Preparation of μ-Diphenylgermyl-μ-carbonyl-bis(tricarbonylcobalt) and Diphenylbis(tetracarbonylcobalt)germanium(IV)

By S. A. FIELDHOUSE, B. H. FREELAND, and R. J. O'BRIEN*

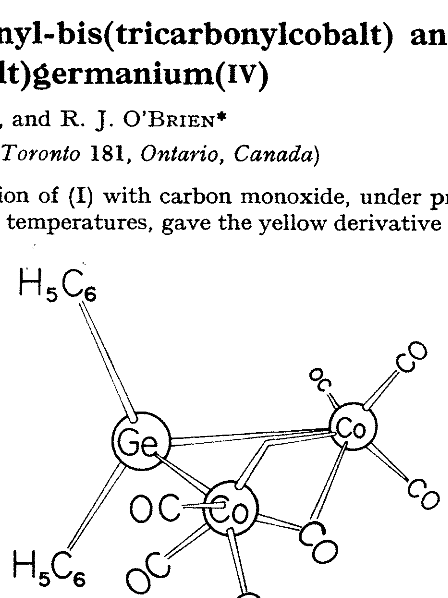
(*Lash Miller Chemical Laboratories, University of Toronto, Toronto* 181, *Ontario, Canada*)

Summary μ-Diphenylgermyl-μ-carbonyl-bis(tricarbonylcobalt) is formed in high yield from diphenylgermane and octacarbonyldicobalt; diphenylbis(tetracarbonylcobalt)germanium(IV) is not an intermediate in the reaction.

THE reaction of silanes with octacarbonyldicobalt[1] affords a very convenient synthesis of tetracarbonylcobalt derivatives of silicon. The analogous preparation of triethyl(tetracarbonylcobalt)germanium(IV) from triethylgermane has also been briefly mentioned.[2] We report a new type of reaction in which a Group IVb metal dihydride gives an heptacarbonyldicobalt derivative on reaction with octacarbonyldicobalt.

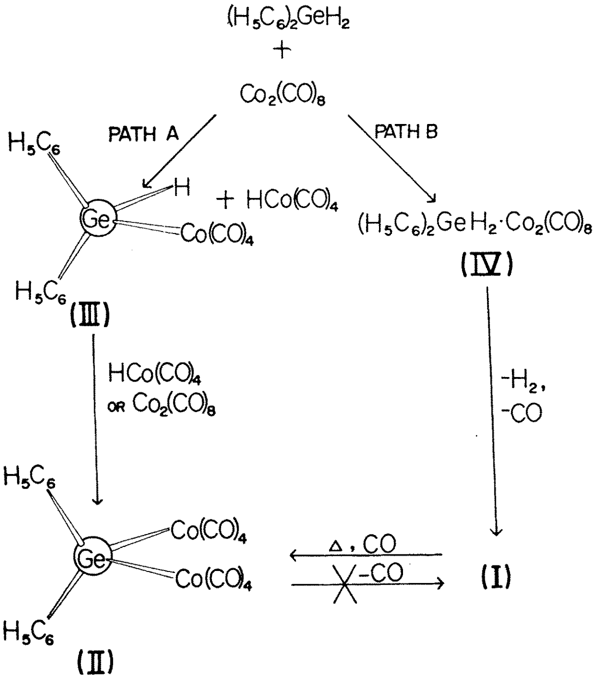
When diphenylgermane and octacarbonyldicobalt were allowed to react in toluene, at room temperature, the only metal carbonyl derivative, obtained in excellent yield, was a stable orange crystalline solid, m.p. 78—80°, for which analysis and mass spectral data indicated the composition $(C_6H_5)_2GeCo_2(CO)_7$. The i.r. spectrum, measured in hexane, showed terminal carbonyl stretching bands at 2100 (s), 2060 (vs), 2036 (vs), 2019 (s), and 2006 (sh, w) cm.$^{-1}$ and a band assigned to a bridging carbonyl group at 1840 (s) cm.$^{-1}$. This spectrum was thus very similar to thos reported for μ-bis(acetylacetonato)tin-μ-carbonyl-bis(tricarbonylcobalt)[3] and μ-tetrafluoroethylidene-μ-carbonyl-bis(tricarbonylcobalt).[4] Accordingly, structure (I) is assigned to the compound, analogous to the tin and carbon compounds above, with a 'bent' cobalt–cobalt bond and a bridging carbonyl group.

Reaction of (I) with carbon monoxide, under pressure at elevated temperatures, gave the yellow derivative (II) (m.p. 135—138° decomp.), which was identified as diphenylbis(tetracarbonylcobalt)germanium(IV) by elemental analysis and its i.r. spectrum, which was similar to those of other bis(tetracarbonylcobalt) derivatives of germanium and tin.[5] The mass spectrum of (II) was also determined. It was found that, in common with tetracarbonylcobalt-tin compounds,[3,6] the heaviest fragment was a $Co_2(CO)_7$-containing species



(I)

which was lighter by one carbonyl group than the expected parent ion. In the case of the corresponding tin derivatives it has been suggested[6] that the stability of the $Co_2(CO)_7$-containing fragment was due to the presence of a bridging carbonyl group. In agreement with this, the mass spectra of (I) and (II) both showed a highest-mass fragment corresponding to $(C_6H_5)_2GeCo_2(CO)_7{}^+$ which decomposed by stepwise loss of seven carbonyl groups. Differences were observed in the mode of cleavage of the phenyl groups from germanium but the significance of this observation is not clear.



The mechanism of the formation of (I) is interesting since it is the only metal carbonyl product of the reaction *irrespective* of the stoicheiometry, or of the rate, or of the order of the addition of the reagents. This appears to rule out a reaction sequence where diphenylgermane is converted into diphenyl(tetracarbonylcobalt)germane† (III) which then reacts further with octacarbonyldicobalt or tetracarbonylcobalt hydride, to give (II), followed by loss of carbon monoxide (path A). Compound (II) is not converted into (I) under the conditions used to isolate (I). The formation of (I) thus appears to involve an intermediate such as (IV), presumably analogous to Chini's aluminium tribromide–octacarbonyldicobalt complex,[7] where bridging carbonyl groups are retained. Loss of hydrogen and carbon monoxide from (IV) could then yield the observed product (I) (path B).

Financial support by the National Research Council of Canada, and by the Government of the Province of Ontario through Province of Ontario Graduate Fellowship to S.A.F. and B.H.F. is gratefully acknowledged. S.A.F. also thanks the University of Manchester Institute of Science and Technology for the award of the Lionel Blundell Overseas Fellowship.

(*Received, August 25th,* 1969; *Com.* 1296.)

---

† This compound has recently been prepared in these laboratories and further studies are in progress.

[1] A. J. Chalk and J. F. Harrod, *J. Amer. Chem. Soc.*, 1967, **89**, 4057; A. P. Hagen and A. G. MacDiarmid, *Inorg. Chem.*, 1967, **6**, 686; S. K. Gondal, A. G. MacDiarmid, F. E. Saalfeld, and M. V. McDowell, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 413; Y. L. Baay and A. G. MacDiarmid, *Inorg. Chem.*, 1969, **8**, 986; R. R. Schrieke and B. O. West, *Austral. J. Chem.*, 1969, **22**, 49.

[2] O. Kahn and M. Bigorne, *Compt. rend.*, 1966, **263**, *C*, 973; *J. Organometallic Chem.*, 1967, **10**, 137.

[3] D. J. Patmore and W. A. G. Graham, *Chem. Comm.*, 1967, 7; *Inorg. Chem.*, 1967, **6**, 1879.

[4] B. L. Booth, R. N. Haszeldine, P. R. Mitchell, and J. J. Cox, *Chem. Comm.*, 1967, 529; *J. Chem. Soc.* (*A*), 1969, 691.

[5] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 983.

[6] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2222.

[7] P. Chini and R. Ercoli, *Gazzetta*, 1958, **88**, 1170.