



Dedicated to Academician Cristian Silvestru
on the occasion of his 70th anniversary

TARGETED SYNTHESIS OF STABLE *tert*-BUTYL-SUBSTITUTED PHOSHAVINYL- AND PHOSHAVINYL(THIOXO)PHOSPHORANES AND THEIR GOLD(I) COMPLEXES

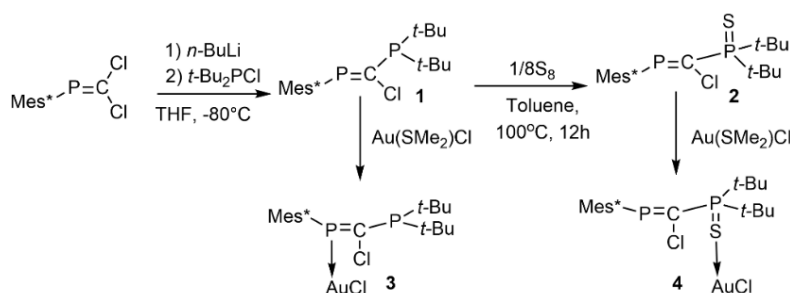
Iulia Andreea AGHION, Raluca SEPTELEAN,* Ionut-Tudor MORARU* and Gabriela NEMES^a

Faculty of Chemistry and Chemical Engineering, Department of Chemistry, “Babeş-Bolyai” University, 11 Arany Janos, 400028 Cluj-Napoca, ROUMANIA

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Two novel *tert*-butyl-substituted phosphavinylphosphoranes, *i.e.*, (Mes*)P=C(Cl)–P(*t*-Bu)₂ **1**, and its sulfonated counterpart, *i.e.*, (Mes*)P=C(Cl)–P(=S)(*t*-Bu)₂ **2**, were synthesized, and fully characterized in solution by multinuclear NMR spectroscopy and HRMS. Their reactivity with gold(I)-based fragments was explored, leading to novel complexes with the [AuCl{(Mes*)P=C(Cl)–P(*t*-Bu)₂}] **3** and [AuCl{(Mes*)P=C(Cl)–P(=S)(*t*-Bu)₂}] **4** formulae, which were isolated and characterized in solution. DFT calculations

were employed to understand the coordination preferences of the investigated P=C–P and P=C–P=S units, emphasizing that for complex **3** the isomer formed via P(*sp*³)→Au is significantly more stable than the one formed through P(*sp*²)→Au donation, while complex **4** exhibits a fluxional behaviour involving a rapid transfer of the AuCl moiety between the S and P(*sp*²) atoms.



INTRODUCTION

Phosphavinylphosphoranes represent a particular class of phosphorus-based species, featuring two different types of P(III) atoms within their P=C–P backbone. Such compounds are renowned for their enhanced electron-donor properties, given the multiple connection sites available in the molecular framework. Hence, the lone pair of electrons (LPs) on both P(*sp*²) and P(*sp*³) atoms, or even the π -component of the P=C

bond, makes them veritable building blocks for new materials with controlled properties.¹ In this regard, phosphavinylphosphoranes have been successfully employed as electron-rich ligands in coordination chemistry, their stabilizing effect on d-block metals being highlighted in various studies.^{2–10}

The stabilization of the P=C–P unit is typically achieved by grafting on the P(*sp*²) atom a bulky organic substituent, such as the 2,4,6-tri-*tert*-butylphenyl (Mes*) group,¹¹ while for the P(*sp*³) phosphorus atom, reported studies indicate that

* Corresponding authors: raluca.septelean@ubbcluj.ro; ionut.moraru@ubbcluj.ro

stabilization is successfully obtained by attaching to it various types of substituents that generally exhibit a synergy of both electronic and steric effects. So far, the reported phosphavinylphosphorane derivatives, of $(\text{Mes}^*)\text{P}=\text{C}-\text{P}(\text{R}_1)(\text{R}_2)$ type, display either identical R_1 and R_2 organic groups, (*e.g.*, phenyl, di-*iso*-propylamine),^{4,8} or a chlorine atom and a bulky organic group (*e.g.*, *t*-Bu, 2,4,6-trimethylphenyl (Mes),¹² or 2,4,6-tri-*iso*-propylphenyl (Trip)¹³ substituents).

In another approach, our research group has conducted a series of studies in which the main strategy for stabilizing phosphavinylphosphorane derivatives was to suppress the reactivity of the $\text{P}(\text{sp}^3)$ atom by incorporating a chalcogen atom in the $\text{P}=\text{C}-\text{P}$ unit. This leads to a new class of derivatives that contain the $\text{P}=\text{C}-\text{P}=\text{X}$ moiety (X = chalcogen atom), known as phosphavinyl(chalcogenoxo)phosphoranes. Given their electron-donor features, provided by the LPs on the $\text{P}(\text{sp}^2)$ and X atoms or by the $\pi(\text{P}=\text{C})$ bond, such species are regarded as potential building blocks for novel materials with tailored electronic properties. In fact, several examples of transition-metal complexes stabilized by $\text{P}=\text{C}-\text{P}=\text{X}$ units have already been reported.^{13–15}

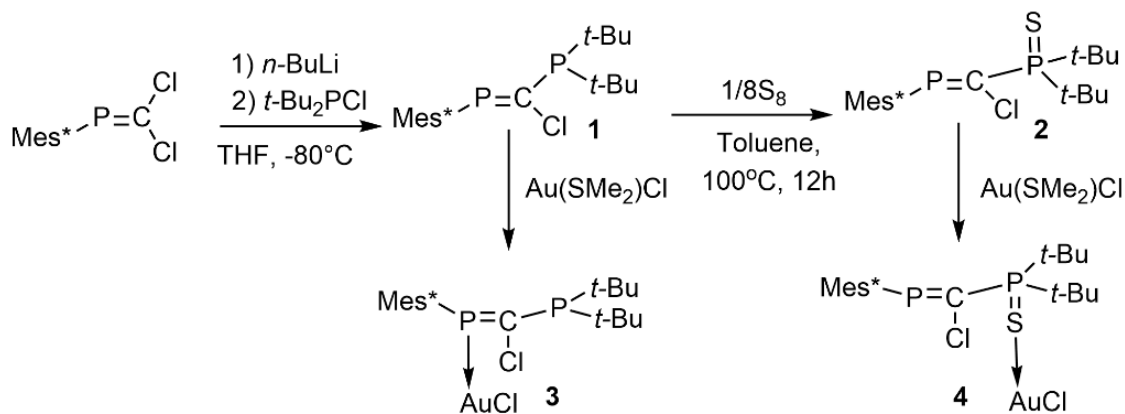
Density functional theory (DFT) studies have been conducted on systems incorporating the $\text{P}=\text{C}-\text{P}$ and the $\text{P}=\text{C}-\text{P}=\text{X}$ fragments, including their complexes with d-block metals, in order to understand their electronic structure, coordination capacity, fluxionality, and so forth.^{14–16} The same theoretical explorations inquired whether the protecting groups grafted on the P atoms can influence the stability and/or reactivity of investigated systems, addressing the role played by both steric and electronic effects. Thus, DFT studies on $\text{P}=\text{C}-\text{P}=\text{O}$ and $\text{P}=\text{C}-\text{P}=\text{S}$ backbones revealed that steric hindrance, due to bulky organic

groups attached to the $\text{P}(\text{sp}^3)$ atom, has an impact not only the stability of these derivatives, but also on their coordination preferences in reaction with different transition metal moieties.^{14,15} Another computational study emphasized that the volume of the substituents grafted on both the $\text{P}(\text{sp}^2)$ and $\text{P}(\text{sp}^3)$ atoms affects the oxidation mechanism of the $\text{P}=\text{C}-\text{P}$ unit.¹⁶ Therefore, the synthetic strategies of the targeted products can be easily adapted by simply playing with the bulkiness of the protecting groups.

The current work consists of a combined experimental/theoretical study reporting the synthesis and characterization of two novel derivatives (*i.e.*, $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(\text{t-Bu})_2$ and $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(=\text{S})(\text{t-Bu})_2$ species), and their ability to form stable gold complexes.

RESULTS AND DISCUSSION

Aiming to obtain new phosphavinylphosphoranes and phosphavinyl (chalcogenoxo)phosphoranes stable compounds, we report herein the synthesis and physicochemical characterization of derivatives $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(\text{t-Bu})_2$ **1** and $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(=\text{S})(\text{t-Bu})_2$ **2** (Mes^* = 2,4,6-tri-*tert*-butylphenyl), and their reactivity with gold-containing fragments. Derivatives **1** and **2** were synthesized by employing a well-known experimental procedure reported by our group.³ The same synthetic strategy has been successfully used to obtain similar derivatives featuring two *iso*-propyl groups on the $\text{P}(\text{sp}^3)$ atom (*i.e.*, $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(\textit{i-Pr})_2$ derivative),¹⁵ or a chlorine atom and an 2,4,6-tri-*iso*-propylphenyl group connected to the same phosphorus atom.¹³ The general synthetic scheme leading to compounds **1** and **2**, as well as their gold complexes **3** and **4**, respectively, is illustrated in Scheme 1.



Scheme 1.

Derivative **1** was obtained by the addition, at low temperature, of an equivalent of bis-*tert*-butylchlorophosphine to a solution of a phosphalkenyllithium derivative, (Mes*)P=C(Li)–Cl (Scheme 1). Phosphavinylphosphorane **1**, separated from the reaction mixture by recrystallisation in hexane, was obtained as a brown powder and completely characterized in solution by multinuclear NMR spectroscopy and HRMS. In the ^{31}P NMR spectrum two signals were observed at 316.6 (doublet) ppm for the phosphorus atom involved in the P=C unit and 52.8 (doublet of multiplets) ppm for the second phosphorus atom, with a $^2J_{\text{P,P}}$ coupling constant of 323.1 Hz, in the expected ranges for similar compounds.¹⁵ In the ^{13}C NMR spectrum, the signals for all the carbon atoms involved in structure of **1** were identified, noteworthy that the sp^2 carbon atom of the P=C–P unit gives a resonance signal at 170.7 ppm, as a doublet of doublets, with $^1J_{\text{P,C}}$ coupling constants of 72.4 Hz and 79.6 Hz respectively. All the resonance signals from the ^1H and ^{13}C NMR were assigned after bidimensional experiments and are presented in experimental part.

The oxidation of derivative **1** with sulfur (using 100% excess) in toluene at 100°C resulted into a novel phosphavinyl(chalcogenoxo)phosphorane compound, Mes*P=C(Cl)–P(=S)(*t*-Bu)₂ **2** (Scheme 1). The reaction was monitored through ^{31}P NMR spectroscopy. After removing the excess of sulfur, and following its precipitation in hexane, **2** was separated as a yellow powder. This compound was also completely characterized in solution, through multinuclear NMR spectroscopy and mass spectrometry. The ^{31}P NMR spectrum reveals two doublet signals, at 82.4 (multiplet) and 343.6 (doublet) ppm, with a $^2J_{\text{P,P}}$ coupling constant of 81.4 Hz. The ^1H and ^{13}C NMR spectra show the specific resonance signals of all the hydrogen and carbon atoms at the expected chemical shifts. In fact, their complete assignation was possible after performing 2D NMR experiments. For instance, the signal corresponding to the sp^2 carbon atom of the P=C–P moiety appears at 159.3 ppm as a doublet of doublets ($^1J_{\text{P,C}} = 85.7$ and $^1J_{\text{P,C}} = 32.1$ Hz). All the NMR data are presented in the experimental part.

In order to understand whether the bulky *t*-Bu organic groups grafted on the P(sp^3) atom influence by steric hinderance and/or electronic effects the

coordination preferences of the –P=C–P< or –P=C–P=S moieties, derivatives **1** and **2** were subsequently reacted with Au(SMe₂)Cl in toluene. The reactions were monitored by ^{31}P NMR. The spectra recorded on the crude reaction mixture of **1** with Au(SMe₂)Cl suggest the near-quantitative formation of complex **3** (Scheme 1), while for the reaction of **2** with Au(SMe₂)Cl the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra reveal rather a mixture between the reactants (signals from derivative **1** at 82.4 ppm and 343.6 ppm) and the newly obtained compound **4**, which is most probably a gold complex (Scheme 1). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** reveals a signal at 78.5 ppm (specific for a P atom involved in a P=C fragment), and another one at 328.2 ppm, which was assigned to the P(sp^3) atom of the P=C–P=S unit. [AuCl{(Mes*)P=C(Cl)–P(*t*-Bu)₂}] complex **3** was completely characterized in solution by multinuclear NMR spectroscopy, and by HRMS spectrometry. The signal of the sp^2 carbon atom shows a dramatic upfield shift (153.7 ppm, dd, $^1J_{\text{P,C}} = 75.8$ Hz, $^1J_{\text{P,C}} = 16.2$ Hz) when compared to the one attributed to the same carbon atom from the starting material **1** (170.7 ppm, dd, $^1J_{\text{P,C}} = 79.6$ Hz, $^1J_{\text{P,C}} = 72.4$ Hz). All the NMR data are presented in detail in the experimental part.

DFT calculations were performed to gain insights into the coordination ability of the P=C–P and P=C–P=S units of **1** and **2**, and to understand the structural and electronic features of gold complexes **3** and **4**. For both **3** and **4**, two different isomers are assessed by theoretical means, in each case. For compound **3**, the investigated complexes involve either the P(sp^3)→Au or the P(sp^2)→Au coordinate bond (Fig. 1). Based on the DFT data, the equilibrium P(sp^2)–Au and P(sp^3)–Au bond distances are of 2.229 and 2.261 Å, values that are slightly larger than the *ca.* 1.86 Å reference length obtained by summing the covalent radii of P and Au atoms.¹⁷ Yet, given that the sum of van der Waals radii for the same atoms is *ca.* 3.56 Å,¹⁸ the coordinate bonds within both model complexes are expected to be significantly strong. In terms of relative stability, the complex involving the P(sp^3)→Au donation is with *ca.* 11.6 kcal mol⁻¹ more stable than the one containing the P(sp^2)→Au bond, meaning that only the former is expected to be obtained during the reaction of **1** with Au(SMe₂)Cl.

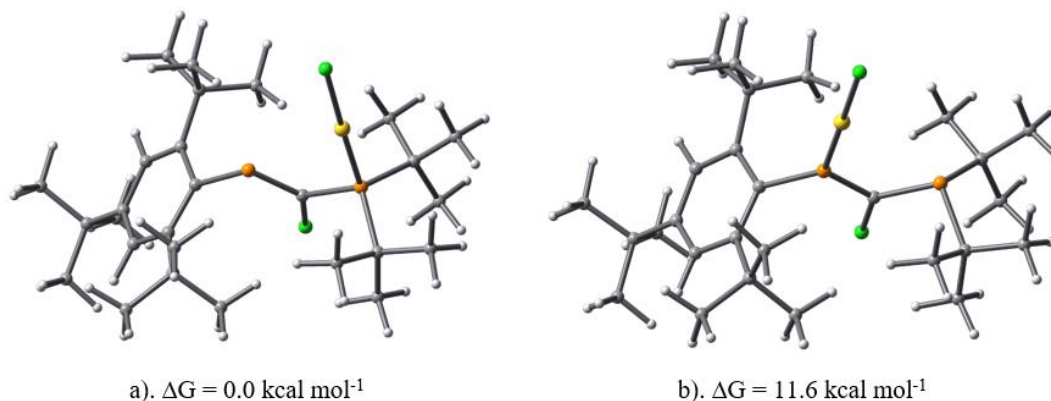


Fig. 1 – Equilibrium geometries of the two model complexes investigated in case of **3**, along with their calculated relative energies; (a) the isomer involving the $P(sp^3)\rightarrow Au$ coordinate bond; (b) the isomer formed via $P(sp^2)\rightarrow Au$ coordinate bond.

Two different isomers are also investigated for complex **4**. The first one involves the $S\rightarrow Au$

donation, while the other structure exhibits a $P(sp^2)\rightarrow Au$ coordinate bond (Fig. 2).

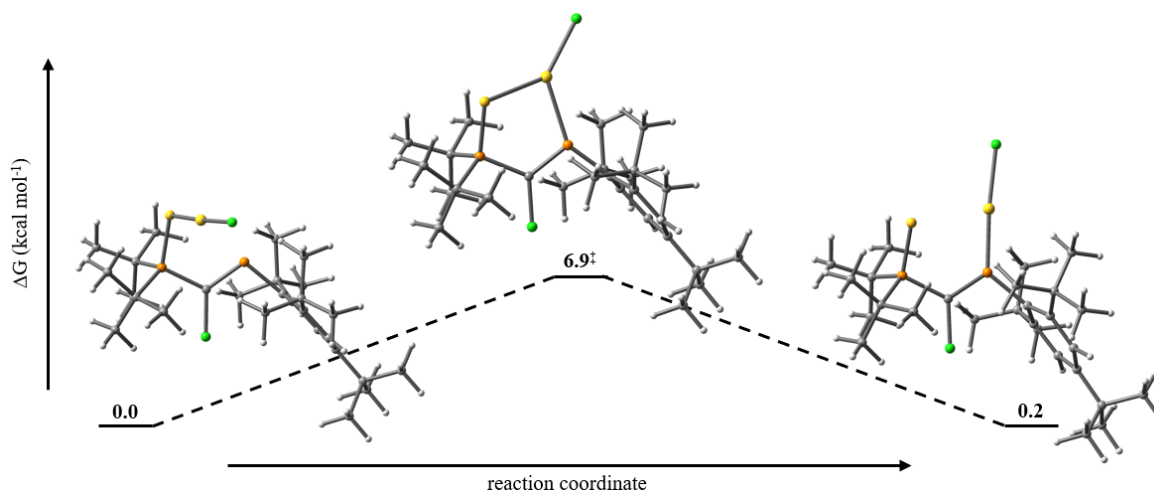


Fig. 2 – Mechanism involving the rapid transfer of the $AuCl$ moiety between the S and $P(sp^2)$ atoms of complex **4**; (left) the complex formed via $S\rightarrow Au$ coordinate bond; (right) the complex obtained through $P(sp^2)\rightarrow Au$ donation; (middle) the TS structure connecting the two isomer geometries.

The computed equilibrium lengths of $S-Au$ and $P(sp^2)-Au$ bonds are 2.261 Å and 2.219 Å, respectively. These bond distances are much closer to lengths obtained by summing the covalent radii of the constituent atoms (*i.e.*, 1.84 Å for $S-Au$ and 1.86 Å for $P-Au$)¹⁷ than to the lengths obtained by summing the van der Waals radii of the same atoms (*i.e.*, 3.55 Å for $S-Au$ and 3.56 Å for $P-Au$),¹⁸ thus highlighting the increased strength of the coordinate bonds formed. Opposite to the case of complex **3**, for **4** the calculated energy difference between the two possible isomers is merely 0.2 kcal mol⁻¹. This suggests that complex **4** exhibits fluxional behavior, which involves a rapid transfer of the $AuCl$ fragment from the S to the $P(sp^2)$ atom. To assess the kinetic accessibility of this structural rearrangement, the transition state (TS) geometry connecting the two isomers is evaluated (Fig. 2).

The TS structure depicts the $P=C-P=S$ unit coordinated to the $AuCl$ moiety in a bridging fashion, with the computed $S-Au$ (2.469) Å and $P(sp^2)-Au$ (2.414 Å) distances being roughly equal. The computed barrier height of <7 kcal mol⁻¹ is highly accessible, thus supporting the fluxional behavior of complex **4** in solution, even at considerably low temperatures.

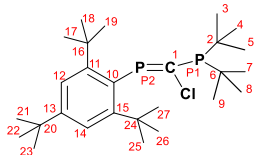
EXPRIMENTAL

The synthesis of all derivatives was performed under inert atmosphere of argon, using Schlenk techniques. The solvents (toluene and hexane) were used after purification through an automatic solvent purification system MBRAUN SBS-800, while the used THF was freshly distilled over $Na/benzophenone$.

Derivatives di-*tert*-butylchlorophosphine and chloro(dimethylsulfide) gold(I) were purchased from Sigma-Aldrich and were used without other purification. Derivative Mes*P=CCl₂ was synthesized according to a reported procedure.¹⁹ The NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at the following frequencies: 400.13 MHz for ¹H, 100.62 MHz for ¹³C, 162.00 MHz for ³¹P, and on a Bruker Avance 600 MHz spectrometer: ¹H (600.13 MHz), ¹³C (150.92 MHz), ³¹P (242.97 MHz) with TMS and H₃PO₄ as references for ¹H, ¹³C and ³¹P. All the spectra were recorded in C₆D₆ and calibrated using the residual peak of the deuterated solvent. High resolution mass spectra were recorded on a LTQ Orbitrap XL mass spectrometer (ThermoScientific) using electrospray ionization.

Synthesis of Mes*P=C(Cl)–P(*t*-Bu)₂ (1)

A solution of *n*-BuLi in hexane (2.36 M, 3.97 mL, 9.37 mmol) was added dropwise to a solution of Mes*P=CCl₂ (3.27 g, 9.37 mmol) in THF, at –80°C. Over the reaction mixture, after 1 hour of stirring at –80°C, (*t*-Bu)₂PCL (1.73 mL, 9.1 mmol) was added and the resulting dark brown solution was allowed to warm to room temperature overnight. The volatiles were evaporated under reduced pressure and the inorganic salts were removed by filtration in hexane. Derivative **1** was obtained as a brown powder from hexane, at low temperature (3.71 g, 87% yield).



¹H NMR (C₆D₆, 400.13 MHz): δ (ppm) = 1.32, s, 9H, CH₃-*para-tert*-butyl; 1.36, d, ³J_{P,H} = 12.1 Hz, 18H, CH₃-*tert*-butyl; 1.59, s, 18H, CH₃-*ortho-tert*-butyl; 7.57, s, 2H, H_{arom}-Mes*.

¹³C NMR (C₆D₆, 100.62 MHz): δ (ppm) = 30.9, d, ²J_{P,C} = 14.7 Hz, C₃-C₅, C₇-C₉; 31.5, C₂₁-C₂₃; 33.5, d, ⁴J_{P,C} = 7.3 Hz, C₁₇-C₁₉, C₂₅-C₂₇; 35.1, C₂₀; 35.4, dd, ¹J_{P,C} = 25.5 Hz, ³J_{P,C} = 16.4 Hz, C₂, C₆; 38.2, C₁₆, C₂₄; 122.6, C₁₂, C₁₄; 137.2, dd, ¹J_{P,C} = 70.3 Hz, ³J_{P,C} = 34.6 Hz, C₁₀; 150.8, C₁₃; 153.8, d, ²J_{P,C} = 2.4 Hz, C₁₁, C₁₅; 170.7, dd, ¹J_{P,C} = 79.6 Hz, ¹J_{P,C} = 72.4 Hz, C₁.

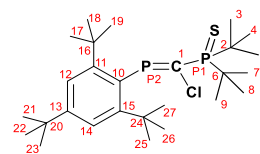
³¹P{¹H} NMR (C₆D₆, 162.00 MHz): δ (ppm) = 52.8, d, ²J_{P,P} = 323.1 Hz, P₁; 311.6, d, ²J_{P,P} = 323.1 Hz, P₂.

³¹P NMR (C₆D₆, 162.00 MHz): δ (ppm) = 52.8, dm, P₁; 311.6, d, ²J_{P,P} = 323.1 Hz, P₂.

HRMS (ESI⁺): C₂₇H₄₇ClP₂ [M+H]⁺ found 469.29382 [M+H]⁺ calcd 469.29143

Synthesis of Mes*P=C(Cl)–P(=S)(*t*-Bu)₂ (2)

A solution of Mes*P=C(Cl)–P(*t*-Bu)₂ **1** (0.68 g, 1.15 mmol) and sulfur (0.1 g, 3.12 mmol) in 15 mL toluene was heated at 100 °C for 2 hours. The solvent was removed under vacuum and the excess sulfur was filtered off from hexane, affording separation of derivative **2** as a yellow powder (0.67g, 92%yield).



¹H NMR (C₆D₆, 400.13 MHz): δ (ppm) = 1.31, s, 9H, CH₃-*para-tert*-butyl; 1.43, d, ³J_{P,H} = 15.6 Hz, 18H, CH₃-*tert*-butyl; 1.50, s, 18H, CH₃-*ortho-tert*-butyl; 7.55, s, 2H, H_{arom}-Mes*.

¹³C NMR (C₆D₆, 100.62 MHz): δ (ppm) = 28.6, C₁₇-C₁₉, C₂₅-C₂₇; 31.4, C₂₁-C₂₃; 33.6, d, ²J_{P,C} = 7.8 Hz, C₃-C₅, C₇-C₉; 35.0, C₂₀; 38.2, C₁₆, C₂₄; 40.6, d, ¹J_{P,C} = 40.5 Hz, C₂, C₆; 122.9, C₁₂, C₁₄; 136.8, dd, ¹J_{P,C} = 70.3 Hz, ³J_{P,C} = 11.3 Hz, C₁₀; 150.8, C₁₃; 154.1, d, ²J_{P,C} = 3.2 Hz, C₁₁, C₁₅; 159.3, dd, ¹J_{P,C} = 85.7 Hz, ¹J_{P,C} = 32.1 Hz, C₁.

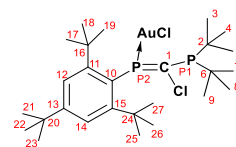
³¹P{¹H} NMR (C₆D₆, 162.00 MHz): δ (ppm) = 82.4, d, ²J_{P,P} = 81.4 Hz, P₁; 343.6, d, ²J_{P,P} = 81.4 Hz, P₂.

³¹P NMR (C₆D₆, 162.00 MHz): δ (ppm) = 82.4, m, P₁; 343.6, d, ²J_{P,P} = 81.4 Hz, P₂.

HRMS (ESI⁺): C₂₇H₄₇ClP₂S [M+H]⁺ found 501.26437 [M+H]⁺ calcd 501.26350

Synthesis of [AuCl{Mes*P=C(Cl)–P(*t*-Bu)₂}] (3)

To a solution of Mes*P=C(Cl)–P(*t*-Bu)₂ **1** (0.42 g, 0.90 mmol) in toluene (8 mL) Au(SMe₂)Cl (0.26 g, 0.90 mmol) was added at room temperature. After 30 minutes of stirring, the volatiles were removed under low pressure, and the solid was washed with pentane when derivative **3** was obtained as a pale-yellow powder (0.57g, 90% yield).



¹H NMR (C₆D₆, 600.13 MHz): δ (ppm) = 1.16, d, ³J_{P,H} = 16.0 Hz, 18H, CH₃-*tert*-butyl; 1.26, s, 9H, CH₃-*para-tert*-butyl; 1.42, s, 18H, CH₃-*ortho-tert*-butyl; 7.49, s, 2H, H_{arom}-Mes*.

^{13}C NMR (C_6D_6 , 150.92 MHz): δ (ppm) = 30.2, d, $^2J_{\text{P,C}} = 5.8$ Hz, C₃-C₅, C₇-C₉; 31.3, C₂₁-C₂₃; 33.5, d, $^4J_{\text{P,C}} = 6.9$ Hz, C₁₇-C₁₉, C₂₅-C₂₇; 35.1, C₂₀; 38.0, C₁₆, C₂₄; 38.6, dd, $^1J_{\text{P,C}} = 23.4$ Hz, $^3J_{\text{P,C}} = 10.4$ Hz, C₂, C₆; 123.0, C₁₂, C₁₄; 134.9, dd, $^1J_{\text{P,C}} = 73.0$ Hz, $^3J_{\text{P,C}} = 20.8$ Hz, C₁₀; 151.8, C₁₃; 153.7, dd, $^1J_{\text{P,C}} = 75.8$ Hz, $^1J_{\text{P,C}} = 16.2$ Hz, C₁; 154.1, d, $^2J_{\text{P,C}} = 2.0$ Hz, C₁₁, C₁₅.

$^{31}\text{P}\{^1\text{H}\}$ NMR (C_6D_6 , 242.97 MHz): δ (ppm) = 81.2, d, $^2J_{\text{P,P}} = 200.9$ Hz, P₁; 343.0, d, $^2J_{\text{P,P}} = 200.9$ Hz, P₂.

^{31}P NMR (C_6D_6 , 242.97 MHz): δ (ppm) = 81.2, dm, P₁; 343.0, d, $^2J_{\text{P,P}} = 200.9$ Hz, P₂.

HRMS (ESI⁺): $\text{C}_{27}\text{H}_{47}\text{AuCl}_2\text{P}_2\text{Na}$ [$\text{M}+\text{Na}$]⁺ found 723.21320 [$\text{M}+\text{Na}$]⁺ calcd 723.20878

Computational Details

All calculations were performed within the framework of the Density Functional Theory (DFT), using the *Gaussian 09* software package.²⁰ The molecular geometries of investigated systems were fully optimized in the gaseous phase without any symmetry constraints, with the optimization criteria being set to *tight*. The hybrid functional developed by Adamo and Barone, PBE0,²¹ and Alrichs's valence triple-zeta quality def2-TZVP^{22–24} basis set were employed in all DFT calculations performed herein. In the case of the gold atoms, the relativistic core electrons were replaced within all calculations by effective core potentials (ECPs),^{25,26} pseudopotentials that include the required relativistic corrections. Vibrational analyses were carried out to characterize the nature of the stationary points (*i.e.*, to confirm whether the investigated species are true minimal or transition state geometries). Frequency calculations were used to compute Gibbs free energies within the framework of the harmonic oscillator approximation for vibrational contribution (further details regarding the thermodynamic equations are available in *Ref. 27*). The integration grid used in all DFT calculations was of 99 radial shells and 950 angular points for each shell (99,950), defined as the "ultrafine" grid in *Gaussian 09*.

CONCLUSIONS

Two novel phosphavinylphosphorane derivatives, $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(t\text{-Bu})_2$ and its sulfur-oxidized analogue $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(=\text{S})(t\text{-Bu})_2$ were synthesized and completely characterized in

solution, using multinuclear NMR spectroscopy and HRMS.

Further, this research, investigated the reactivity of these compounds with gold-containing fragments, specifically $\text{Au}(\text{SMe}_2)\text{Cl}$. Derivative $\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(t\text{-Bu})_2$ **1** readily formed a stable gold complex, $[\text{AuCl}\{\text{Mes}^*\text{P}=\text{C}(\text{Cl})-\text{P}(t\text{-Bu})_2\}]$, **3**, and DFT calculations revealed a strong preference for the coordination through the $\text{P}(sp^3)$ atom. This $\text{P}(sp^3)\rightarrow\text{Au}$ bond was found to be significantly more stable (by approximately 11.6 kcal mol⁻¹) indicating selective coordination behavior for compound **1**. In contrast, the reaction of derivative **2** with $\text{Au}(\text{SMe}_2)\text{Cl}$ yielded a gold complex **4** exhibiting fluxional behavior in solution. DFT calculations for complex **4** demonstrated a very small energy difference (0.2 kcal mol⁻¹) between two possible isomers: one coordinated via the $\text{S}\rightarrow\text{Au}$ and another via the $\text{P}(sp^2)\rightarrow\text{Au}$. A low calculated activation barrier (<7 kcal mol⁻¹) for the interconversion between these isomers further supports the rapid transfer of the AuCl fragment between the S and $\text{P}(sp^2)$ atoms, even at low temperatures.

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