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LETTER

# Synthesis and reactivity of digermylruthenium complexes $Me_2\overline{Ge(CH_2)_nGe(Me_2)Ru}(CO)_4$ ($n = 1$ or 2)

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

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

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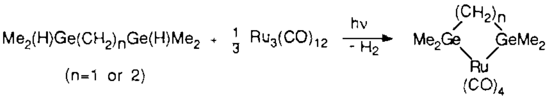
The interactions of transition-metal complexes with the $M_{14}$ atom have long been an area of interest involving both stoïchiometric and catalytic transformations of the $M_{14}$ atom compounds. Many $M_{14}$–M′ (M′ = transition-metal) are now well known, but few four- of five-ring heterocycles havig the $M_{14}$–$M'_8$–$M_{14}$ catenation have been reported [1–11]. Following our previous studies on the bis(dimethylgermyl)alkane-iron tetracarbonyls $Me_2\overline{Ge(CH_2)_nGe(Me_2)Fe}(CO)_4$ ($n = 1$ or 2) [9, 10] and on the dimethylgermyldimethylsilylmethane-di-iron octacarbonyl [11], the synthesis, spectroscopic analyses and reactivity of bis(dimethylgermyl)alkane-ruthenium tetracarbonyls have been investigated in this work.

The bis(dimethylgermyl)alkane-ruthenium tetracarbonyls are obtained starting from the germanium hydrides $(Me_2(H)Ge(CH_2)_nGe(H)Me_2$ ($n = 1$ or 2) [12] and $Ru_3(CO)_{12}$. The cyclization reactions are practically over after several hours of UV irradiation at ambient temperature and the resulting compounds are purified by distillation.

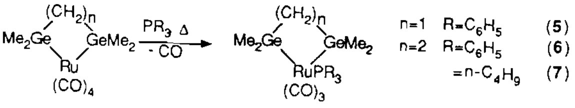


n=1 (1) n=2 (2)

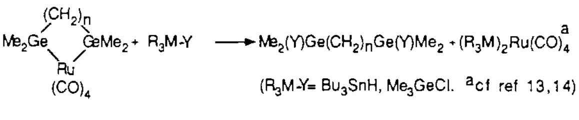
The complexes 1 and 2 are characterized by mass, IR and NMR spectroscopies (1: IR ($C_6H_6$) νCO $cm^{-1}$ = 2100(m), 2080(f), 2040(F), 2000(F); $^1H$ NMR ($C_6D_6$) δ ppm: 1.64 ($CH_2$), 0.66 ($CH_3$); $^{13}C$ NMR ($C_6D_6$) δ ppm: 201.55 ($CO_{ax}$), 193.26 ($CO_{eq}$), 25.42 ($CH_2$), 5.46 ($CH_3$). 2: IR ($C_6H_6$) νCO $cm^{-1}$: 2080(m), 2060(f), 2020(F), 1990(F); $^1H$ NMR ($C_6D_6$) δ ppm: 1.18 ($CH_2$), 0.58 ($CH_3$); $^{13}C$ NMR ($C_6D_6$) δ ppm: 197.63 ($CO_{ax}$), 193.90 ($CO_{eq}$), 19.89 ($CH_2$), 3.56 ($CH_3$)). The appearance of four carbonyl bands with the usual intensity pattern for $M_{14}$–M′–$M_{14}$ species in the IR and of sharp proton NMR singlets for methyl and methylenic or ethylenic protons of the germyl ligands are characteristic of $C_{2v}$ local symmetry at ruthenium in these compounds.

The heterocycles 1 and 2 have high potential in organometallic synthesis but are less reactive than their iron homologues [9, 10].

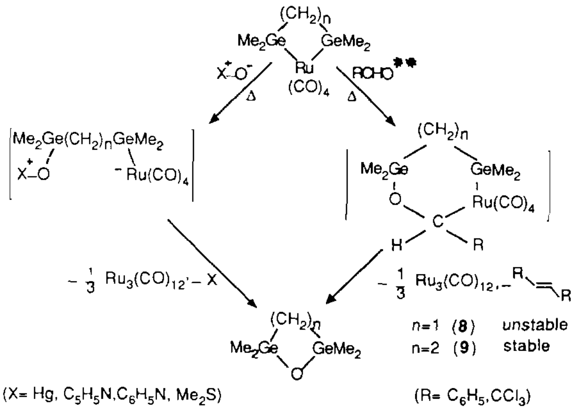
CO substitution reactions with various phosphines are obtained under thermic effects. New compounds 5–7 were characterized by IR, NMR, mass spectroscopy and elemental analysis.



Ge–Ru bond cleavage reactions are observed with various halogens, alcohols, organic halides and more interestingly with organometallic halides.



The reactions with oxides and organic carbonyl compounds lead to the heterocycles **8** or **9** which are stable or unstable at room temperature depending on the size of the heterocycle [9, 10, 12, 15].



As their iron homologues [10] compounds 1 and 2 react with 1,2-quinones through a one electron mechanism producing the digermylated dioxepane 10 [10] and dioxocane 11 [10] that are formally the adducts of biradicals $Me_2\dot{G}e(CH_2)_n\dot{G}eMe_2$ ($n = 1$ or

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*Author to whom correspondence should be addressed.

**The mechanism of this reaction may be viewed as an insertion reaction of the aldehyde in the Ge–Ru bond in a first step, followed by a thermic decomposition of the resulting adduct as demonstrated in the case of bis(dimethylgermyl)methane-iron tetracarbonyl [10].

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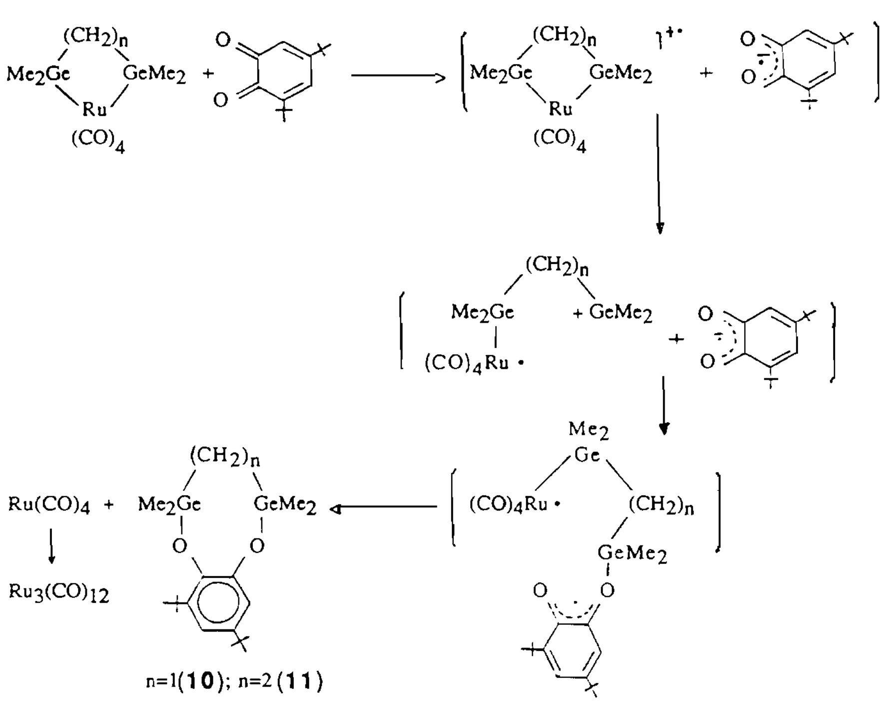
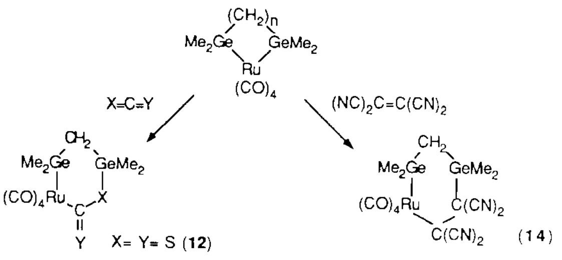


n=1(**10**); n=2(**11**)

2) with quinones. The transient semiquinonic radical involved can be detected by ESR spectroscopy either as the anion radical or ion paired with the metal ($g=2.0029$, $a^H$ 2.8 G).

Compound **1** reacts at room temperature with $CS_2$, PhNCO and $(NC)_2C{=}C(CN)_2$ to give heterocyclic expansion reactions. Adducts **12**–**14** are stable at ambient temperature and characterized by NMR, IR and mass spectrometry analyses. $^1H$ NMR data ($C_6D_6$): **12**: $\delta$ 0.58 (s, $CH_3GeRu$), 0.44 (s, $CH_3GeS$) and 0.75 (s, $CH_2$) ppm; **13**: $\delta$ 0.14 (s, $CH_3GeRu$), 0.60 (s, $CH_3GeO$), 1.45 (s, $CH_2$) and 7.4 ($C_6H_5$) ppm; **14**: $\delta$ 0.12 (s, $CH_3GeRu$), 0.50 (s, $CH_3GeC$), 1.20 (s, $CH_2$) ppm. IR data ($C_6H_6$): **12**: $\nu$CO $cm^{-1}$ 2080(m), 2010(f), 2000(F), 1990(F); $\nu$CS $cm^{-1}$ 1500(m). **13**: $\nu$CO $cm^{-1}$ 2080(m), 2060(f), 2000(F), 1960(F), 1650(f); $\nu$CN $cm^{-1}$ 1600. **14**: $\nu$CO $cm^{-1}$ 2080(m), 2020(f), 1990(F), 1960(F); $\nu$CN $cm^{-1}$ 2160(m).



X= Y= S (12)
X= O Y= N-Ph (13)
(14)

The new metalla heterocycles **12** and **13** decompose thermally to form the previously reported heterocycles $(Me_2GeX)_3$ and $Me_2\overline{GeCH_2Ge(Me_2)C}H_2$ suggestive of $Me_2\overline{GeCH_2Ge(Me_2)X}$ (X = O, S) and then, as observed, $[Me_2Ge{=}X]$ and $[Me_2Ge{=}CH_2]$ intermediates [9, 12, 15].

## References

1 C. S. Candy and M. F. Lappert, *J. Chem. Soc., Chem. Commun.,* (1972) 445.
2 L. Vancea and W. A. G. Graham, *Inorg. Chem., 13* (1974) 511.
3 C. S. Liu and C. W. Cheng, *J. Am. Chem. Soc., 97* (1975) 6746.
4 W. Fink, *Helv. Chim. Acta, 59* (1976) 606.
5 J. Greene and D. Curtis, *Inorg. Chem., 17* (1978) 2324.
6 H. Sakurai, T. Kobayashi and Y. Nakadaira, *J. Organomet. Chem., 162* (1978) C43.
7 T. H. Hseu, Y. Chi and C. S. Liu, *Inorg. Chem., 20* (1981) 199.
8 F. H. Carré and J. J. E. Moreau, *Inorg. Chem., 21* (1982) 3099.
9 J. Barrau, N. Ben Hamida, A. Agrébi and J. Satgé, *Organometallics, 8* (1989) 1586.
10 J. Barrau, N. Ben Hamida and J. Satgé, *Inorg. Chem., 29* (1990) 1674.
11 J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem., 387* (1990) 65.
12 J. Barrau, N. Ben Hamida and J. Satgé, *J. Organomet. Chem., 282* (1985) 315.
13 J. D. Cotton, S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A,* (1968) 2758.
14 S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A,* (1971) 2874.
15 J. Barrau, N. Ben Hamida, A. Agrébi and J. Satgé, *Organometallics, 6* (1987) 659.