) used for chromatography and Kieselgur (Kieselgur, gereinigt, gegläht, Erg. B.6, Riedel de Haën AG) used for filtration were degassed at 1 mbar at 130 °C for 12 h and saturated with argon. – NMR: Bruker Avance DPX 200 at 200.13 MHz (¹H), 50.323 MHz (¹³C{¹H}), 81.015 MHz (³¹P{¹H}); chemical shifts (δ) in ppm with respect to [D₆]DMSO (¹H: δ = 2.50; ¹³C: δ = 39.4) and [D₆]acetone (¹H: δ = 2.05; ¹³C: δ = 206.2), respectively, as internal standards and to 85% H₃PO₄ (³¹P: δ = 0) as external standard. – IR: Bruker FT-IR IFS-66; CaF₂ cells. – UV/Vis/NIR: Perkin–Elmer Lambda 19; cells (0.2 cm; Hellma 110 suprasil). – MS (FAB): Finnigan MAT 8400; Nibeol matrix (4-nitrobenzyl alcohol). – Elemental analysis: Microanalytical Laboratory of the Organisch-Chemisches Institut, Universität Heidelberg. – Melting points: Gallenkamp MFB-595 010; the values are not corrected. – Chemicals: The metallates Na₂[M₂(CO)₁₀]^[5] (M = Cr, W) and GeI₂^[19] were prepared by literature methods. All other chemicals were commercially obtained and used without further purification. – Analytical and

spectroscopic data are given in Table 2, Table 5, and Table 6. X-ray data are given in Tables 3, 4, and 7.

Na₂[(OC)₅M]I₂Ge–GeI₂{M(CO)₅} ([Na⁺]₂-1a**, M = Cr; [Na⁺]₂-**2a**, M = W):** To a stirred orange solution of Na₂[M₂(CO)₁₀] (M = Cr: 430 mg, 1 mmol; M = W: 694 mg, 1 mmol) in THF (50 mL) was added solid GeI₂ (326 mg, 1 mmol) in one portion. The orange solution turned red immediately. After stirring for 1 h, the GeI₂ had completely dissolved and a clear red solution had formed. The reaction mixture was filtered through Kieselgur (3 cm). The resulting red solution was concentrated in vacuo (5 mL) and chromatographed on silica gel (15 cm, Ø = 3 cm; THF). Elution with THF gave one yellow band that contained [M(CO)₆] and Na[M(CO)₅I] (M = Cr, W: identification by IR spectroscopy^[20]). A red band remained on the top of the column that was eluted with ethanol. The resulting solution was taken to dryness. [Na⁺]₂-**1a** and [Na⁺]₂-**2a**, respectively, were obtained as deep orange oils. The identity of the sodium salts **1a** and **2a** is inferred from metathesis to the corresponding [Ph₄P] salts, which may be fully characterised by various methods, including elemental analysis. The $\tilde{\nu}_{\text{CO}}$ -IR patterns of the sodium salts and the phosphon-

Table 5. Analytical data for the compounds **1–2**

	m.p. / °C	MS; m/z (%)	UV / nm (DMA)	mol. formula	elemental analysis
		[fragment]	λ_{max} (ε [l mol ⁻¹ cm ⁻¹])	(mol. Mass)	
[Ph ₄ P ⁺] ₂ - 1a	234–235	980 (7)	296 (25000);	C ₅₈ H ₄₀ O ₁₀ P ₂ Cr ₂ Ge ₂ I ₄	calcd. C 40.60 H 2.35
	(dec.)	[(M-2PPh ₄ -2CO)] ⁺	366 (3200); 425 (1600)	(1715.67)	found C 40.75 H 2.51
[Ph ₄ P ⁺] ₂ - 1b ^[a]	247–248	609 (29)	318 (22200);	C ₅₈ H ₄₀ O ₁₀ P ₂ Cr ₂ Ge ₂ Cl ₄	calcd. C 51.61 H 2.99 ^[a]
	(dec.)	[(M-2PPh ₄ -CO-Cl)] ⁺	379 (9800)	(1349.92)	found C 50.42 H 2.95
[Ph ₄ P ⁺] ₂ - 2a	201–203	852 (49)	288 (10000);	C ₅₈ H ₄₀ O ₁₀ P ₂ W ₂ Ge ₂ I ₄	calcd. C 35.19 H 2.04
	(dec.)	[(M-2PPh ₄ -W(CO) ₅ -I)] ⁺	311 (7600); 405 (2000)	(1974.40)	found C 34.61 H 2.08
[nBu ₄ N ⁺] ₂ - 2a	197–198	1173 (15)	290 (15000);	C ₄₂ H ₇₂ O ₁₀ N ₂ W ₂ Ge ₂ I ₄	calcd. C 28.25 H 4.06
	(dec.)	[(M-2nBu ₄ N-I)] ⁺	324 (9500); 406 (1500)	(1785.54)	found C 28.21 H 3.88
[Ph ₄ P ⁺] ₂ - 2b ^[a]	207–208	852 (54)	-	C ₅₈ H ₄₀ O ₁₀ P ₂ W ₂ Ge ₂ Cl ₄	calcd. C 43.17 H 2.50 ^[a]
	(dec.)	[(M-2PPh ₄ -3CO)] ⁺	-	(1613.59)	found C 42.18 H 2.46

^[a] Partial substitution of Cl by I: calculated formula for [Ph₄P⁺]₂-**1b**: C₅₈H₄₀Cl_{3.6}Cr₂Ge₂I_{0.4}O₁₀P₂; calculated formula for [Ph₄P⁺]₂-**2b**: C₅₈H₄₀Cl_{3.6}Cr₂Ge₂I_{0.4}O₁₀P₂

Table 6. ¹H-, ³¹P{¹H}-, and ¹³C{¹H}-NMR spectroscopic data for the compounds **1–2**

	¹ H					³¹ P{ ¹ H}		¹³ C{ ¹ H} ^[i]					
	H _{arom.} ^[d]	H _α ^[e]	H _β ^[f]	H _γ ^[g]	H _δ ^[h]	CO _{ax}	CO _{eq}	CO _{ax}	CO _{eq}	C _{para}	C _{ortho}	C _{meta}	C _{ipso}
								CO _{ax}	CO _{eq}	C _α	C _β	C _γ	C _δ
[Ph ₄ P ⁺] ₂ - 1a ^[a]	7.95–7.74	-	-	-	-	23.5	-	219.6	135.2	134.5	130.4	117.6	
[Ph ₄ P ⁺] ₂ - 1a ^[b]	8.00–7.85	-	-	-	-	23.3	-	222.1	136.5	135.8	131.5	119.1	
[Ph ₄ P ⁺] ₂ - 1b ^[a]	7.97–7.69	-	-	-	-	23.3	227.7	220.0	135.2	134.4	130.3	117.6	
[Ph ₄ P ⁺] ₂ - 2a ^[a]	7.96–7.68	-	-	-	-	23.6	-	201.2	135.2	134.4	130.3	117.6	
[Ph ₄ P ⁺] ₂ - 2a ^[c]	7.97–7.60	-	-	-	-	22.8	-	202.6	136.3	135.6	131.3	-	
[nBu ₄ N ⁺] ₂ - 2a ^[a]	-	3.17	1.58	1.32	0.94	-	-	201.3	57.4	23.0	19.1	13.3	
[nBu ₄ N ⁺] ₂ - 2a ^[b]	-	3.44	1.84	1.42	0.98	-	-	210.1	202.7	59.4	24.5	20.4	13.9
[Ph ₄ P ⁺] ₂ - 2b ^[a]	8.02–7.55	-	-	-	-	23.6	205.3	200.0	135.2	134.4	130.3	117.6	

^[a] [D₆]DMSO. – ^[b] [D₆]acetone. – ^[c] CD₃CN. – ^[d] Non-resolved multiplets. – ^[e] t, 2 H. – ^[f] m, 2 H. – ^[g] m, 2 H. – ^[h] t, 3 H. – ^[i] In case of [PPH₄] salts: C_{para} [d, ⁴J(³¹P, ¹³C) = 3 Hz]; C_{ortho} [d, ⁴J(³¹P, ¹³C) = 10 Hz]; C_{meta} [d, ⁴J(³¹P, ¹³C) = 13 Hz]; C_{ipso} [d, ⁴J(³¹P, ¹³C) = 13 Hz]; in case of [nBu₄N] salts: C_α, C_β, C_γ, C_δ: carbon atoms of *n*-butyl substituent.

Table 7. Crystal structure data for the compounds 1–3

compound	[Ph ₄ P ⁺] ₂ ·1a	[Ph ₄ P ⁺] ₂ ·1b	[Ph ₄ P ⁺] ₂ ·2a	[Ph ₄ P ⁺] ₂ ·2b	3
formula:	C ₃₈ H ₄₀ O ₁₀ P ₂ Cr ₂ Ge ₂ I ₄	C ₃₈ H ₄₀ O ₁₀ P ₂ Cr ₂ Ge ₂ Cl ₄	C ₃₈ H ₄₀ O ₁₀ P ₂ W ₂ Ge ₂ I ₄	C ₃₈ H ₄₀ O ₁₀ P ₂ W ₂ Ge ₂ Cl ₄	C ₂₀ H ₈ O ₁₀ N ₂ W ₂ Ge ₂ I ₂
molecular mass [g]:	1715.67	1349.88	1979.40	1613.59	962.37
crystal dimension [mm]	0.30·0.30·0.30	0.30·0.30·0.30	0.20·0.20·0.20	0.30·0.30·0.30	0.20·0.30·0.20
crystal system:	triclinic	triclinic	triclinic	triclinic	monoclinic
space group (no.):	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)	<i>P</i> 2 ₁ / <i>n</i> (14)
<i>a</i> [pm]	1196.0 (2)	1117.4 (2)	1204.9 (2)	1122.8 (3)	939.6 (2)
<i>b</i> [pm]	1217.5 (1)	1211.0 (1)	1226.2 (3)	1215.2 (3)	1900.0 (2)
<i>c</i> [pm]	1298.1 (2)	1240.7 (2)	1276.3 (3)	1249.9 (3)	1649.3 (2)
α [°]	70.43 (1)	71.57 (1)	90.39 (3)	70.93 (1)	90.00 (0)
β [°]	88.13 (1)	88.83 (1)	110.91 (3)	88.91 (2)	92.58 (2)
γ [°]	60.65 (1)	68.68 (1)	111.00 (3)	69.02 (2)	90.00 (0)
cell volume [10 ⁶ pm ³]:	1532.4 (4)	1475.3 (4)	1624.7 (6)	1497.7 (7)	2941.7 (9)
molecular units / cell:	1	1	1	1	4
density (calculated) [g cm ⁻³]	1.859	1.519	2.023	1.791	2.716
temperature [K]:	200	200	293	200	200
no. rflns. for cell parameter refinement:	30	33		34	37
scan range:	3.4° ≤ 2 θ ≤ 51.0°	3.9° ≤ 2 θ ≤ 48.2°	3.5° ≤ 2 θ ≤ 52.2°	3.9° ≤ 2 θ ≤ 56.0°	3.3° ≤ 2 θ ≤ 49.0°
scan speed (ω) [° min ⁻¹]:	12	12		10	12
integration time [sec/frame]			5		
no. rflns. measured:	5767	5081	19872	8097	5185
no. unique rflns.:	5484	4805	6249	7024	4861
no. rflns. observed (≥ 2 σ):	4839	3886	3294	6229	3111
no. parameters refined:	353	432	353	348	314
residual electron density [$\cdot 10^{-6}$ e pm ⁻³]:	0.96 / -1.53	1.61 / -0.56	0.67 / -1.38	3.27 / -4.76	4.36 / -2.08
<i>R</i> _i / <i>R</i> _w [%] (refinement on <i>F</i> ²)	3.4 / 11.7	4.5 / 13.1	4.5 / 8.8	5.4 / 17.6	6.7 / 17.7

ium salts are similar enough to leave no doubt about the nature of the organometallic anions **1a** and **2a**.

[Ph₄P]₂[(OC)₅M]I₂Ge–GeI₂{M(CO)₅} ([Ph₄P⁺]₂·1a, M = Cr; [Ph₄P⁺]₂·2a, M = W): To a stirred orange solution of [Na⁺]₂·1a (541 mg, 0.5 mmol) or [Na⁺]₂·2a (673 mg, 0.5 mmol), respectively, in ethanol (10 mL) was added a suspension of [Ph₄P]I (933 mg, 2 mmol) in ethanol (30 mL). The corresponding yellow [Ph₄P] salts of **1a** or **2a** precipitated immediately. After stirring for 30 min, the solid was separated from the mother liquor by filtration and washed with ethanol (2 × 5 mL), diethyl ether (2 × 5 mL) and dried in vacuo leaving the salts of [Ph₄P⁺]₂·1a and [Ph₄P⁺]₂·2a as yellow powders. Yield: [Ph₄P⁺]₂·1a: 394 mg, 0.23 mmol, 46%; [Ph₄P⁺]₂·2a: 456 mg, 0.23 mmol, 46% (with respect to GeI₂). In order to grow single crystals of [Ph₄P⁺]₂·1a and [Ph₄P⁺]₂·2a the yellow powder was dissolved in DMA (5 mL) and overlaid with ethanol (20 mL). Within 5 d at 20 °C yellow single crystals suitable for X-ray analysis were obtained.

[Ph₄P]₂[(OC)₅M]Cl₂Ge–GeCl₂{M(CO)₅} ([Ph₄P⁺]₂·1b, M = Cr; [Ph₄P⁺]₂·2b, M = W): To a stirred orange solution of [Na⁺]₂·1a (541 mg, 0.5 mmol) or [Na⁺]₂·2a (673 mg, 0.5 mmol) in ethanol (30 mL) was added solid [Ph₄P]Cl (750 mg, 2 mmol). The corresponding yellow [Ph₄P] salts of **1b** or **2b** precipitated immediately. Further workup and the growth of single crystals of [Ph₄P⁺]₂·1b or [Ph₄P⁺]₂·2b were achieved following the methods described for [Ph₄P⁺]₂·1a. Yield: [Ph₄P⁺]₂·1b: 310 mg, 0.23 mmol, 46%; [Ph₄P⁺]₂·2b: 370 mg, 0.23 mmol, 46% (with respect to GeI₂). The exchange of iodide versus chloride is almost complete under these conditions, as shown by elemental analysis and X-ray analysis.

[nBu₄N]₂[(OC)₅W]I₂Ge–GeI₂{W(CO)₅} ([nBu₄N⁺]₂·2a): To a stirred orange solution of [Na⁺]₂·2a (673 mg, 0.5 mmol) in ethanol

(30 mL) was added solid [nBu₄N]I (739 mg, 2 mmol). The corresponding yellow [nBu₄N] salt of **2a** precipitated immediately. The subsequent workup followed the method described for [Ph₄P⁺]₂·2a. Yield: [nBu₄N⁺]₂·2a: 482 mg, 0.27 mmol, 54% (with respect to GeI₂).

[(OC)₅W]I₂Ge–Ge(bipy){W(CO)₅} (3): Na₂[W₂(CO)₁₀] (694 mg, 1 mmol) was dissolved in THF (50 mL) and solid GeI₂ (326 mg, 1 mmol) and solid 2,2'-bipyridine (156 mg, 1 mmol) were added in one portion. The initially clear orange solution turned deep red immediately (GeI₂ dissolved in a period of minutes). After stirring for 1 h, the reaction mixture was filtered through Kieselgur (3 cm). The resulting red solution was concentrated to 5 mL in vacuo and chromatographed on silica gel (15 cm, Ø = 3 cm; diethyl ether). Elution with diethyl ether gave a red band, which was identified by IR spectroscopy to consist of [W(CO)₆] and [(OC)₄W(bipy)].^[17,20] Elution with THF gave a second red band containing **3**. This fraction was taken to dryness to leave **3** as a red oil. Single crystals of **3** were obtained by the following procedure: A concentrated THF solution of **3** (348 mg in 5 mL of THF) was shared out between three test tubes (Ø = 1 cm), which were each placed into a Schlenk tube (250 mL). Diethyl ether (30 mL), which was in the Schlenk tube, was allowed to diffuse through the gas phase into the THF solutions (12 h at 20 °C). After this period of time the diethyl ether was replaced by petroleum ether (boiling range 40–60 °C; 50 mL). Vapour diffusion of the petroleum ether for 4 d gave red single crystals of **3** that were suitable for X-ray structure analysis. All operations were carried out in the dark. While the identity of **3** could be determined by X-ray analysis of these crystals at 200 K, dissolving these crystals in CD₂Cl₂ or [D₆]acetone at 20 °C resulted in red solutions that contained bipy ligands in three different coordination environments. The ¹H-NMR spectra show three sets of

signals that, although not individually resolved, provide evidence that compound **3** disintegrates at least in part under the given experimental conditions. In addition, a satisfactory elemental analysis could not be obtained for **3**.

[Ph₄P]₂[(OC)₅Cr]₆Ge₆] ([Ph₄P⁺]₂-4**):** To a stirred orange solution of [Na⁺]₂-**1a** (541 mg, 0.5 mmol) in THF (30 mL) was added a solution of Na₂[Cr₂(CO)₁₀] (430 mg, 1 mmol) in THF (30 mL) in 10-mL portions during a period of 3 h. During the addition the colour of the solution turned to red-brown. The reaction mixture was filtered through Kieselgur (3 cm), concentrated to 5 mL in vacuo and chromatographed on silica gel (15 cm, Ø = 3 cm; THF). Elution with THF gave a broad yellow band containing Na[Cr₂(CO)₁₀H], which was identified by IR spectroscopy.^[5,18] A deep red band remained on top of the column and this was eluted with ethanol. The resulting deep red solution was taken to dryness in vacuo and redissolved in ethanol (10 mL). Addition of solid [Ph₄P]Cl (375 mg, 1 mmol) led to the corresponding red-brown [Ph₄P]⁺ salt of **4**, which precipitated immediately. The solid was separated from the mother liquor by filtration, washed with ethanol (2 × 5 mL), diethyl ether (2 × 5 mL) and dried in vacuo. Yield: [Ph₄P⁺]₂-**4**: 151 mg, 0.07 mmol, 40% (with respect to GeI₂). Single crystals of [Ph₄P⁺]₂-**4** could be obtained by layering a concentrated DMA solution of [Ph₄P⁺]₂-**4** (3 mL) with ethanol (20 mL).

X-ray Structure Determinations: The measurements for [Ph₄P⁺]₂-**1a**, [Ph₄P⁺]₂-**2b**, and **3** were carried out with a Siemens P4 four-circle diffractometer, data for [Ph₄P⁺]₂-**2a** were collected with a Nonius Kappa CCD diffractometer, all using Mo-K_α radiation. In the case of the Siemens P4 four-circle diffractometer, measurements of the intensities of three check reflections (measured every 100 reflections) remained constant throughout the data collection, thus indicating crystal and electronic stability. The data collected using a scintillation counter measuring device (Siemens P4) were corrected in the usual way including experimental absorption correction. The data from the CCD device (Nonius Kappa CCD) were processed by the standard Nonius software.^[21] All calculations were performed using the SHELXT PLUS software package. Structures were solved by direct methods with the SHELXS-86 program and refined with the SHELXL-93 program.^[22] The program XPMa^[23] was used for graphical handling of the data. The structures were refined in fully or partially anisotropic models by full-matrix least-squares calculations. Hydrogen atoms were introduced at calculated positions. Table 7 compiles the data for the structure determinations. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-135292 ([Ph₄P⁺]₂-**1a**), -135293 ([Ph₄P⁺]₂-**1b**), -135291 ([Ph₄P⁺]₂-**2a**), -135295 ([Ph₄P⁺]₂-**2b**), -135294 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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