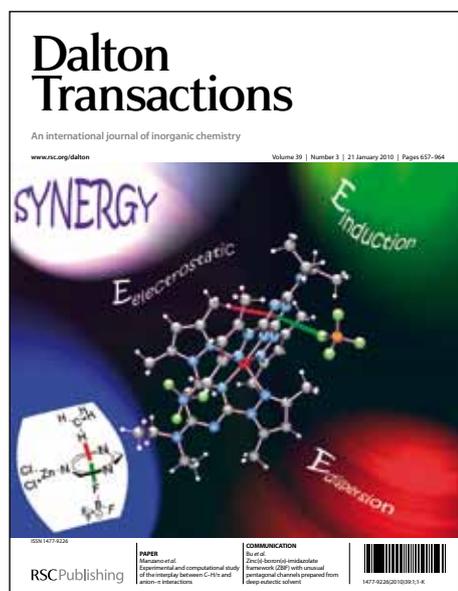


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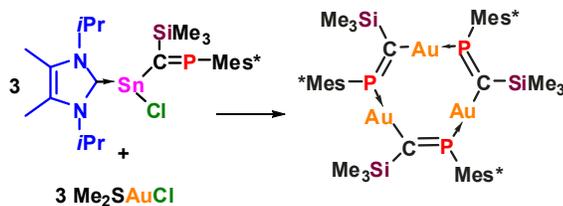
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N-Heterocyclic Carbene Stabilized Phosphaalkenyl(chloro)stannylene

Tibor-Gabor Kocsor, Gabriela Nemeş*, Nathalie Saffon, Sonia Ladeira, David Madec, Annie Castel and Jean Escudié



The first phosphaalkenyl(chloro)tin(II) compound stabilized through complexation with a N-heterocyclic carbene was fully characterized, and its reaction with Me_2SAuCl led to the formation of an unprecedented P=C-bridged trinuclear gold complex.

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T.-G. Kocsor,^{a,b} G. Nemes,^{b*} N. Saffon,^c S. Mallet-Ladeira,^c D. Madec,^a A. Castel^a and J. Escudé^a

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The new phosphaalkenyl(chloro)tin(II) compound NHC–Sn(Cl)[C(SiMe₃)=PMes*] was isolated and fully characterized including molecular structure determination by a single crystal X-ray diffraction analysis. Its reaction with Me₂SAuCl led to the formation of an unprecedented P=C-bridged trinuclear gold complex [AuC(SiMe₃)=PMes*]₃ through the transfer of the phosphaalkenyl substituent to the gold atom.

The use of electron-donating N-heterocyclic carbenes (NHC) as stabilizing ligand for reactive main group species has attracted growing interest in the last decade.¹ Number of fascinating and unusual group 14-based compounds have been reported as NHC complexes of low-valent, low-oxidation state or charged derivatives.² In this context, we synthesized and structurally characterized hypermetallyl- and phosphaalkenylmetallylenes: NHC–E[M₁₄(SiMe₃)₃]₂³ and NHC–E[(C(Cl)=PMes*)]₂⁴ (E = Ge, Sn). In the tin series, the reported examples remain scarce in comparison with the silicon and germanium analogues. Some years ago, carbene–tin complexes NHC–SnCl₂ and NHC–SnAr₂ (Ar = 2,4,6-*i*Pr₃C₆H₂; NHC = (MeCN*i*Pr)₂C:) were prepared and structurally characterized.⁵ A zwitterionic carbene–stannylene adduct was obtained by cleavage of a dibenzotetraazafulvalene by a diaza–stannylene.⁶ Since then, various NHC bearing sterically demanding groups on nitrogen atoms such as Dip (2,6-

*i*Pr₂C₆H₃)^{2d} and Mes (2,4,6-Me₃C₆H₂)⁷ have been used. Recently, two examples of unstable entities stabilized by coordination to NHC have been isolated: the tin(II)dihydride in the form of the carbene-tungsten bis-adduct NHC–SnH₂W(CO)₅⁸ and the amidochloride-carbene adduct NHC–Sn(Cl)NHDip (NHC = (HCNDip)₂C).⁹ In all cases, the carbene coordination is one of the key factors to obtain divalent species in their monomeric state. With this in mind, we envisioned to prepare N-heterocyclic carbene stabilized phosphaalkenyl(chloro)stannylene: NHC–Sn(Cl)[C(SiMe₃)=PMes*] bearing both trimethylsilyl and chloride moieties in order to gain access to a tin(II)phosphaallene Sn=C=P by elimination of the trimethylchlorosilane. Moreover, based on the ability of phosphaalkenyl moieties to give various types of coordination reactions with transition-metals,¹⁰ we investigated the ability of this new tin(II) compound to coordinate a gold complex.

We first synthesized the phosphaalkenyl(chloro)stannylene using the method described for the diphosphaalkenyl tin(II) compound.^{4b} The addition of NHC–SnCl₂ **1** in 1:1 equivalent ratio to a solution of Mes*P=C(Li)SiMe₃ (obtained by addition of *t*-BuLi to Mes*P=C(Cl)SiMe₃)¹¹ in THF at low temperature afforded the product **2** (Scheme 1). The detection of a single signal in the ³¹P NMR spectra at 344.9 ppm (²J_{P-Sn} = 298.9 Hz) indicates the formation of only one stereoisomer, that could be assigned to the *E* isomer for steric reasons. By contrast, when using two equivalents of the lithium derivative, the expected homoleptic stannylene NHC–Sn[C(SiMe₃)=PMes*]₂ was not obtained.

Compound **2** was isolated as an air- and moisture-sensitive yellow powder in 70% yield. **2** is moderately soluble in benzene and toluene, but is highly soluble in THF in which it remains stable under heating for several hours up to 50 °C. However, a higher heating temperature causes a partial decomposition of complex **2** without elimination of Me₃SiCl. Compound **2** could be fully characterized by ¹H, ¹³C, ²⁹Si, ³¹P, ¹¹⁹Sn NMR spectroscopy in solution and the structure in solid state was established by X-ray

^a Université de Toulouse, UPS, CNRS, LHFA, UMR 5069, 118 Route de Narbonne, F-31062 Toulouse cedex 09, France

^b Facultatea de Chimie și Inginerie Chimică, Universitatea Babeș-Bolyai, Str. M. Kogălniceanu, Nr: 1, RO-400084, Cluj-Napoca, Romania.

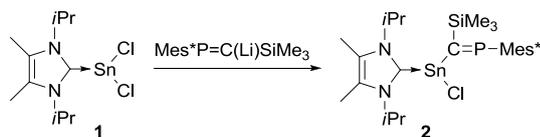
E-mail :sgabi@chem.ubbcluj.ro

^c Université de Toulouse, UPS, Service Commun Rayons X, ICT-FR2599, 118 Route de Narbonne, F-31062 Toulouse cedex 09, France

† Electronic supplementary information (ESI) available: Synthesis and characterization data of new compounds and crystallographic data. CCDC-973089 for **2** and CCDC-973090 for **3**. For ESI and crystallographic data in CIF see DOI: 10.1039/c000000x/

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diffraction studies on single crystals obtained from toluene at low temperature (Figure 1).



Scheme 1 Synthesis of phosphalkenyl(chloro)stannylenes NHC–Sn(Cl)[C(SiMe₃)=PMes*]

The ¹H NMR spectrum exhibits a broad signal belonging to the four CH₃ of the *i*Pr groups and a well-resolved septet corresponding to the CH moiety reflecting some steric hindrance in this chlorostannylenes. In the ¹³C NMR spectrum, the carbenic carbon signal is upfield-shifted (178.6 ppm) in comparison to that of the free carbene¹² (206 ppm) in agreement with a carbene coordination to group 14 element.¹³ Due to the presence of the chlorine atom, the ¹¹⁹Sn NMR spectrum of the phosphalkenyl(chloro)stannylenes **2** displays a signal at 52.2 ppm lowfield-shifted by comparison with that of its analogue containing two P=C units (-130.8 ppm).^{4b} In the ²⁹Si NMR spectrum a signal was observed at -9.3 ppm with a ²J_{Si-P} coupling constant of 20.9 Hz.

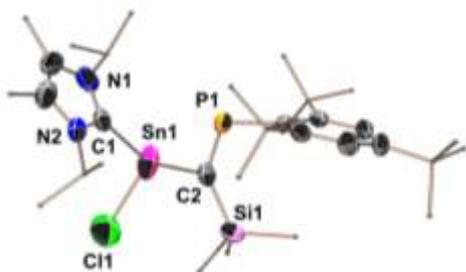
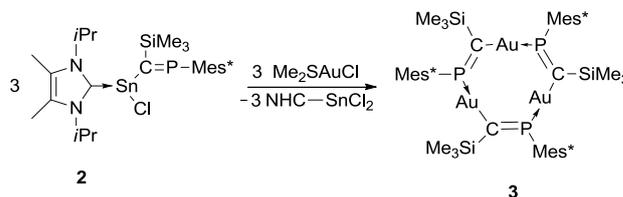


Fig. 1 Molecular structure of compound **2** in the solid state (50 % probability level for the thermal ellipsoids). The asymmetric unit contains two independent molecules; only one is shown here. For clarity, hydrogen atoms are omitted and methyl/isopropyl/*t*-Bu groups are simplified. Selected bond distances [Å] and bond angles [deg]: Sn1–C1 2.289(7), Sn1–C2 2.247(7), Sn1–Cl1 2.431(3), P1–C2 1.650(8), Si1–C2 1.880(8), C1–Sn1–C2 98.8(3), C1–Sn1–Cl1 95.4(2), C2–Sn1–Cl1 101.4(2), Sn1–C2–P1 103.8(4), Sn1–C2–Si1 117.1(3), P1–C2–Si1 136.6(4)

The X-ray structure analysis confirms the *E* configuration of the P=C double bond and reveals a three-coordinate tin center with a flattened pyramidal geometry (sum of the bond angles of 302.19°) (Figure 1). The Sn–C_{carbene} distance (2.289(7) Å) is very similar to the one found in NHC–SnCl₂ (2.290(5) Å)^{5a} (NHC = (MeCN*i*Pr)₂C:) and slightly shorter than those of the previously reported homoleptic stannylenes^{4b} (2.316(2) Å) and amido(chloro)stannylenes-carbene adduct NHC–Sn(Cl)NHDip⁹ (2.3220(19) Å) (NHC = (HCNDip)₂C:). The Sn–Cl bond length (2.431(3) Å) is close to the average of Sn–Cl distance (2.445 Å) in NHC stabilized chlorostannylenes^{5a, 7}

Due to both the lone pair of electrons on the phosphorous atom and the unsaturated P=C bond, **2** appears as a promising building block in organometallic and coordination chemistry. Preliminary study of its reactivity towards a gold complex was performed in order to evaluate its behavior as ligand for transition metal

complexes. The reaction of **2** with Me₂SAuCl in equimolar amount, performed at low temperature in toluene, led to air-stable yellow crystals after successive crystallization processes. The ³¹P NMR spectrum shows a singlet at 249.5 ppm without coupling constant with the tin atom. The low-field chemical shift indicates that the P=C double bond is still present¹⁴ and the ¹H NMR spectrum reveals a very symmetrical molecule with the complete absence of the carbene moiety. The single crystal X-ray structure analysis showed the unexpected formation of the phosphalkenyl-bridged trinuclear gold complex **3** (Scheme 2).



Scheme 2 Synthesis of the P=C-bridged trinuclear gold complex **3**

Trimer **3** contains a nearly planar nine-membered ring with a mean deviation to this plane of 0.0126 Å (maximum deviation for Au2 (0.0282 Å) and minimum for C1 (0.0005 Å)) (Figure 2). Mes* groups are orthogonal to this plane probably to minimize the steric congestion. The geometry around the gold atom is almost linear with the C–Au–P bond angles ranging from 174.5(2) to 177.8(2)°. The Au–P bond distances (Au1–P1 2.282(2), Au2–P2 2.291(2) and Au3–P3 2.294(2) Å) are comparable to those of the dinuclear complex {Au[*i*PrMe₂Si]₂C=P]₂N} (2.3051(8) and 2.2971(8) Å)¹⁵ in agreement with the coordination of Au(I).

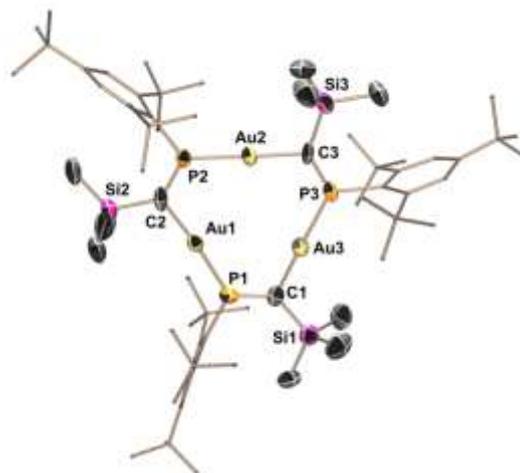


Fig. 2 Molecular structure of compound **3** in the solid state (50% probability level for the thermal ellipsoids). For clarity, hydrogen atoms and the co-crystallized solvent molecules (benzene) are omitted and Mes* groups are simplified. Selected bond distances [Å] and bond angles [deg]: C2–Au1 2.037(6), C3–Au2 2.016(8), C1–Au3 2.012(9), C1–P1 1.690(8), C2–P2 1.609(8), C3–P3 1.655(1), Au1–P2 2.282(2), Au2–P2 2.291(2), Au3–P3 2.294(2), C1–Si1 1.856(7), C2–Si2 1.912(9), C3–Si3 1.892(9), C2–Au1–P1 177.8(2), C3–Au2–P2 177.6(2), C1–Au3–P3 174.5(2), C1–P1–Au1 120.4(3), C2–P2–Au2 122.8(3), C3–P3–Au3 121.8(3), Au1–C2–P2 117.5(4), Au2–C3–P3 114.4(5), Au3–C1–P1 114.9(3)

The formation of **3** was also supported by NMR data. The ^{31}P NMR resonance (249.5 ppm) is in agreement with the values reported for similar systems. For example, in the case of phosphasilapropene gold complexes,¹⁶ the ^{31}P NMR spectra display signals in the range of 253 to 260 ppm for the phosphorous atom of the P=C bond coordinated to the gold atom. In the ^{29}Si NMR spectrum, the presence of a doublet of doublet at -8.9 ppm ($^2J_{\text{Si-P}} = 22.8$ Hz, $^3J_{\text{Si-P}} = 8.3$ Hz) with two different coupling constants with the phosphorous atoms confirmed that the P=C groups are connected. Complex **3** could also be obtained by the direct reaction between the organolithium derivative $\text{Mes}^*\text{P}=\text{C}(\text{Li})\text{SiMe}_3$ and Me_2SAuCl ; nevertheless, as often reported in the literature,¹⁷ the use of organolithium compound as transmetallating reagent lowered the yield in **3** (5%) and the main products were the *E* and *Z* form of the hydrolyzed product, $\text{Mes}^*\text{P}=\text{C}(\text{H})\text{SiMe}_3$.

The formation of **3** seems to result from the transfer of the phosphalkenyl substituent to the gold center. The use of organotin(IV) compounds as aryl transfer reagents to various transition-metals (platinum, palladium and gold) constitutes an useful route for the preparation of organo-transition metal complexes,¹⁷⁻¹⁸ but to the best of our knowledge, there is only one example of such transmetallation reaction with tin(II) compounds: the formation of the copper tetramer $[(\text{Me}_3\text{Si})_2\text{N}]_4\text{Cu}_4$ by reaction between the acyclic stannylene $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{Sn}$ and the copper(I) chloride.¹⁹ Such transfer was more often observed in the germylene series in the reaction of bis-germavinylidene $[(\text{Me}_3\text{SiN}=\text{PPh}_2)_2\text{C}=\text{Ge}\rightarrow\text{Ge}=\text{C}(\text{PPh}_2=\text{NSiMe}_3)_2]$ with a molybdenum carbonyl complex²⁰ and recently by our group²¹ in the reaction of a bis(amidinato)germylene with a rhodium complex. The phosphalkenyl groups such as $\text{Mes}^*\text{P}=\text{C}$ are also known to coordinate to gold(I) complexes^{16,22} but no similar trimeric structure containing the C–Au–P fragment was reported until now. In the case of $[\text{Au}_2(\text{CC-}t\text{-Bu})\{\mu_3\text{-(MeO)}_2\text{PCHP(OMe)}_2\}]_n$ ($n = 3$),²³ the formation of a trimer was supposed but the structure was not unambiguously determined by X-ray diffraction studies.

In summary, the first phosphalkenyl(chloro)tin(II) compound stabilized by intermolecular coordination of a N-heterocyclic carbene was isolated and fully characterized including molecular structure determination by a single crystal X-ray diffraction analysis. Its reactivity towards a gold complex mainly showed the transfer of the phosphalkenyl substituent to the gold atom leading to the formation of an unprecedented P=C-bridged trinuclear gold complex. The reactivity study of **3** with various transition-metals is currently under progress.

Acknowledgments

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Notes and references

† Crystal data²⁴ for **2**: $\text{C}_{33}\text{H}_{58}\text{ClN}_2\text{PSiSn}$, $M = 696.01$, Triclinic, $P\bar{1}$, $a = 13.9436(13)$, $b = 15.6575(14)$, $c = 19.2277(18)$ Å, $\alpha = 99.241(4)$, $\beta = 105.189(4)$, $\gamma = 103.438(4)^\circ$, $V = 3829.0(6)$ Å³, $Z = 4$, 79615 reflections

collected, 12408 unique ($R_{\text{int}} = 0.0411$), R_1 (observed data) = 0.0706, wR_2 (all data) = 0.1749. **3**·**4**(C_6H_6): $\text{C}_{66}\text{H}_{114}\text{Au}_3\text{P}_3\text{Si}_3$, $4(\text{C}_6\text{H}_6)$, $M = 1988.10$, Monoclinic, Cc , $a = 20.3176(12)$, $b = 30.5474(16)$, $c = 17.6840(10)$ Å, $\beta = 122.067(2)$, $V = 9301.0(9)$ Å³, $Z = 4$, 57843 reflections collected, 16169 unique ($R_{\text{int}} = 0.0462$), R_1 (observed data) = 0.0352, wR_2 (all data) = 0.0764.

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