1,1-Dimetallagermacyclopent-3-enes: Precursors to Transition Metal Substituted Germylenes (Germanediyls)

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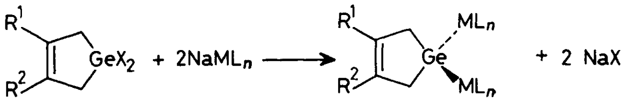
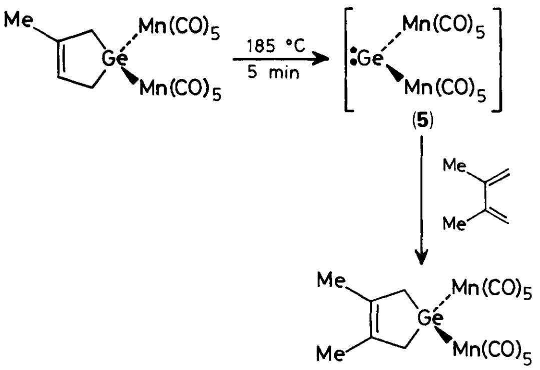
Transition metal substituted germylenes have been generated by pyrolysis of 1,1-dimetallagermacyclopent-3-enes and by the metathesis reaction between GeI_2 and $[Mo(CO)_3Cp]^-$ (Cp = C_5H_5).

The chemistry of silylene and germylene reactive intermediates has been intensely studied in recent years, with particular emphasis on the preparation of suitable generators,[1] trapping reagents,[2] and their rearrangement reactions.[3] However, the work has been confined almost exclusively to the study of silylenes and germylenes containing electronegative substituents. The sole exception is the recent generation of a transition metal substituted silylene, {:Si[Fe(CO)$_2$Cp]-Me} (Cp = C_5H_5), by Marietti-Migrami and West,[4] which was trapped by reaction with benzophenone. Since heavy carbene



(1) $R^1 = R^2 = Me, ML_n = Mn(CO)_5$
(2) $R^1 = R^2 = Me, ML_n = Fe(CO)_2Cp$
(3) $R^1 = R^2 = Me, ML_n = Co(CO)_4$
(4) $R^1 = Me, R^2 = H, ML_n = Mn(CO)_5$

Scheme 1

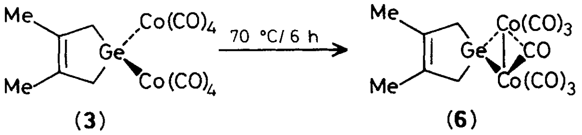


Scheme 2

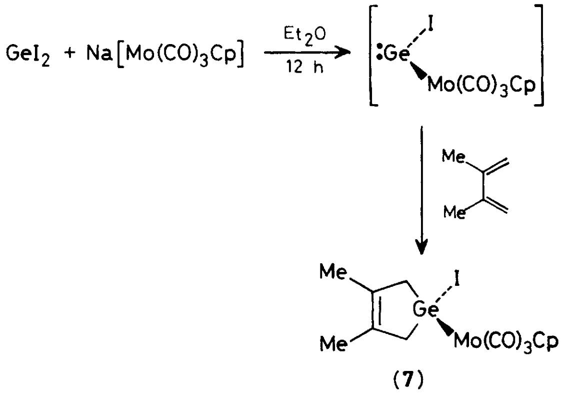
analogues containing electropositive substituents are likely to exhibit interesting chemistry,[5] we are examining methods to prepare precursors for transition metal substituted germylenes, $\{:Ge[ML_n]_2\}$. 1,1-Disubstituted germacyclopent-3-enes seem to be suitable precursors since dimethylgermylene[6] and dichlorogermylene[7] have been cleanly extruded under relatively mild conditions.

A series of 1,1-ditransition metal substituted germacyclopent-3-enes have been prepared according to the metathesis reaction of Scheme 1. When reactions were carried out over short periods (30 min), mixtures of mono- and di-substituted products were obtained. However, the 1,1-disubstituted species, (**1**)—(**4**), were isolated in high yields after a reaction period of 12 h as colourless or pale yellow solids that gave satisfactory spectroscopic and elemental analytical data.†

Thermogravimetric analyses of (**1**)—(**4**) indicate that the onset of weight loss occurs at ~150 °C and is complete by ~250 °C.‡ After pyrolysis in the solid state at 165 °C for five minutes in a sealed tube, (**1**) generated 2,3-dimethylbuta-1,3-diene as shown by ^1H n.m.r. spectroscopy of the reaction products, implying the possible extrusion of $\{:Ge[Mn(CO)_5]_2\}$ (**5**). In order to determine whether transition metal substituted germylenes are extruded intact, a number of trapping experiments have been carried out. Scheme 2 is typical of these experiments. Compound (**4**) was pyrolysed in the presence of a large excess of 2,3-dimethylbuta-1,3-diene diluted with toluene solution and sealed in an ampoule *in vacuo*. After heating to 185 °C for 5 min,§ the volatile components were removed *in vacuo* and the whole reaction mixture dissolved in $[^2H_6]$benzene. Methyl and methylenic ^1H n.m.r. resonances corresponding to an authentic sample of (**1**) could be unequivocally identified, together with resonances due to unchanged (**4**) and a small amount of polydiene. After this short pyrolysis, at least 30% of (**5**), extruded from (**4**), had been trapped to form (**1**).¶ This experiment provides quantitative evidence that is consistent with the extrusion of the transition metal substituted germylene, $\{:Ge[Mn(CO)_5]_2\}$, upon pyrolysis of (**4**) and demonstrates that both the Ge–Mn and Mn–CO bonds are kinetically stable to the reaction conditions employed. It has previously been reported[8] that compound (**3**) extrudes $\{:Ge[Co(CO)_4]_2\}$ between 40 and 60 °C. However, we found that heating (**3**) for 6 h at 70 °C resulted only in the quantitative extrusion of CO to form (**6**), according to Scheme 3. Elimination of 2,3-dimethylbuta-1,3-diene occurs at a significant rate only above 170 °C.



Scheme 3



Scheme 4

Additional evidence for the generation of transition metal substituted germylenes has been obtained from trapping reactions according to Scheme 4. Compound (**7**) was isolated in 30% yield after reaction for 12 h at room temperature in diethyl ether and was characterized by ^1H n.m.r. spectroscopy.‖ Since the reaction of GeI_2 with 2,3-dimethylbuta-1,3-diene is negligible over this period at room temperature (significant reaction occurs only ⩾50 °C), and the reaction of $Na[Mo(CO)_3Cp]$ with 1,1-di-iodo-3,4-dimethylgermacyclopent-3-ene is only 20% complete after three days (control experiment using Et_2O as solvent under similar conditions to those of Scheme 4), we conclude that $\{:GeI[Mo(CO)_3Cp]\}$ (**8**) must be a relatively long-lived species under the conditions of

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† *Selected spectroscopic data*: (**1**) ^1H n.m.r. δ 2.44 (s, 4H, CH_2), 1.82 (s, 6H, Me); i.r. ν(C–O) (cm^{-1}), 2100m, 2067m, 2032s, br., 1950sh. (**2**) ^1H n.m.r. δ 2.48 (s, 4H, CH_2), 2.06 (s, 6H, Me), 4.40 (s, 5H, Cp); i.r. ν(C–O)(cm^{-1}), 1983s, 1933sh, 1917s, 1900sh. (**3**) ^1H n.m.r. δ 2.47 (s, 4H, CH_2), 1.66 (s, 6H, Me); i.r. ν(C–O) (cm^{-1}) 2100s, 2081s, 2032s, 1944s, br. (**4**) ^1H n.m.r. δ 2.30 (s, 2H, CH_{2a}), 2.46 (s, 2H, CH_{2b}), 1.88 (s, 3H, Me), 5.88 (s, 1H, CH); i.r. ν(C–O) (cm^{-1}) 2075m, 2010s, 2001s, br., 1986s, br.

‡ Data were recorded from 40—400 °C with a heating rate of 10 °C/min and from 40—900 °C with a heating rate of 40 °C/min. No weight change was observed above 250 °C.

§ A twenty-fold excess of trapping reagent was used and the experiment carried out at high dilution [~0.1 mM in (**4**)] to reduce the possibility of polymerization of the dienes.

¶ This is the minimum extent of conversion as determined by comparison of the ^1H n.m.r. integration of resonances due to unchanged (**4**) and (**1**). However, it is likely that more than 30% of (**4**) reacted.

‖ (**6**), ^1H n.m.r. δ 2.46 (s, 4H, CH_2), 1.46 (s, 6H, Me); i.r. ν(C–O) (cm^{-1}) 1999s, br.; 2041s, 2088s, 1836s. (**7**) ^1H n.m.r. δ 2.57 (d, 2H, J_{HH} 16 Hz, CH_{2a}), 2.36 (d, 2H, CH_{2b}), 1.68 (s, 6H, Me).

Scheme 4. The isolation of only the mono-substituted product is probably the result of the large steric demands of the $[Mo(CO)_3Cp]^-$ moiety.

Further studies on the thermal rearrangements of this interesting class of compounds and the reactivity of transition metal substituted germylenes are in progress.

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5 For example, it has been suggested that silylenes, when substituted with electropositive substituents, may exhibit triplet electronic ground states, M. E. Colin, J. Breulet, and H. F. Schaefer, *Tetrahedron*, 1985, **41**, 1434.

6 D. Lei and P. P. Gaspar, unpublished results.

7 S. P. Kolesmikov, I. S. Royozhin, M. G. Safarov, and O. M. Nefedov, *Izv. Akad, Nauk, SSSR, Ser. Khim*, 1981, **6**, 1423, *Engl. transl.*, 1981, 1143. Dichlorogermylene was extruded at ~500 °C.

8 We have isolated compound (**3**) as a colourless crystalline solid, according to the reaction of Scheme 1, and recrystallized it from n-pentane at −30 °C. The previous report of this compound refers to it as a yellow–brown oil that decomposes upon distillation at 60 °C and 5×10^{-1} mmHg. A. Castel, P. Riviere, J. Satge, J. J. E. Moreau, and R. J. P. Corriu, *Organometallics*, 1983, **2**, 1498.