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Carbenes

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Electronic Properties and Reactivity of an Isolable Phosphagermaheterocyclic Carbene**

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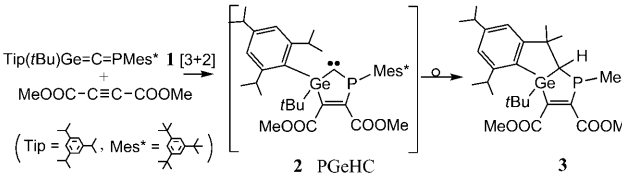
In memory of Dumitru Ghereg

Carbenes have been considered for a long time as unstable intermediates until the pioneering work of Bertrand and co-workers[1,2] with the isolation of a stable noncyclic push–pull carbene and of Arduengo and co-workers[3] with the isolation of an N-heterocyclic push–push carbene (NHC). Today, stable carbenes, particularly NHCs, govern a large part of modern chemistry,[4] especially in coordination chemistry with many applications: first of all in the field of catalysis, where NHCs successfully replace phosphines,[5] but also in medical chemistry,[6] in nanoscience,[7] and in the development of new luminescent compounds,[8] where their role is also dramatically increasing.

To develop and enhance the applications of NHCs, one of the main objectives has been to modulate their electronic properties (acceptor and mainly donor), which are one of the key characteristics of such carbenes. In the case of a typical NHC system, the easiest variation concerns the substituents on the nitrogen atoms bonded to the carbene center, which affects the steric and electronic properties of the ligands;[9] recently, interesting works on the backbone of NHCs have been reported.[10] However, a greater impact on the electronic properties of such types of heterocyclic carbenes could be obtained by the replacement of the nitrogen atoms on the carbenic centre by other heteroelements: the only reported example of such an isolated nitrogen-free NHC-type carbene comes from Bertrand and co-workers, with the synthesis of a highly basic, means strongly σ-donor, diphosphinocarbene.[11]

Recently we published the unprecedented 1,3-dipole behavior of the phosphagermaallene Tip(*t*Bu)Ge=C=PMes* (**1**; Tip = 2,4,6-triisopropylphenyl; Mes* = 2,4,6-tris-*tert*-butylphenyl) towards dimethyl acetylenedicarboxylate, leading surprisingly to a new type of nitrogen-free carbene, the transient phosphagermaheterocyclic carbene (PGeHC) **2**; the latter undergoes, even at low temperature, a rearrangement by insertion of the carbenic carbon atom into a CH bond of an *ortho*-*i*Pr of the Tip group to lead to the heterocyclic compound **3** (Scheme 1).[12a]

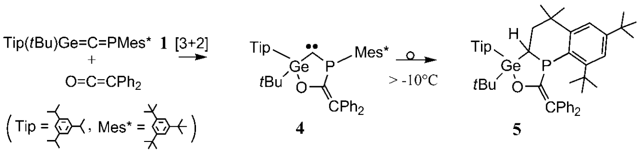


Scheme 1. 1,3-Dipole behavior of the phosphagermaallene **1** towards dimethyl acetylenedicarboxylate.

The synthesis of an isolable PGeHC compound is a major objective to determine its electronic properties and to study its reactivity. Herein we report the first example of an isolable and spectroscopically evidenced PGeHC, which constitutes the second nitrogen-free NHC-type carbene, its electronic properties, its chemical behavior, and the structure of the corresponding Rh complex.

Stable cyclic PGeHC **4** was obtained according to a similar procedure as that for **2**, by addition of one equivalent of diphenylketene ($Ph_2C{=}C{=}O$) to phosphagermaallene **1** at −80 °C in diethyl ether (Scheme 2). As in the case presented in Scheme 1, the formation of carbene **4** can only be explained by a 1,3-dipole behavior of the phosphagermaallene **1** giving a [3+2] cycloaddition with the C=O bond of the diphenylketene.

Monitoring the reaction by dynamic ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy between −80 °C and room temperature showed



Scheme 2. Reaction of Tip(*t*Bu)Ge=C=PMes* **1** with $Ph_2C{=}C{=}O$.

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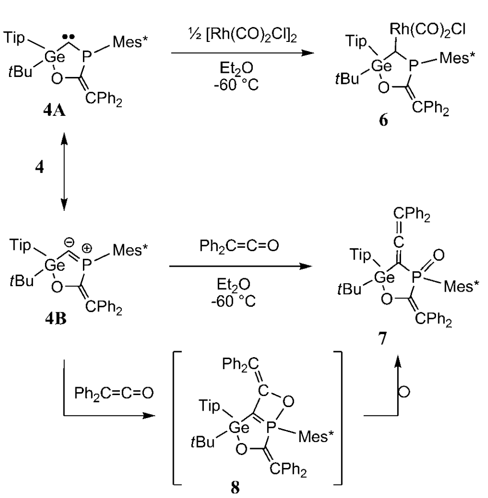
that carbene **4** was nearly quantitatively obtained at −30 °C. The product was physicochemically evidenced by a singlet at $\delta = 119.1$ ppm in the ^{31}P NMR spectrum. Unfortunately, the ^{13}C signal of the carbenic carbon could not be attributed because of the presence of many aromatic carbon atoms in the expected field. At −80 °C carbene **4** is nearly insoluble in diethyl ether and can be isolated as a white stable solid. It showed no degradation during three weeks in ether solution at −30 °C but at higher temperatures (0 °C) it slowly undergoes in solution a C−H insertion into an *o*-*t*Bu group of the Mes* group leading to the sole compound **5** (δ^{31}P = −22.9 ppm, $^2J_{\mathrm{PH}} = 17.6$ Hz)[13] (Scheme 2); such an insertion into a C−H bond has been observed recently for other unstable PGeHC compounds.[12] The difference of reactivity with carbene **2** (insertion into an *o*-*i*Pr of the Tip group) is due to a different geometry of the heterocyclic carbene **4**, the insertion occurring into the closest C−H bond. Tricyclic compound **5** was characterized by an X-ray structural study (see the Supporting Information). Bond lengths are in the normal range with the exception of the Ge–O bond, which is slightly elongated (1.839(2) Å; standard Ge–O: 1.75–1.80 Å).[14] In the tricyclic unit, the aromatic ring and the central six-membered ring are in a same plane, except the former carbenic carbon atom, which is 0.599 Å out of this plane.

Tetracarbonyl-di-μ-chloridodirhodium(I) was added to a solution of carbene **4** in Et_2O cooled to −60 °C to evaluate its σ-donor properties;[15] this reaction leads nearly quantitatively to rhodium complex **6** (Scheme 3).[13]

Complex **6** was evidenced in the ^{13}C NMR spectrum by a signal doublet of doublet at low field for the carbenic carbon atom ($\delta = 196.68$ ppm, $^1J_{\mathrm{CRh}} = 34.9$ Hz, $^1J_{\mathrm{CP}} = 3.1$ Hz). One of the most interesting features for this compound was obtained from the IR spectrum, which displays vibrations for the carbonyl groups at similar wave numbers (1985 and 2061 cm^{-1}) to that of Bertrand's P-heterocyclic carbene (1985 and 2059 cm^{-1}).[11] Thus, from these low values, strong basic character for carbene **4** can be deduced, which explains its high reactivity.



Scheme 3. Reaction of carbene **4** with a rhodium complex and with $Ph_2C{=}C{=}O$.

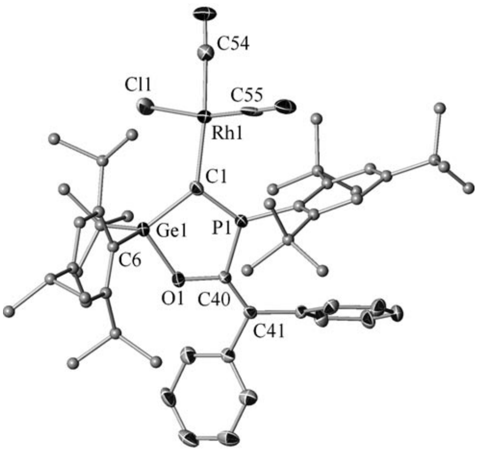


Figure 1. Structure of **6**. Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted, and Tip, *t*Bu, and Mes* groups have been simplified for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.862(4), O1–C40 1.362(6), C40–P1 1.804(6), P1–C1 1.639(6), Ge1–C1 1.978(6), Ge1–C6 1.996(6), Ge1–C2 1.988(6), P1–C21 1.798(6), C40–C41 1.351(8), C1–Rh1 2.113(6), Rh1–Cl1 2.310(8), Rh1–C54 1.869(8), Rh1–C55 1.832(12), P1-C40-O1 107.1(4); C40-O1-Ge1 121.3(4); O1-Ge1-C1 94.9(2); Ge1-C1-P1 104.4(3); C1-P1-C40 111.9(3); Ge1-C1-Rh1 134.1(3); P1-C1-Rh1 120.4(3).

Structural analysis (Figure 1) of rhodium complex **6** shows a germanium carbon distance (Ge1−C1 1.978(6) Å) corresponding to a standard single bond,[14] illustrating the lack of electronic stabilization by the germanium atom. By contrast, the short phosphorus carbon distance (P1−C1 1.639(6) Å) is characteristic of a standard P=C double bond.[16] This situation can be best described by form **4B** in Scheme 3. The sum of angles around the phosphorus atom ($\Sigma = 360°$) and the P1−C21 bond situated in the nearly planar five-membered ring Ge1-C1-P1-C40-O1 support this interpretation. The very short P1−C1 distance observed in **6** is also in good agreement with calculations that predicted a P−C bond length of 1.63 Å for the closely related phosphagermacarbene **2**.[12a]

From these special geometrical characteristics, we could expect high reactivity of this formal P=C double bond: this is the case for the addition of one equivalent of $Ph_2C{=}C{=}O$ to the carbene **4** to afford the new allenic derivative **7**[13] (Scheme 3 and Figure 2). The first step was probably a Wittig-type reaction, leading to transient bicyclic compound **8**, followed by rearrangement. The same result was obtained by addition of two equivalents of diphenylketene to the starting phosphagermaallene **1** at −80 °C. Derivative **7** was evidenced in the ^{31}P NMR spectrum by a signal at $\delta = 30.6$ ppm, convenient for a RR′R″P(O) derivative and in the ^{13}C NMR spectrum by a characteristic low-field shifted signal for the sp carbon atom of the allenic unit ($\delta = 207.77$ ppm, $^2J_{\mathrm{PC}} = 1.0$ Hz). The structure of **7** was unambiguously proved by X-ray analysis. The allenic unit displays a typical bond angle of 177.9(3)° for C20-C21-C22, which is close to 180°, with short C20–C21 and C21–C22 bond lengths; as expected, the P1–C20 distance (1.832(2) Å) lies in the normal range, which is in marked contrast with the short corresponding bond in the rhodium complex **6** (1.639(6) Å).

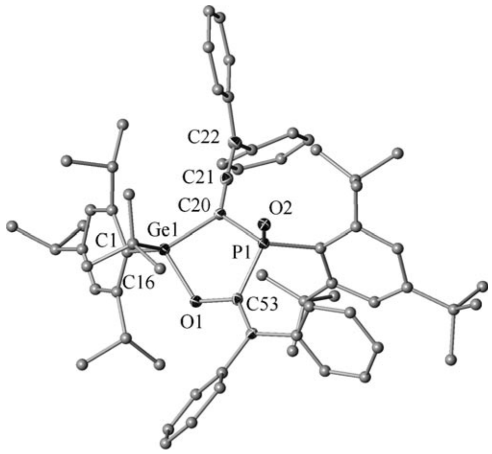
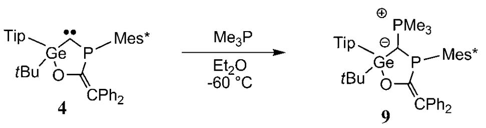


Figure 2. Structure of **7**. Ellipsoids are set at the 50% probability level. Hydrogen atoms are omitted, and Tip, *t*Bu, Ph, and Mes* groups have been simplified for clarity. Selected bond lengths [Å] and angles [°]: Ge1–O1 1.833(2), O1–C53 1.379(3), C53–P1 1.849(2), P1–C20 1.832(2), C20–Ge1 1.979(2), Ge1–C1 1.967(2), Ge1–C16 1.995(2), P1–O2 1.485(2), C20–C21 1.291(3), C21–C22 1.322(3); P1-C53-O1 114.6(2); C53-O1-Ge1 117.5(2); O1-Ge1-C20 91.1(1); Ge1-C20-P1 107.2(1); C20-P1-C53 97.5(1); C20-C21-C22 177.9(3).

The four atoms O1-C53-P1-C20 are in a plane, while the germanium atom Ge1 is slightly out from this plane; surprisingly, the two bulkiest groups, Tip and Mes*, are in a *cis* disposition.

Addition of trimethylphosphine to the carbene **4** at −60 °C led to transient complex **9** (Scheme 4). Because of its low stability (crystallization attempts failed owing to its decomposition back to the starting products), this complex could not be isolated but was evidenced in the ^{31}P NMR spectrum by the presence of two doublets at $\delta = 5.3$ ppm (PMe_3) and $\delta = 8.3$ ppm (PMes*) with a rather high $^2J_{PP}$ coupling constant (181 Hz). This reaction proves that the carbene **4** also presents an electrophilic character.



Scheme 4. Reaction of the carbene **4** with trimethylphosphine.

In conclusion, the surprising 1,3-dipole behavior of phosphagermaallene **1** towards unsaturated reagents constitutes a good route to a new type of carbenes such as phosphagermacarbene **4** (PGeHC). The latter compound, which is highly basic, can also behave as electrophile and is particularly active in Wittig-type reactions. The study of this compound and the generalization of this route to the synthesis of other PGeHCs are now under active investigation.

Experimental Section

Syntheses of **4** and **5**: To a solution of phosphagermaallene **1**[17] (1 mmol) in Et_2O (20 mL) cooled to −80 °C was slowly added one equivalent of diphenylketene dissolved in Et_2O (10 mL). The reaction was monitored by dynamic ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy between −80 °C and room temperature. The NMR spectroscopic analysis showed the nearly quantitative formation of the carbene **4** at −30 °C. Owing to the slow rotation of the Tip and Mes* groups, their signals were generally extremely broad. By cooling to −80 °C, **4** is insoluble in Et_2O and can be isolated as a white powder (0.71 g, 87 %). By warming the Et_2O solution of **4** to room temperature, the signals of carbene **4** slowly disappeared and were replaced by those of the insertion product **5**. The solvent was removed under reduced pressure and replaced by 30 mL of pentane. LiF was eliminated by filtration. After concentration, white crystals of **5** (0.64 g, 78 %) were obtained by cooling to −20 °C from pentane. **4**: ^{31}P NMR ($CDCl_3$): $\delta = 119.1$ ppm. **5**: ^{1}H NMR ($CDCl_3$): δ = GeCHP = 2.08–2.27 (m), CH_2P = 1.73–1.89 (m) and 2.28–2.48 ppm (m); ^{31}P NMR ($CDCl_3$): $\delta = -22.9$ ppm, $^2J_{PH} = 17.6$ Hz.

Synthesis of **6**, **7**, and **9**: To a solution of carbene **4**, prepared in situ as previously described or by starting from the isolated carbene, cooled to −60 °C, was added half an equivalent of $[\{Rh(CO)_2Cl\}_2]$ dissolved in Et_2O (or one equivalent of $Ph_2C{=}C{=}O$ in Et_2O, or a tenfold excess of Me_3P). The reaction mixture was warmed to room temperature and treated as above. **6**: ^{13}C NMR ($CDCl_3$): $\delta = 184.28$ (dd, $^3J_{CP} = 9.6$ Hz, $^1J_{CRh} = 74.1$ Hz, CO), 185.33 (d, $^1J_{CRh} = 56.7$ Hz, CO), 196.68 ppm (dd, $^1J_{CP} = 3.1$ Hz, $^1J_{CRh} = 34.9$ Hz, GeCP); ^{31}P NMR ($CDCl_3$): $\delta = 140.2$ ppm (d, $^2J_{PRh} = 3.8$ Hz); IR: $\tilde{\nu} = 1985.6$ and 2061.3 cm^{-1} (CO). **7**: ^{13}C NMR ($CDCl_3$): $\delta = 97.83$ (d, $^1J_{CP} = 66.8$ Hz, Ge$C{=}C{=}CPh_2$), 207.77 ppm (d, $^2J_{CP} = 1.0$ Hz, Ge-$C{=}C{=}CPh_2$); ^{31}P NMR ($CDCl_3$): $\delta = 30.6$ ppm. **9**: ^{31}P NMR ($CDCl_3$): $\delta = 5.3$ (dd, $^2J_{PP} = 181.0$ Hz, $^2J_{PH} = 11.2$ Hz, PMe_3), 8.3 ppm (d, $^2J_{PP} = 181.0$ Hz, PMes*).

CCDC 821063 (**5**), 821064 (**6**), and 821065 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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