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The formation of mixed germanium-cobalt carbonyl clusters: an electrospray mass spectrometric study, and the structure of a high-nuclearity $[Ge_2Co_{10}(CO)_{24}]^{2-}$ anion.

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Synopsis

A high nuclearity cluster anion with semi-encapsulated germanium atoms within a Ge_2Co_{10} core was prepared and structurally characterised, following initial detection by electrospray mass spectrometry.

Abstract.

The reaction of $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ with $[Co(CO)_4]^-$ has been monitored by electrospray mass spectrometry to detect the cluster anions generated. Conditions giving known mixed Ge-Co carbonyl clusters were established, and a new high nuclearity cluster anion, $[Ge_2Co_{10}(CO)_{24}]^{2-}$ was detected. Conditions for its formation were optimised and it was subsequently isolated as its $[Et_4N]^+$ salt and characterised by single-crystal X-ray crystallography. The Ge_2Co_{10} cluster core has a novel geometry with the two germanium

atoms in semi-encapsulated positions, forming seven formal Ge-Co bonds. There are also eighteen formal Co-Co bonds. Corresponding reactions of [μ_4-Si{$Co_2(CO)_7$}$_2$] with [$Co(CO)_4$]$^-$ were also investigated.

Introduction.

The systematic synthesis of high-nuclearity metal carbonyl clusters is still a developing goal[1-3]. This is partly because the mechanisms of cluster-building reactions are poorly understood, since *in situ* monitoring of them is usually difficult. Carbonyl-region infrared spectra of different species often overlap and provide little structural information for large clusters, while other techniques such as NMR are very limited. Determining reaction pathways has relied heavily on crystallising intermediate species from solutions and carrying out single-crystal structure analyses. Compounds characterised in this way are restricted to those that crystallise well, and may sometimes not be representative of the major species formed during reactions.

We have previously described reactions in which cobalt carbonyl clusters have been built up around the group 14 elements silicon and germanium as templates[4-11]. In particular, the reaction of [$Co(CO)_4$]$^-$ with [μ_4-Ge{$Co_2(CO)_7$}$_2$] (**1**), (which is formed[4] in near-quantitative yield from GeH_4 and $Co_2(CO)_8$) led[5,6] to the isolation of two anionic clusters with four-coordinate germanium, **2** and **3**, and one with five-coordinate germanium **4**. In contrast, the corresponding reaction with [μ_4-Si{$Co_2(CO)_7$}$_2$] has only given the paramagnetic anion [$SiCo_9(CO)_{21}$]$^{2-}$, still a unique example of a metal carbonyl cluster with a fully encapsulated silicon atom[7]. Indeed there are very few examples of encapsulated heavier group 14 atoms in discrete clusters, in contrast to the large number of carbido clusters. For germanium, the five-coordinate atoms in **4** and in the [Co_4{μ_4-

$GeCo(CO)_4\}_2(CO)_{11}]$ cluster **5** can be regarded as semi-encapsulated[5, 8], with only $[GeNi_{10}(CO)_{20}]^{2-}$ and $[GeNi_{12}(CO)_{22}]^{2-}$as fully encapsulated examples[12].

Recently it has been demonstrated that the relatively new technique of electrospray mass spectrometry (ESMS) is useful for characterising metal carbonyl anions in solutions, since ions are transferred directly into the source with minimum fragmentation[13-16]. Each mass spectral peak therefore corresponds to a distinct species. Most common solvents are tolerated so reaction mixtures can be sampled directly, and conditions can be arranged so that exposure to air is avoided. It is therefore potentially a powerful new technique for studying cluster syntheses reactions. An added advantage arises from the small samples needed -- reactions can be monitored on a very small scale.

We now report our re-examination of the $[Co(CO)_4]^-$/ $[\mu_4\text{-}E\{Co_2(CO)_7\}_2]$ reaction (E = Si or Ge) using ESMS methods, and the full characterisation of a novel, high-nuclearity mixed metal cluster.

Experimental

All reactions were carried out in re-distilled solvents under nitrogen, using standard Schlenk techniques. $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$, **1**, $[\mu_4\text{-}Si\{Co_2(CO)_7\}_2]$, and $Et_4N[Co(CO)_4]$ were prepared using literature procedures[4,5,9].

Electrospray mass spectra were recorded on a VG Platform II spectrometer operating in negative ion mode. The mobile phase was 1,2-$C_2H_4Cl_2$, which had been distilled from CaH_2 under nitrogen and stored in a reservoir under an argon atmosphere. This was found to provide more consistent spectra than CH_2Cl_2 or $CHCl_3$, possibly because of its lower volatility and smoother vaporisation in the electrospray source. The mobile phase was pumped at 0.02 mL min^{-1} using a SpectraPhysics P1000 pump. For monitoring reactions, *ca* 0.5 mL samples of the mixture were extracted by syringe, diluted under argon with 1,2-$C_2H_4Cl_2$, and injected into the spectrometer via a Rheodyne valve with a 10 μL loop. The source temperature was 60°C, and nitrogen was used as both nebulising and drying gas. Skimmer cone voltage was maintained at a low value (typically 5 V) to minimise fragmentation of ions.

Peaks were assigned from the *m/z* values, and by comparison of the isotope envelope patterns with those simulated using the ISOTOPE program[18].

Small scale reactions monitored by ESMS. A typical reaction used $[\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ (0.030 g, 0.0.043 mmol) and $Et_4N[Co(CO)_4]$ (0.026 g, 0.086 mmol) in either CH_2Cl_2 or Et_2O (10 mL). If required, the mixtures were gently heated using an oil bath. Aliquots were removed at intervals and analysed by ESMS.

Preparation of $[Et_4N]_2[Ge_2Co_{10}(CO)_{24}]$(**6**). $\mu_4\text{-Ge}\{Co_2(CO)_7\}_2]$ (0.210 g, 0.30 mmol) and $Et_4N[Co(CO)_4]$ (0.180 g, 0.60 mmol) were dissolved in CH_2Cl_2 (20 mL) and heated under reflux for 5-6 hours, by which time ESMS on an extracted aliquot showed the Ge_2Co_{10} dianion **6** was the dominant species in solution. The mixture was concentrated to *ca* 5 mL under vacuum and Et_2O was added dropwise to precipitate the product, (0.199 g, 38%). ν_{CO} (CH_2Cl_2), 2066 m,sh, 2028 vs, br, 2007 m,sh 1730 w, br. Crystallographic quality crystals were obtained by layering a solution of the product in CH_2Cl_2 with Et_2O and storing under nitrogen at -20°C.

X-ray crystal structure of $[Et_4N]_2[Ge_2Co_{10}(CO)_{24}].1.5CH_2Cl_2.0.5Et_2O$.

Intensely red crystals were obtained as described above and one measuring 0.22 x 0.18 x 0.12 mm was transferred on a glass fibre to the cold nitrogen stream of the diffractometer with minimum exposure to air.

Crystal data: $C_{40}H_{40}Co_{10}Ge_2N_2O_{24}.1.5CH_2Cl_2.0.5(C_2H_5)_2O$, M = 1831.67, orthorhombic, a = 30.3922(6), b = 23.5597(5), c = 17.2684(3) Å, U 12364.7(4) Å^3, T 203 K, space group Pcca, Z = 8, μ(Mo-Kα) 3.8 mm^{-1}, 74629 reflections collected, 10909 unique (R_{int} 0.0398) used after correction for absorption ($T_{max, min}$ 0.845, 0.649). Refinement on F^2 gave R_1 0.0595 (9539 data with $I > 2\sigma(I)$) and wR_2 0.1618 (all data). The refinement was complicated by disorder in the $[Et_4N]^+$ cations, and a poorly resolved solvent molecule which was assigned to Et_2O.

Results and discussion

Electrospray mass spectra

The course of the reaction between $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ (**1**) and $Et_4N[Co(CO)_4]$ is solvent-dependent. In Et_2O, there is a fairly rapid reaction to give the previously characterised[5] $[GeCo_5(CO)_{16}]^-$ cluster (**4**), as shown by the immediate growth of the peak at *m/z* 817. This species then slowly disappears, to be replaced by peaks at *m/z* 1047 and 1147 which can be assigned to the known[6] anions $[GeCo_7(CO)_{20}]^-$ (**3**) and $[Ge_2Co_2(CO)_{21}]^-$ (**2**). There are then few subsequent changes over several hours.

In CH_2Cl_2, there is no peak attributable to the $[GeCo_5(CO)_{16}]^-$ ion **4** at any stage, with the two Co_7 clusters **2** and **3** being the first ones observed. What is more interesting, is the subsequent decay of these two signals, with a new peak at *m/z* 704 arising from a doubly charged ion of mass 1408 (see Figure 1; there is also a weak peak at *m/z* 1408 corresponding to the monocharged equivalent arising from oxidation in the mass spectrometer source). This can be assigned from the mass and distinctive isotope pattern to a species $[Ge_2Co_{10}(CO)_{24}]^{2-}$, (**6**), a previously undetected cluster. Monitoring of the reaction mixture on a larger scale allowed optimisation for the formation of this large cluster, and subsequent isolation and full characterisation by X-ray crystallography (see below).

It should be emphasised that the information concerning the changes taking place during reaction is not available by means other than ESMS. Although the three smaller anions had been previously isolated and characterised[5,6], they came from different reactions and the inter-relationships were never evident, and the large cluster was not even suspected. Infrared spectroscopy of the reaction mixture is not very helpful, all of the clusters **2**-**4**, **6** giving one main broad band at around 2025 cm^{-1}, with only minor differences in the weak bands distinguishing them; this is characteristic for large clusters[18]. The information provided by ESMS is also complete, in that we can be confident that there are no other anionic species involved in significant quantities at any stage. It should be noted that *neutral* compounds are invisible to the ESMS technique under the conditions used, so their involvement in the process needs to be deduced rather than detected.

To our knowledge, **6** is the first example where an unsuspected cluster anion has been first detected using ESMS and subsequently isolated and fully characterised.

The ESMS data allow us to rationalise the sequence of reactions, as summarised in Scheme 1. Initial addition of $[Co(CO)_4]^-$ to $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ (**1**) (or to $[(OC)_4CoGeCo_3(CO)_9]$, **7**, a known[4,19] decarbonylation product of **1** under mild conditions) gives the $GeCo_5$ cluster **4**. This is apparently reasonably stable in Et_2O but not in CH_2Cl_2. Breakdown of **4** would give rise to "$Co_2(CO)_7$", (which would dimerise to generate $[Co_4(CO)_{12}]$), and a $[GeCo_3(CO)_9]^-$ ion. This latter species is isoelectronic with the known $[AsCo_3(CO)_9]$ which is a highly reactive Lewis base towards CO-displacement reactions, including with itself to generate cyclic trimers[20]. By analogy, $[GeCo_3(CO)_9]^-$ is expected to be a stable intermediate, but even more reactive as a Lewis base because of the negative charge. It is not detected by ESMS, but rapidly reacts with either **1** or **7** in the system to generate the Ge_2Co_7 anion **2** or with the $[Co_4(CO)_{12}]$ formed to give the $GeCo_7$ anion **3**, both of which are indefinitely stable in Et_2O solution. In CH_2Cl_2 however the cluster **2** releases more $[GeCo_3(CO)_9]^-$ which adds to the $GeCo_7$ anion **3** to give, after CO loss and condensation, the Ge_2Co_{10} dianion **6**.

Consistent with this, addition of PPh_3 to a mixture of the two anions **2** and **3** increases the rate of formation of **6**. This is envisaged to involve reaction of **2** with PPh_3 according to Scheme 2, with the released $[GeCo_3(CO)_9]^-$ reacting as before with **3**.

This overall scheme can explain the specificity for the Ge_2Co_{10} product **6**, without any species of intermediate nuclearity. The suggestion of $[GeCo_3(CO)_9]^-$ as a key building block can also explain the marked difference between the analogous reactions of $[\mu_4\text{-}Ge\{Co_2(CO)_7\}_2]$ and $[\mu_4\text{-}Si\{Co_2(CO)_7\}_2]$ (see below); $[GeCo_3(CO)_9]^-$ is formally Ge(II) so the analogous Si(II) species $[SiCo_3(CO)_9]^-$ is presumably much less favoured as an intermediate.

The reaction of $[\mu_4\text{-}Si\{Co_2(CO)_7\}_2]$ with $[Co(CO)_4]^-$ differs from that found for the corresponding germanium system. Initially (15-30 minutes) at reflux in CH_2Cl_2 the ESMS shows a peak at *m/z* 771 which can be assigned to the previously unknown $[SiCo_5(CO)_{16}]^-$, presumably with the same structure as the analogous germanium species **4**. As the reaction proceeds a second anionic species with *m/z* 1029 is detected. Unambiguous assignment is complicated by Si and CO both having nominal mass of 28, so either $[Si_2Co_7(CO)_{20}]^-$ or $[SiCo_7(CO)_{21}]^-$ are possible for this peak. There are subtle differences for these in the detailed isotope pattern, with relative intensities100/33/16/4 for the former and 100/29/12/2 for the latter, compared with the experimental ratio of 100/33/16/5. These small differences tentatively favour the Si_2Co_7 option. On the other hand, the fact that subsequent cluster build-up leads to species with only one silicon atom would favour the $SiCo_7$ option, since a sequence $SiCo_x \rightarrow Si_2Co_y \rightarrow SiCo_z$ is perhaps unlikely. Neither of the two species corresponds to any anions in the germanium system, and attempts to isolate crystals for further characterisation were unsuccessful, so the structure of this *m/z* 1029 species remains unknown.

As the reaction progresses further, two more anionic products form simultaneously, a dianion with *m/z* 573, and a monoanion with *m/z* 1175. These can be assigned with confidence to the previously characterised[7] $[SiCo_9(CO)_{21}]^{2-}$ and the previously unknown $[SiCo_9(CO)_{22}]^{-}$. The latter is the electron-precise (130 CVE) version of the former, which is paramagnetic with 129 CVE, so will have the same capped square-antiprism core with an encapsulated silicon atom. It is not clear how the $SiCo_9$ clusters form, but the ESMS results indicate unequivocally that this mono-capped square-antiprism core is the only higher-nuclearity cluster formed, with no sign of either a $SiCo_8$ square-antiprism analogous to the carbido cluster[21] $[CCo_8(CO)_{18}]^{2-}$, nor a bi-capped square-antiprism analogous to the $[ERh_{10}(CO)_{22}]^{3-}$ anions (E = P, As)[22].

The silicon system does not give an analogue of the Ge_2Co_{10} cluster **6**, nor does the germanium system give a cluster corresponding to the $SiCo_9$ core, emphasising the very different cluster building processes in these two similar systems.

The structure of the $[Ge_2Co_{10}(CO)_{24}]^{2-}$ anion.

The asymmetric unit of the crystal lattice of the Et_4N^+ salt of the anion contains the anion **6**, two cations, 1.5 molecules of CH_2Cl_2 and 0.5 molecules of Et_2O, with significant disorder associated with the cations and solvent molecules. However the anion itself is well-defined.

The overall structure of the anion is illustrated in Figure 2, with the Ge_2Co_{10} core shown on Figure 3. The geometry of the cluster is unique, and cannot be readily classified in terms of the regular polyhedra normally associated with high-nuclearity clusters. It has essentially C_2 symmetry with the axis passing through the mid-points of the Co(4)-Co(5) and Co(6)-Co(7) bonds, so the two germanium atoms are equivalent. Each forms six short Ge-Co bonds (2.346-2.406 Å) and one longer one (Ge(1)-Co(4) 2.611, Ge(2)-Co(5) 2.623 Å), arranged so that one side of the germanium atoms is 'naked'. In this sense the germanium atoms can be regarded as semi-interstitial, with a similarity to the phosphorus atom in the cluster $[PCo_6(CO)_{16}]^-$, reported earlier from Chini's group[23]. Semi-encapsulated antimony atoms have recently been demonstrated in the $[Ni_{31}Sb_4(CO)_{40}]^{6-}$ anion, with formal 8- and 10-connectivities[24].

Within the Ge_2Co_{10} cluster there are 18 formal Co-Co bonds ranging from 2.548-2.853 Å. The 24 CO groups can be divided into sixteen terminal ones, four symmetrically bridging [CO(23), CO(42), CO(52), and CO(63)], and four semi-bridging [CO(11), CO(22), CO(81), and CO(91)], arranged so as to approximately maintain the overall C_2 symmetry.

The core geometry is not readily understood by any of the usual electron-counting schemes[25]. Including the germanium atoms as contributing 4 electrons to the total count, the anion has 148 cluster valence electrons, which gives 12 skeletal electron pairs for the

12 vertex structure. With Wade's rules this would predict a mono-capped 11-vertex geometry, which is clearly not observed.

Another way of interpreting the core is to identify a central Ge_2Co_4 octahedron capped on four faces by Co(1), Co(2), Co(8) and Co(9), with two of the new faces further capped by Co(3) and Co(10).

It is interesting to compare the 148-electron $[Ge_2Co_{10}(CO)_{24}]^{2-}$ ion with other $M_{10}E_2$ clusters. When E is C or N, condensed structures with the main group elements fully encapsulated are the norm. For example, the recently reported[26] 142-electron $[Co_{10}N_2(CO)_{19}]^{4-}$ anion has a stacked trigonal prismatic arrangement with nitrogen atoms fully encapsulated in two of the three interstitial sites. A similar arrangement for the germanium example is presumably precluded by the size of the atom (r = 1.22 Å), too large to fit within a cavity made up from six cobalt atoms[27]. The 134-electron cluster $[Os_{10}S_2(CO)_{23}]$ is the only other $M_{10}E_2$ example we are aware of with heavier main group E elements. This has a compact core of osmium atoms with the S atoms on the surface linked to only four Os atoms[28], more as a four-electron ligand than as a semi-encapsulated atom.

Conclusion

Electrospray mass spectrometry is a useful way of monitoring reaction progress in anion condensation reactions since it directly samples all species in solution. A detailed study of the $[\mu_4\text{-}E\{Co_2(CO)_7\}_2]/[Co(CO)_4]^-$ systems has helped rationalise previous results, has highlighted differences for the E= Ge or Si examples, and has led to the discovery of a novel, high-nuclearity, mixed Ge-Co cluster anion **6** with an unprecedented core geometry.

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Captions to figures

Figure 1. The electrospray mass spectrum of the anionic products observed in the reaction of $[\mu_4\text{-Si}\{Co_2(CO)_7\}_2]$ (**1**) with $[Co(CO)_4]^-$. Inset: isotope envelope for the peak centred at *m/z* 704 showing the 0.5 amu spacing associated with the 2- ion.

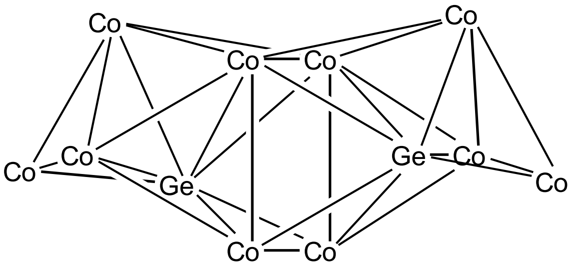
Figure 2. The structure of the $[Ge_2Co_{10}(CO)_{24}]^{2-}$ (**6**) ion, showing atom labelling.

Figure 3. The detailed structure of the metallic core of the $[Ge_2Co_{10}(CO)_{24}]^{2-}$ (**6**) ion

Table 1

Metal-metal bond distances in the anion $[Ge_2Co_{10}(CO)_{24}]^{2-}$.

Ge(1)-Co(1)	2.3940(12)	Ge(2)-Co(4)	2.4055(13)
Ge(1)-Co(2)	2.3662(13)	Ge(2)-Co(6)	2.4026(13)
Ge(1)-Co(3)	2.3890(12)	Ge(2)-Co(7)	2.3990(13)
Ge(1)-Co(5)	2.3643(12)	Ge(2)-Co(8)	2.3765(13)
Ge(1)-Co(6)	2.3951(12)	Ge(2)-Co(9)	2.3939(13)
Ge(1)-Co(7)	2.3971(13)	Ge(2)-Co(10)	2.3463(13)
Ge(1)-Co(4)	2.6107(13)	Ge(2)-Co(5)	2.6230(12)
Co(1)-Co(2)	2.6701(15)	Co(1)-Co(3)	2.8050(15)
Co(1)-Co(4)	2.5645(14)	Co(1)-Co(5)	2.7106(14)
Co(2)-Co(3)	2.6688(15)	Co(2)-Co(4)	2.6663(14)
Co(2)-Co(7)	2.6454(14)	Co(4)-Co(5)	2.6499(14)
Co(4)-Co(7)	2.8137(14)	Co(4)-Co(9)	2.6677(14)
Co(5)-Co(6)	2.8194(14)	Co(5)-Co(8)	2.6412(14)
Co(5)-Co(9)	2.5477(14)	Co(6)-Co(7)	2.8526(14)
Co(6)-Co(8)	2.6507(14)	Co(8)-Co(9)	2.7052(14)
Co(8)-Co(10)	2.7104(14)	Co(9)-Co(10)	2.7514(14)



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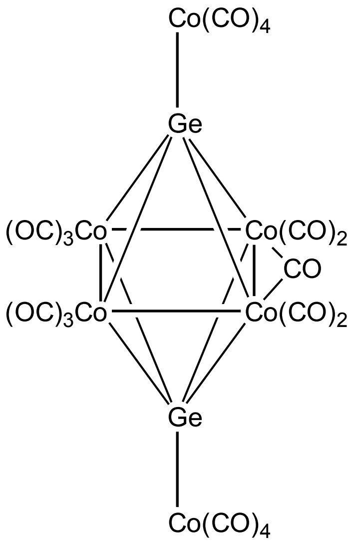

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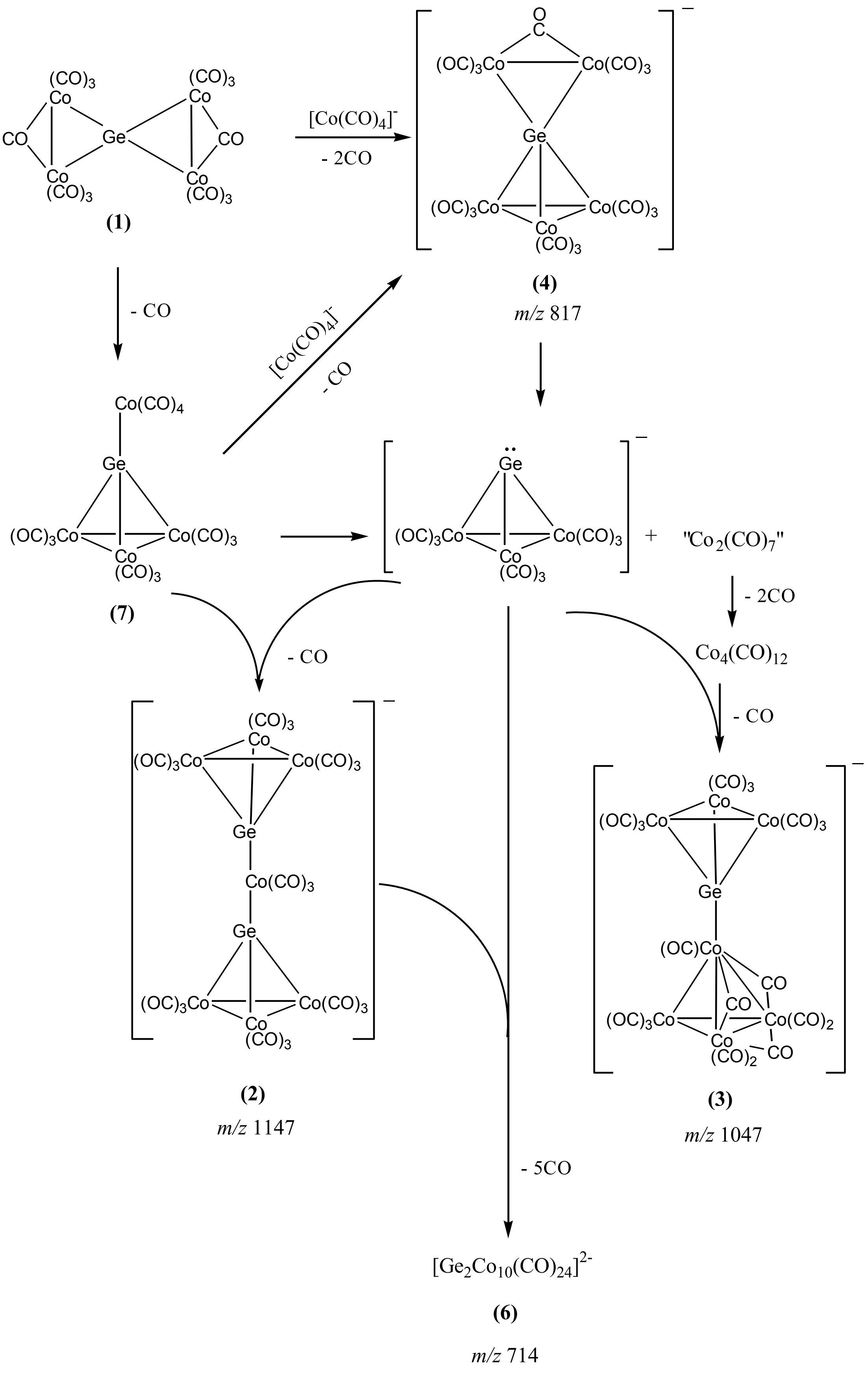
(1)
[Co(CO)4]-
- 2CO
(4)
m/z 817
- CO
[Co(CO)4]-
- CO
(7)
+
"Co2(CO)7"
- 2CO
Co4(CO)12
- CO
- CO
(2)
m/z 1147
(3)
m/z 1047
- 5CO
[Ge2Co10(CO)24]2-
(6)
m/z 714