

Figure 2. ^2H NMR spectrum of *cis*-methylcyclopentane-2- d_1 (δ 1.01) and *trans*-methylcyclopentane-2- d_1 (δ 1.68), the hydrolysis products obtained in the cyclization of **1**- d_1 .

$^\circ\text{C}$. Quenching with bipyridine at -100°C yields cyclized compounds that are stable at room temperature and can be obtained in greater than 90% yields. To demonstrate that the cyclization occurred under the same conditions as polymerization, the reaction of **1** with ethylaluminum dichloride cocatalyst was carried out in the presence of ethylene at -100°C . After rapid quenching, ethylene oligomers capped with cyclopentyl groups were obtained.⁸

Since this carefully designed polymerization system results in the insertion of an α -olefin into a titanium-carbon bond under polymerization conditions, the measurement of an isotope effect on stereochemistry of polymerization can be accomplished. This represents the most direct and precise method for the study of a step in a catalytic reaction in which a stereocenter is produced.

Insertion of an α -olefin into a metal alkyl bond that is monodeuterated at the α -position generates diastereomers as shown below for one enantiomer. Although there may be a kinetic isotope effect in the Cossee mechanism, the stereochemically determined isotope effect in this situation should be 1.0. If the α -hydrogens are involved in activation prior to insertion, the symmetry of the CHD is broken, and the ratio of diastereomers will reflect the ratio of C-H to C-D activation. This is demonstrated in Figure 1 for one enantiomer and one orientation of the inserting olefin. Choice of olefin orientation is unimportant in the example since, if α -activation is important, *one direction of attack* by the olefin will be highly favored. This is particularly true in this case, since bicyclic transition states are involved. Consequently, if α -CH activation is important in M-C activation and in the control of stereochemistry, the ratio of diastereomers should not equal 1; i.e., there will be an isotope effect reflected in the diastereomer ratio.⁵

This isotope effect on the stereochemistry was measured using the titanocene alkenyl chlorides described above. Cyclization of the α -deuterated analogue at -100°C using EtAlCl_2 produces *cis*- α -diastereomers, as shown above. The ^2H spectra of the isomeric organometallic products, as well as the *cis* and *trans* methylcycloalkanes which result from protonolysis of the organometallic are readily distinguishable at 76 MHz.^{9,10} In all cases, the ratio of *cis* to *trans* isomers is 1.00 ± 0.05 (Figure 2). This result demonstrates that α -activation is not a significant effect in either the rate or stereochemistry of this olefin insertion reaction which takes place under polymerization conditions in a polymerization system.

Although Ziegler polymerization and olefin metathesis have been linked from the beginning as related processes, it is now

(8) The oligomers were analyzed by GC-MS and by capillary GC, using authentic products for comparison.

(9) ^2H NMR analysis of the hydrolysis products of the cyclization with **1**- d_1 showed a 1:1 mixture of *cis*-methylcyclopentane-2- d_1 (δ 1.01) and *trans*-methylcyclopentane-2- d_1 (δ 1.68). This is in agreement with literature values. Lipnick, R. L. *J. Am. Chem. Soc.* **1974**, *96*, 2941.

(10) After quenching with bpy, the organometallic product from the cyclization with **2**- d_1 was analyzed by ^2H NMR. The spectrum showed a 1:1 mixture of the *trans* and *cis* products at δ 1.54 and 0.69, respectively. Hydrolysis of the mixture gave again a 1:1 mixture of *trans*-methylcyclohexane-2- d_1 (δ 1.60) and *cis*-methylcyclohexane-2- d_1 (δ 0.80).

apparent from this work and our metathesis studies with titanocene systems that the basic steps are different. Metathesis is the chemistry of titanium carbon double bonds while Ziegler polymerization is that of titanium carbon single bonds.

Acknowledgment. Support of the National Science Foundation (CHE-8214668) and the Southern California Regional NMR Facility (CHE-7916324) is gratefully acknowledged.

2,2-Dimesityl-1-(2,4,6-tri-*tert*-butylphenyl)germaphosphene: The First Stable Compound with a Germanium-Phosphorus Double Bond[†]

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Received December 28, 1984

Currently, there is great deal of interest in group 14 and 15 elements in low coordination states. In organophosphorus and organogermanium chemistry, several very interesting new compounds with $p\pi-p\pi$ bonds between heteroatoms have been reported: $\text{P}=\text{C}$,¹ $\text{P}=\text{N}$,^{1b} $\text{P}=\text{P}$,^{2,3} $\text{P}=\text{As}$,² $\text{P}=\text{Sb}$,² and $\text{Ge}=\text{Ge}$.⁴

It seems quite evident that the stability of these compounds is intimately related to the accessibility of the double bond. Indeed, such compounds could be stabilized when reactive sites are protected by bulky substituents.

Metallaphosphenes [$>\text{M}=\text{P}-$, M = group 14 (Si, etc.)] have long been speculated as reactive intermediates and could only be characterized by trapping reactions (M = Si,⁵ Ge,⁶ Sn⁷). Very recently, the first stable silaphosphene ($>\text{Si}=\text{P}-$) has been reported.⁸

In the present paper, we describe the synthesis of 2,2-dimesityl-1-(2,4,6-tri-*tert*-butylphenyl)germaphosphene (**1**), the first stable compound containing a germanium-phosphorus double bond. The highly air-sensitive germaphosphene **1** has been isolated in pure form and characterized by its physicochemical data and its expected trend in chemical reactivity.

The first step in the synthesis of **1** involves the preparation in nearly quantitative yields of (halo)germylphosphines **5** by addition of the lithiophosphine **3** [prepared by reacting *tert*-butyllithium (1.6 M in pentane) with (2,4,6-tri-*tert*-butylphenyl)phosphine (**2**)]

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

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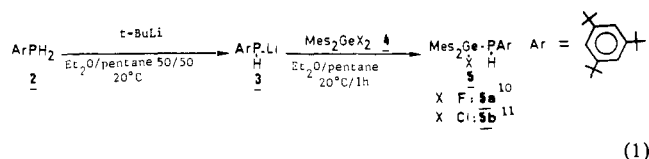
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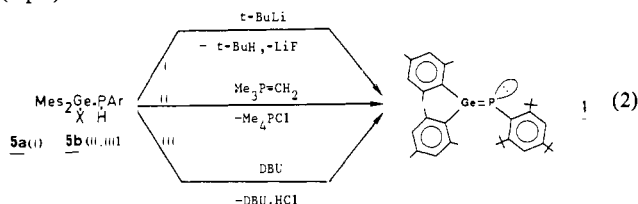
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to dimesityldihalogermanes⁹ **4** (eq 1).



Dehydrohalogenation of **5** was accomplished using different strong bases: (i) *tert*-butyllithium, (ii) trimethylmethylenephosphorane, and (iii) 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU)¹² (eq 2).



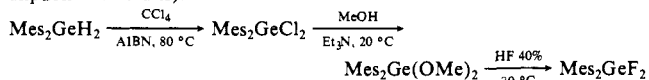
(i) An equivalent of *t*-BuLi was added to an equivalent of **5a** in ethereal solution at -15 °C, under an argon atmosphere. An orange color developed immediately; ³¹P NMR investigation of the solution showed the nearly quantitative formation of **1** [δ ³¹P +175.4 (H₃PO₄)]. Centrifugation of lithium fluoride and removal of ether/pentane solvents under vacuum afforded an air-sensitive crude material. Recrystallization of crude **1** from pentane gave pure orange crystals of **1**.¹³

(ii) An equimolar quantity of trimethylmethylenephosphorane (Me₃P=CH₂) (in pentane) was added to a solution of **5b** in the same solvent at 20 °C. The reaction mixture was filtered to remove Me₄PCl. ³¹P NMR analysis of the filtrate showed the formation of **1** (30%) and **6** (35%) and the presence of unreacted starting material **5b** (30%). The adduct **6**¹⁴ presumably results from the addition of trimethylmethylenephosphorane to **1** (see further).

(iii) Addition of 1 equiv of DBU to **5b** in pentane solution afforded **1** in small amount (~15%); the yield of **1** cannot be improved even with a large excess of DBU.

The structure of **1** was corroborated by its chemical behavior. A preliminary investigation reveals the expected polarity¹⁵ of the

(9) Mes₂GeCl₂ and Mes₂GeF₂ have been obtained as followed (Riviere, P., unpublished results):



(10) **5a**: ¹H NMR (60 MHz, C₆D₆) δ 1.45 (s, 9 H, para *t*-Bu) 1.60 (s, 18 H, ortho *t*-Bu), 2.13 (s, 6 H, *p*-Me), 2.30 (s, 12 H, *o*-Me), 6.70 (br s, 4 H Ar Mes); ³¹P NMR (36.4 MHz, C₆D₆) δ -110.6 (¹J_{PH} = 209, ²J_{PF} = 9 Hz); IR (pentane) ν (PH) 2330 cm⁻¹. Anal. Calcd for C₃₆H₅₂FGeP: C, 71.19; H, 8.63; F, 3.13. Found: C, 71.30; H, 8.84; F, 3.40.

(11) **5b**: ¹H NMR (60 MHz, C₆D₆) δ 1.38 (s, 9 H, *p*-*t*-Bu), 1.50 (s, 18 H, *o*-*t*-Bu), 2.05 (s, 6 H, *p*-Me), 2.35 (s, 12 H, *o*-Me), 6.69 (br s, 4 H Ar Mes); ³¹P NMR (C₆D₆) δ -90.9 (¹J_{PH} = 215 Hz); IR (pentane) ν (PH) 2360 cm⁻¹. Anal. Calcd for C₃₆H₅₂ClGeP: C, 69.31; H, 8.40; Cl, 5.68. Found: C, 69.08; H, 8.57; Cl, 5.82.

(12) Attempts to dehydrochlorinate **5b** by amines such as trimethylamine, triethylamine, or 1,4-diazabicyclo[2.2.2]octane were unsuccessful.

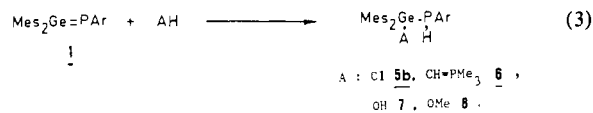
(13) **1** presents as highly air-sensitive orange crystals (mp 155-160 °C, sealed tube) soluble in usual organic solvents and stable at room temperature. ¹H NMR (C₆D₆) δ 1.38 (s, 9 H, *p*-*t*-Bu), 1.77 (s, 18 H, *o*-*t*-Bu), 1.98 (s, 6 H, *p*-Me), 2.12 (s, 6 H, *o*-Me of Mes'), 2.60 (s, 6 H, *o*-Me of Mes''), 6.58 and 6.73 (two br s, 4 H Ar Mes), 7.47 (d, 2 H, Ar Ar, ⁴J_{PH} = 6.0 Hz). Mesityl groups are nonequivalent (no rotation about Ge=P bond). Mes' is probably the mesityl group cis with the lone pair on phosphorus; similar deshielding has already been observed in 2-germaphospholanes (Courret, C.; Escudie, J.; Satge, J.; Redoules, G. C. R. Acad. Sci. Ser. 3 1974, 279, 225-228). ³¹P NMR (C₆D₆) δ +175.4; mass spectrum (EI), *m/e* 606 (M).

(14) **6**: ¹H NMR (60 MHz, C₆D₆) δ 0.20 (m, 1 H, CHGe), 1.0 (d, 9 H, ²J_{PH} = 13.0 Hz, PMe₃), 1.32 (s, 9 H, *p*-*t*-Bu), 1.53 (s, 18 H, *o*-*t*-Bu), 2.13 (s, 6 H, *p*-Me), 2.47 (s, 12 H, *o*-Me), 6.77 (br s, 4 H, Ar Mes); ³¹P NMR (C₆D₆) δ -5.5 (PMe), -81.2 (PAr, ¹J_{PH} = 206 Hz); mass spectrum (EI), *m/e* 677 (M).

(15) The reactivity of the Ge=P double bond is in good agreement with the polarity predictions arising from calculations made in collaboration with J. C. Barthelat (Laboratoire de Physique Quantique, Toulouse); this theoretical investigation has now been achieved and submitted to publication.

Ge=P bond with germanium as the more positive partner.

Reactivity of **1** is very high particularly toward compounds with active hydrogens, e.g., water, methanol, hydrogen chloride, and trimethylmethylenephosphorane, which add to the germanium-phosphorus double bond; addition of these reagents to an orange solution of **1** in pentane at room temperature resulted in immediate decoloration of reaction mixture and afforded respectively the adducts **7**,¹⁶ **8**,¹⁷ **5b**,¹¹ and **6**¹⁴ in nearly quantitative yields (eq 3).



Germaphosphene **1** is the first isolated compound with a double bond between germanium and phosphorus. Further investigations of its chemical and spectroscopic properties are now in progress.

(16) **7**: ¹H NMR (C₆D₆) δ 1.21 (s, 9 H, *p*-*t*-Bu), 1.40 (s, 18 H, *o*-*t*-Bu), 2.05 (s, 6 H, *p*-Me), 2.22 (s, 12 H, *o*-Me), 6.65 (br s, 4 H, Ar Mes); ³¹P NMR (C₆D₆) δ -105.6 (¹J_{PH} 209 Hz); mass spectrum (desorption), *m/e* 606 (M).

(17) **8**: ¹H NMR (C₆D₆) δ 1.20 (s, 9 H, *p*-*t*-Bu), 1.38 (s, 18 H, *o*-*t*-Bu), 2.00 (s, 6 H, *p*-Me), 2.13 (s, 12 H, *o*-Me), 6.60 (br s, 4 H Ar Mes); ³¹P NMR (C₆D₆) δ -107.0 (¹J_{PH} = 212 Hz); mass spectrum (EI), *m/e* 619 (M).

Resonance Raman Studies of the Photoreduction of Horseradish Peroxidase Compounds I and II

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Horseradish peroxidase (HRP) (EC 1.11.1.7) catalyzes the oxidation of substrates by hydrogen peroxide without the formation of ternary complexes.¹⁻³ Instead, the enzyme is first oxidized by peroxide to form an intermediate referred to as compound I which is deficient from the resting enzyme by two electrons. Resting HRP contains high-spin, five-coordinate ferriheme. The most widely held view is that, on oxidation to compound I, one electron is removed from the iron atom and one oxygen atom of peroxide is retained to form an oxyferryl ion, while the second electron is abstracted from the porphyrin ring to form a π -cation radical. Compound I is catalytically active and its porphyrin radical abstracts one electron from the substrate to form a second intermediate, called compound II, which is subsequently reduced back to the resting enzyme by one-electron oxidation of a second molecule of substrate.

Resonance Raman (RR) spectroscopy has proven to be a valuable tool for the study of heme proteins⁴ and has been applied to HRP and its intermediates.⁵⁻¹⁴ Compound I has long been

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