Germanium Complexes of Ruthenium and Osmium Dodecacarbonyls: Metal–Metal Heterocycles: Crystal Structure of $[Me_2GeRu(CO)_3]_3$

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Summary Pyrolysis of the compounds $(Me_3Ge)_2M'(CO)_4$ [M' = Ru or Os] affords polynuclear complexes $[Me_2GeM'(CO)_3]_3$ shown to contain heterocyclic rings of six metal atoms, and the anion $[Me_3GeRu(CO)_4]^-$ reacts with various metal halides to give *inter alia* pentanuclear $[Me_3GeRu(CO)_4]_2Hg$.

DEPENDING on the reaction conditions (u.v. irradiation or heat, and the ratio of the reactants), trimethylgermane and the dodecacarbonyls of ruthenium or osmium, $M'_3(CO)_{12}$, afford the complexes $(Me_3Ge)_2M'(CO)_4$ (I), $Me_3GeOs(CO)_4H$ (II), $[Me_3GeRu(CO)_4]_2$ (III), and $[Me_3GeM'(CO)_3(\mu\text{-}GeMe_2)]_2$ (IV).

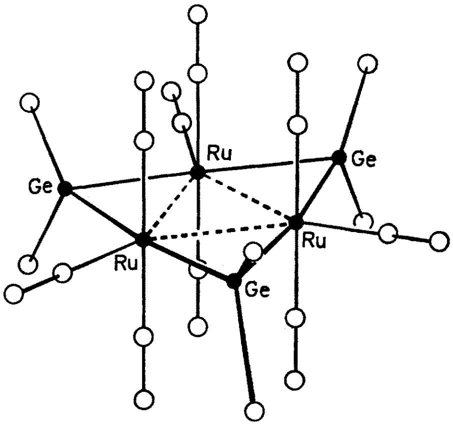
Complex (III) has a molecular structure similar to that of its silicon analogue.[1] This follows from the nature of its i.r. spectrum [ν_{max}(CO)(cyclohexane): 2046w, 2017s, and 2008w cm^{-1}] and for example the ready cleavage of the ruthenium–ruthenium bond to form the anion $[Me_3GeRu(CO)_4]^-$ (V). The overall molecular structure, however, is being established.[2] Complex (IV) (M' = Ru) is isomorphous[2] and almost certainly isostructural with its tin analogue[3] and, therefore, contains a four membered heterocyclic ring $\overline{Ru\cdot Ge\cdot Ru\cdot Ge}$.

Pyrolysis of (I) affords small amounts of polynuclear species $[M'(CO)_3]_2(\mu\text{-}GeMe_2)_3$ (VI) and good yields of compounds of molecular formula $Me_6Ge_3M'_3(CO)_9$ (VII). The ruthenium and osmium complexes (VI) have spectroscopic properties [M' = Ru, ν_{max}(CO): 2029s and 1919s, br (cm^{-1}); ^{1}H n.m.r. τ 8·7s] very similar to those of the compound $[Fe(CO)_3]_2(\mu\text{-}GeMe_2)_3$, the molecular structure of which consists of two $Fe(CO)_3$ groups linked by three bridging Me_2Ge groups.[4]

The colours and solubilities of the compounds (VII) are remarkably similar to those of the parent carbonyls. Their ^{1}H n.m.r. spectra show chemical shifts [τ, 8·76 (M' = Ru) and 8·73 (M' = Os)] very close to those of the bridging Me_2Ge groups found in complexes of type (IV) [τ, 8·85 (M' = Ru) and 8·77 (M' = Os)]. Both species (VII) show five carbonyl stretching bands in their i.r. spectra (at 2046s, 2038w, 2017s, 2011w, and 1986m cm^{-1} for M' = Ru). These properties suggest a molecular structure based on a triangular cluster M_3' with each side bridged by Me_2Ge groups, and this has been firmly established by a single-crystal *X*-ray diffraction study of the ruthenium compound (Figure).

Crystals of $[Me_2GeRu(CO)_3]_3$ are hexagonal, $P6_3/m$, with two trimer molecules in a unit cell of dimensions a = 10·92, c = 12·18Å. The three germanium atoms are coplanar with the three ruthenium atoms which form an equilateral triangle, while two of the carbonyl groups on each ruthenium atom are almost mutually *trans* and perpendicular to the Ru_3Ge_3 plane. The Me_2Ge bridges are symmetrical and the Ge–Ru distance is 2·47 Å. The molecule possesses idealised symmetry $\bar{6}m2$ (D_{3h}). The Ru–Ru distance (2·93 Å) is only 0·08 longer than that in $Ru_3(CO)_{12}$[5] where bridging groups are absent. In the compound $[Me_3SnRu(CO)_3(\mu\text{-}SnMe_2)]_2$, the diamagnetism of which also demands a spin pairing of electrons between ruthenium atoms, the Ru–Ru distance is 3·12 Å. The Ru–Ge–Ru bond angle (72·6°) in (VII) [M' = Ru] is considerably distorted from regular tetrahedral and may be compared with the $M'\cdot M\cdot M'$ angles in $[Me_3SnRu(CO)_3(\mu\text{-}SnMe_2)]_2$ and $[Fe(CO)_3]_2(\mu\text{-}GeMe_2)_3$ of 71·5°[3] and 69·8°,[4] respectively.

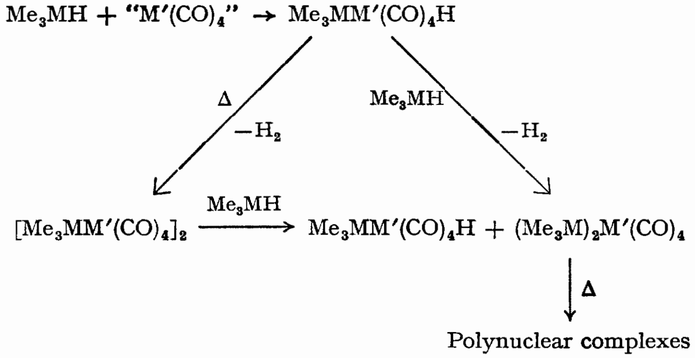
Complexes (VII) represent the first examples of heterocyclic metal-ring systems involving six metal atoms; an M'_3 triangle being part of a $(M'\cdot Ge)_3$ hexagon. Very recently examples of five-membered metal–metal heterocycles have been reported.[6]



FIGURE

The new compounds reported herein have an extensive chemistry. For example, the anion (V) has been used to prepare $Hg[Ru(CO)_4GeMe_3]_2$, the first carbonyl complex containing a pentanuclear chain of metal atoms, as well as $Me_3GeRu(CO)_4Re(CO)_5$, $Me_3GeRu(CO)_4AuPPh_3$, *etc.*

Moreover the interconversion of (I)—(IV) has delineated the various processes involved in reactions between Me_3MH (M = Si, Ge or Sn) and $M'_3(CO)_{12}$. Under u.v. irradiation Me_3GeH and $Ru_3(CO)_{12}$ afford mostly (III) with a low yield of (I) (M' = Ru). Using excess of Me_3GeH, complex (I) is formed in high yield (80%) with only a trace of (III) and (IV) (M' = Ru). Moreover, (III) reacts directly with Me_3GeH to give (I). Under various conditions Me_3GeH and $Os_3(CO)_{12}$ yield only (II), (I) (M' = Os), and small amounts of (IV) (M' = Os). Complex (II) reacts rapidly under mild conditions with Me_3GeH to give (I) (M' = Os), and also decomposes in isolation to give the same complex. In contrast $Me_3SiOs(CO)_4H$ decomposes thermally to give $[Me_3SiOs(CO)_4]_2$. On no occasion has a species $[Me_3MM'(CO)_4]_2$ been observed to decompose in isolation to afford $(Me_3M)_2M'(CO)_4$, and it seems unlikely, therefore that (I) (M' = Os) forms from (II) *via* $[Me_3GeOs(CO)_4]_2$, which has not been isolated. These observations suggest that the reactions follow the accompanying scheme where excess of Me_3MH and increasingly vigorous conditions favour formation of $(Me_3M)_2M'(CO)_4$ and polynuclear species, respectively. The initial process would involve an oxidative-addition reaction to co-ordinatively unsaturated $M'(CO)_4$, rather than reaction of the hydride with $M_3'(CO)_{12}$.



If the latter occurred there seems no reason why species such as $Me_3Si[Os(CO)_4]_nH$ ($n = 2$ or 3) should not have been isolated, since such complexes would be expected to be stable and analogous to $H[Os(CO)_4]_nH$[7] and Ph_3PAu-$[Os(CO)_4]Cl$.[8]

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