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Preliminary communication

A NEW GERMANIUM TETRACOBALT CARBONYL : $GeCo_4(CO)_{14}$

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SUMMARY

The room-temperature reaction of $NaCo(CO)_4$ with halogermanes, or of $Co_2(CO)_8$ with GeH_4, gives $GeCo_4(CO)_{14}$ which is assigned a $Ge[Co_2(CO)_7]_2$ structure on infrared evidence. This new species eliminates one CO at 50°C to give $(CO)_4CoGeCo_3(CO)_9$ and adds further $Co(CO)_4^-$ to give anionic $[GeCo_6(CO)_n]^{2-}$.

INTRODUCTION

A number of Group IV-cobalt carbonyls of the $MCo_4(CO)_n$ family have been reported (M = Si,Ge,Sn,Pb). Schmid et al have established that the n=13 members formed by silicon [1] and germanium [2,3] are clusters $(CO)_4CoGeCo_3(CO)_9$, while tin [4,5] and lead [4] form the n=16 members with the completely open structures $M[Co(CO)_4]_4$ which do not condense to the n=13 clusters. Schmid [3,6] has discussed this constrasting behaviour in terms of the size of the Group IV atoms.

We now report that germanium forms a third member of the family with n=14 which is stable at room temperature.

RESULTS AND DISCUSSION

When GeI_4 and $NaCo(CO)_4$ (ca 1:5 mole ratio) were reacted in 1:2 benzene/hexane at 25°C for 3 hours a deep brown solution resulted. Filtration, evaporation of solvents, and recrystallisation from CH_2Cl_2, gave deep-red crystals of $GeCo_4(CO)_{14}$ in 50% yield. Similarly, the reaction in Et_2O of $NaCo(CO)_4$ with $Cl_3GeCo(CO)_4$ or $ClGe[Co(CO)_4]_3$[7] gave $GeCo_4(CO)_{14}$ as the major product, together with a component showing ν_{CO} [2079vs, 2030(m,sh) 2020 vs, 2000 vw] within 2 cm^{-1} of the frequencies reported for $Sn[Co(CO)_4]_4$[5]. An alternative synthesis of $GeCo_4(CO)_{14}$ involved reaction of GeH_4 with $Co_2(CO)_8$ (1:2 mole ratio) in hexane in a sealed tube for 15 weeks at room temperature. This reaction also yielded a small amount of $(CO)_4CoGeCo_3(CO)_9$[2].

$GeCo_4(CO)_{14}$ is a deep-red solid which is stable indefinitely under nitrogen at -20°C, or for short periods in air. The mass spectrum shows the parent ion (m/e = 698 – 704); 73% of the total ion current is carried by $GeCo_4(CO)_n^+$ (n=0–14).

Solid $GeCo_4(CO)_{14}$ under vacuum slowly evolves CO (1 mole equivalent) at 50°C; after 45 hours near-quantitative conversion to $(CO)_4CoGeCo_3(CO)_9$[2] is achieved. In hexane solution carbonyl loss is more rapid giving $(CO)_4CoGeCo_3(CO)_9$ in 2 hours at 55-60°C. Thus Schmid & Etzrodt's isolation of 62% $(CO)_4CoGeCo_3(CO)_9$ from the reaction between $GeBr_4$ and $NaCo(CO)_4$[2] was a consequence of their reaction temperature of 55°C.

We suggest a structure for $GeCo_4(CO)_{14}$ of the type $Ge[Co_2(CO)_7]_2$ with the germanium acting as a common bridge replacing one CO in each of two $Co_2(CO)_8$ units. By comparison with other X_2Ge bridged $Co_2(CO)_7$ molecules [8], where the dihedral angle between the $GeCo_2$ plane and the bridging carbonyl plane is about 95°, this would predict C_2 symmetry. However the relatively simple infrared spectrum of $GeCo_4(CO)_{14}$ [ν_{CO} (hexane) 2079(vs) 2061(m) 2040(m) 2032(s) 2023(m) 2005w 1848m] indicates a higher symmetry structure. One possibility is the approximately D_{2d} arrangement where the bridging CO is in the $GeCo_2$ plane in each half of the molecule.

Reaction of $GeCo_4(CO)_{14}$ (or $GeCo_4(CO)_{13}$) with further $Co(CO)_4^-$ [<u>ca</u> 1:2 mole ratio] in CH_2Cl_2 or THF occurred readily to give an anionic species which could be isolated as the Et_4N^+ salt [ν_{CO} (nujol) 2050(w), 2016(vs), 1836(m), 1804(m)]. The same species was a co-product of the reaction of GeI_4 with $Co(CO)_4^-$ in benzene/hexane. Accurate analysis proved difficult due to air-sensitivity but preliminary data indicate a Et_4N^+ : Co ratio of 2:6 and confirms the presence of germanium, making a formulation $[Et_4N]_2[GeCo_6(CO)_n]$ most reasonable. This may have a "semi-interstitial" arrangement similar to the iso-electronic $[Co_6P(CO)_{16}]^-$[9].

The rich variety of germanium-cobalt carbonyl chemistry is being further explored and Xray structural analyses of both $GeCo_4(CO)_{14}$ and $[GeCo_6(CO)_n]^{2-}$ are under way.

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