Inorganica Chimica Acta, *178* (1990) 141–142

Inorganica Chimica Acta
LETTER

A cobalt–cobalt bond with bridging bis(dimethylgermyl)alkane and carbon monoxide

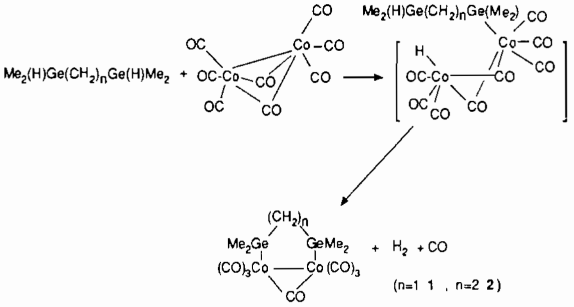
J. Barrau* and **N. Ben Hamida**

Laboratoire de Chimie des Organominéraux, U.R.A no. 477 C.N.R.S. Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse (France)

(Received October 26, 1990)

Only a few compounds of cobalt with ^{14}M–X–^{14}M–Co linkages are known [1–5]. Thus after our studies on the bis(dimethylgermyl)alkane iron and ruthenium tetracarbonyls $Me_2Ge(CH_2)_nGe(Me_2)M(CO)_4$ (M = Fe or Ru; $n = 1$ or 2) [6–8] and on the dimethylgermyldimethylsilylmethane-di-iron octacarbonyl [9] $Me_2Ge(CH_2)_nSi(Me_2)Fe(CO)_4Fe(CO)_4$ we have investigated in this work synthesis, spectroscopic analyses and some aspects of the reactivity of new polynuclear germylated clusters the bis(dimethyl)alkane dicobalt heptacarbonyls $Me_2Ge(CH_2)_nGe(Me_2)Co_2(CO)_7$ ($n = 1$ (**1**), $n = 2$ (**2**)).

These dicobalt heptacarbonyl complexes **1** and **2** are readily obtained by reaction of the bis(dimethylgermyl)alkanes $Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n = 1$ or 2) [10] with $Co_2(CO)_8$.



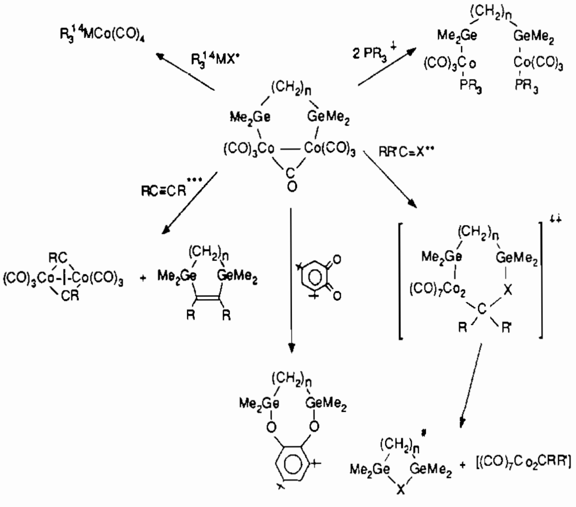
This reaction, irrespective of the stoichiometry and comparable with the reaction of Ph_2GeH_2 with $Co_2(CO)_8$ [11, 12] can be rationalized by (i) cleavage of the cobalt–cobalt bond of $Co_2(CO)_8$ by a Ge–H bond of the digermane with formation of a hydridocarbonyl group; (ii) intramolecular elimination of H_2 and elimination of carbon monoxide. There, is no evidence for preliminary formation of intermediate $Me_2Ge[Co(CO)_4](CH_2)_nGe[Co(CO)_4]Me_2$ which could spontaneously lose one carbonyl group. Complexes like $Me_2{}^{14}M[Co(CO)_4]$–X–$^{14}M[Co(CO)_4]Me_2$ (x = O, ^{14}M = Si or Ge; X = C_2H_4, 14M = Si) [1, 2] are known; they are thermally labile giving $CO_4(CO)_{12}$.

The complexes **1** and **2** are characterized by mass, Ir and NMR spectroscopies. **1**: IR (CCl_4) νCO (cm^{-1}) = 2080(m), 2020(m), 1990(F), 1850(m); ^1H NMR (C_6D_6) δ (ppm) = 1.44(CH_2), 0.70(CH_3); ^{13}C NMR (C_6D_6) δ (ppm) = 201.21 (bridged CO), 199.95 (CO_t), 22.70 (CH_2), 8.57(CH_3). **2**: IR (CCl_4) νCO (cm^{-1}) = 2070(m), 2010(m), 1980(F), 1850(m); ^1H NMR ($CDCl_3$) δ (ppm) = 1.40(CH_2), 0.75(CH_3); ^{13}C NMR (C_6D_6) δ (ppm) = 201.50 (bridged CO), 200.06 (CO_t), 21.24(CH_2), 4.80(CH_3).

The cobalt complexes **1** and **2** undoubtedly have the structure in which the germylated group replaces a bridging carbonyl in the parent dicobaltoctacarbonyl. This structure is indicated in IR by the band at 1850 cm^{-1} showing the presence of the bridging carbonyl and by the pattern of four strong bands in the terminal carbonyl region.

In this structure the two methyl groups are nonequivalent, thus the observation of a single sharp methyl resonance in the NMR at room temperature of **1** and **2** indicates that these molecules are fluxional.

Several rearrangements pathways might explain this observation. Adams and Cotton have shown that



Scheme 1. *^{14}M = Si,Sn R = X = Cl; ^{14}M = Si, R = Me X = Cl. **X = O, R = H, R′ = Ph, CCl_3; X = S, R·C·R′ = C = S. ***R = Ph, $EtCO_2$. #$n = 1$ unstable, $n = 2$ *stable* [6, 7]. +R = Ph, n-Bu. ++All these intermediate adducts are unstable at room temperature unlike those obtained in the reactions of the same unsaturated compounds RR′C=X with bis(dimethylgermyl)alkane iron or ruthenium tetracarbonyls [7, 8].

---

*Author to whom correspondence should be addressed.

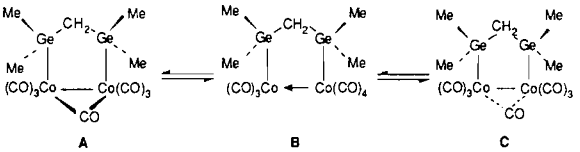
0020-1693/90/$3.50

the bis(germylene) complex $[Me_2Ge]_2Co_2(CO)_6$ has a temperature dependent NMR spectrum and have postulated a pseudo-rotation mechanism but not excluded one involving terminal germylene exchange [3].

In addition to these two mechanisms Job and Curtis have postulated but not demonstrated a rapid bridged–non-bridged–bridged interconversion for the germylated compound $Me_2GeCo_2(CO)_7$ [4].

To discuss the mechanism we have examined the ^{13}C NMR spectrum of 1 as a function of temperature. The single peak observed at 35 °C for the methyl groups collapses and separates at 0 °C into two peaks of equal intensities; at -50 °C we can observe four other methyl resonances and in the meantime the carbonyl resonances collapse, then the bridged carbonyl peak decreases and two carbonyl resonances remain.

These results seems to provide proof that bridged–non-bridged interconversion occurs. So the complex 1 may average the environments of the methyl groups via a terminal-bridged carbonyl exchange in which the new cobalt–carbonyl–cobalt bridge is formed on the opposite side of the Ge–Co–Co–Ge plane.



These new polynuclear heterocycles with high moisture- and oxygen-sensitivity are more reactive than the corresponding iron and ruthenium clusters [6, 7] and the complexes $R_3{}^{14}MCo(CO)_4$ ($^{14}M = Si$, Ge). They have high potential in organometallic synthesis and for example can lead to organogermanium heterocycles as well as to polynuclear clusters having ^{14}M–M bonds. Various CO substitution reactions with phosphines, Ge–Co cleavages by organometallic halides and insertion reactions have been observed as summarized in Scheme 1.

References

1 J. Greene and D. Curtis, *Inorg. Chem.*, *17* (1978) 2324.
2 L. Vancea and W. A. G. Graham, *Inorg. Chem.*, *13* (1974) 511.
3 R. D. Adams and F. A. Cotton, *J. Am. Chem. Soc.*, *92* (1970) 5003.
4 R. C. Job and M. D. Curtis, *Inorg. Chem.*, *12* (1973) 2514.
5 A. J. Cleland, S. A. Fieldhouse, B. H. Freeland and R. J. O'Brien, *J. Organomet. Chem.*, *32* (1971) C15.
6 J. Barrau, N. Ben Hamida, A. Agrebi and J. Satgé, *Organometallics*, *8* (1989) 1585.
7 J. Barrau, N. Ben Hamida, A. Agrebi and, J. Satgé, *Inorg. Chem.*, *29* (1990) 1674.
8 J. Barrau and N. Ben Hamida, *Inorg. Chim. Acta*, *175* (1990) 159.
J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem.*, *395* (1990) 27.
9 J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem.*, *387* (1990) 65.
10 J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem.*, *282* (1985) 315.
11 S. A. Fieldhouse, B. H. Freeland and R. J. O'Brien, *Chem. Commun.*, (1969) 127.
12 R. Ball, M. J. Bennett, E. H. Brooks, W. A. G. Graham, J. Hoyano and S. M. Illingworth, *Chem. Commun.*, (1970) 592.