Cleavage of the Au−P Bond in Au-Substituted Phosphines

Rui Wei, Xin-Feng Wang and Liu Leo Liu*[a]

Dedicated to Prof. Douglas W. Stephan on the occasion of his 70th birthday

Abstract: Three protocols that involve the cleavage of the Au−P bond in Au-substituted phosphines (AuPhos) have been demonstrated, namely i) direct demetallation with a strong anionic base; ii) protonation followed by demetallation with a neutral base; iii) oxidation-triggered metal migration. Specifically, direct demetallation of (CAAC)AuPPh$_2$ (**1a**) (CAAC = cyclic (alkyl)(amino)carbene) with KP(TMS)$_2$ or LiC(N$_2$)TMS yields (CAAC)AuPTMS$_2$ (**2**) or (CAAC)AuC(N$_2$)TMS (**3**), respectively. Treatment of (NHC)AuPPh$_2$ (**1b**) (NHC = N-heterocyclic carbene) with HOTf followed by the corresponding neutral phosphine gives scarce examples of aurophosphonium salts [(NHC)AuPHAd$_2$][OTf] (**5**) and [((NHC)Au)$_2$PPh$_2$][OTf] (**6**). Oxidation of **1a** or **1b** with Se affords LAuSeP(Se)Ph$_2$ (L = CAAC, **7a**; NHC, **7b**).

Introduction

Terminal transition metal (TM)-phosphido complexes bearing a tri-coordinate phosphorus atom as an X-type ligand have attracted considerable interest due to their huge potential as either effective catalysts or reactive intermediates in phosphination reactions.[1] Numerous terminal early TM-phosphido complexes have been known. According to the hard and soft acids and bases (HSAB) concept, the mismatch of the hard early TM and the soft phosphorus center renders the metal-phosphorus bond in these complexes highly reactive with a predominantly ionic character.[2] Indeed, such metal-phosphorus bonds have been shown to readily add to unsaturated chemical bonds to construct novel organophosphorus compounds.[3] By contrast, late TMs are softer in nature, and consequently, the late TM-phosphorus bond is more covalent and shows distinct reactivity.[1c, 1d, 1g, 4] However, examples of the terminal late TM-phosphido complexes are rare. Because of relativistic effects, gold has an electronegative value of 2.54, the highest of any TM. This significantly enhances the covalency of Au−P bonds, and thus the terminal Au-phosphido complexes can be regarded as Au-substituted phosphines (AuPhos). These AuPhos were first isolated by Toste, Bergman and co-workers[5] in 2013 as well as recently by the Corrigan,[6] Bertrand and Grützmacher groups,[7] in which a Au center is supported by a singlet carbene ligand. In 2022, we systematically investigated a series of AuPhos.[8] Such compounds have proved one of the extremely electron-rich phosphorus superbases owing to the d-p lone pair repulsion. Unlike the ionic M−P bonds in TM phosphido complexes,[3] AuPhos contain a highly covalent Au−P bond and are not sensitive to alcohol, amine and water.[8] We now describe three methods that effect the cleavage of the Au−P bond, which include 1) direct demetallation with a strong anionic base; 2) protonation followed by demetallation with a neutral base; 3) oxidation-triggered metal migration.

[a] Dr. R. Wei; X.-F. Wang; Prof. Dr. L. L. Liu
Department of Chemistry and Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China
E-mail: liuleoliu@sustech.edu.cn

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Results and Discussion

A handful of reports documented the feasible insertion of a Au−E (E = H,[9] F,[10] N,[5] B,[11] Si,[12] Al[13]) bond with unsaturated chemical bonds (e.g. C≡C, N=N, C=O). These precedents prompt the question: does the Au−P bond in AuPhos undergo similar insertion? To begin, we looked at the reaction of **1a** (Figure 1a) with phenylacetylene, styrene, benzophenone or carbon dioxide. Yet, no reaction was identified in all cases. These also stand in stark contrast to the fact that the Cu−P bond in copper phosphido complexes readily adds to the polarized multiple bonds.[14] As aforesaid, the Au−P bond in AuPhos is highly covalent. Indeed, even in the presence of protic substrates (e.g. EtOH, H$_2$O), this Au−P bond is robust.[8] It is noteworthy that the intermediacy of [Pd]−PR$_2$ was proposed in Pd-catalyzed hydrophosphination reactions, which was postulated to add to unsaturated bonds as a key step.[15] However, considering the high electronegative nature of Pd (χ = 2.2) as well, [Pd]−PR$_2$ is very unlikely to engage in such insertion reactions.

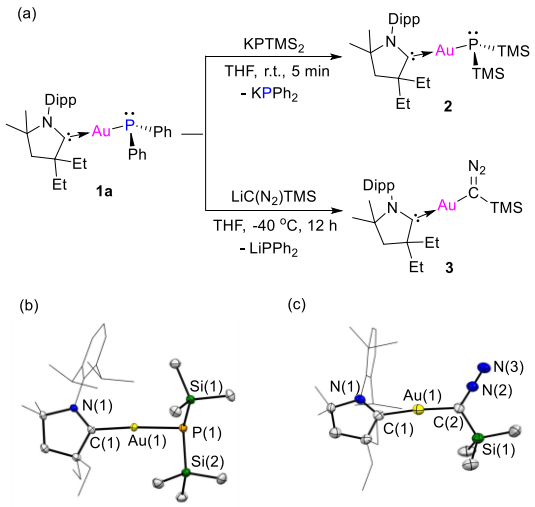
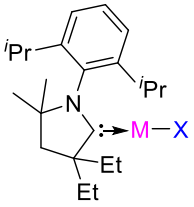


Figure 1. (a) Synthesis of **2** and **3**. (b) Solid-state structure of **2**. (c) Solid-state structure of **3**. Thermal ellipsoids are set at the 40% probability level.

We then conducted density functional theoretical (DFT) calculations (M06-2X/def2-SVP) to understand the distinction between the Au−P (Table 1, entry 1) and M−E (M = Au, Cu; E = N, P) bonding (entries 2-4). The highest covalent character of the

Au−P bond in **1a** among these four species is reflected by the smallest charge difference between Au and P (0.05 a.u.) and the largest Wiberg bond index of Au−P (0.60). Besides, quantum theory of atoms in molecules (QTAIM) analysis corroborates the covalent nature of the Au−P bond in **1a** with the smallest energy density of -0.044 a.u. at the Au-P bond critical point (BCP). As a result, heterolysis of the Au-P bond in AuPhos should be challenging.

Table 1. Natural bond orbital (NBO) and quantum theory of atoms in molecules (QTAIM) analyses on model complexes.[a]



Entry	M−X	*q* (M)[b]	*q* (N/P)[b]	WBI[c]	*H*(r)[d]
1	Au−NPh_2	0.467	-0.798	0.41	-0.003
2	Au−PPh_2	0.272	0.202	0.60	-0.044
3	Cu−PPh_2	0.610	0.056	0.43	-0.041
4	Au−$\overset{\oplus}{P}(H)Ph_2$	0.349	0.646	0.50	-0.016

a] Computations were conducted at the M06-2X/def-SVP level of theory. [b] NBO charges are given in a.u. [c] Wiberg bond index of M−X bond. [d] Energy density at the bond critical point of M−X bond.

AuPhos **1a** was found inert in the presence of ^{t}BuOK. Nonetheless, combining **1a** with the strong anionic base $KP(TMS)_2$ in THF at room temperature gave rise to the ligand exchange at Au affording **2** (^{31}P NMR: -233.1 ppm) in 41% yield (Figure 1). Crystals suitable for X-ray crystallography obtained from a pentane solution allowed the solid-state structure of **2** to be determined, confirming the formation of a disilyl substituted AuPhos **2**. Species **2** features a pyramidalized tricoordinate P(1) atom with the sum of angles of 308.4°. The Au(1)−P(1) bond length is 2.3253(5) Å. These values are close to those of $IDippAuP(TMS)_2$ (307.8°; 2.3197(6) Å) (IDipp = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene), which was synthesized by the elimination of TMSCl from a reaction of IDippAuCl and $P(TMS)_3$.[6] The utility of **1** as a $[LAu]^+$ donor via scission of the Au−P bond was further indicated by its reaction with $LiC(N_2)TMS$ at -40 °C, which smoothly produced **3** in 43% yield. The infrared spectrum of **3** displayed a characteristic infrared absorption at 1989 cm^{-1} ascribing to the CN_2 stretching vibration. X-ray diffraction revealed **3** to be a Au-substituted diazomethane. The Au(1)−C(1) distance (2.037(8) Å) compares favorably for typical Au−C single bonds (1.99 Å)[16] but is longer than that for $[(CH_2)(NDipp)]_2PC(N_2)Au(^{Me}IDipp)$ (1.945(3) Å)[17] (^{Me}IDipp = 1,3-bis(2,6-diisopropylphenyl)-4,5-dimethyl-imidazol-2-ylidene).

We reasoned that the Au−P bond polarity would be enhanced if P is protonated. Based on the theoretical data (Table 1, entries 2 and 4), the Au−P bond in the protonated cation $[LAuP(H)Ph_2]^+$ is much more polarized than that of AuPhos **1**. Experimentally, this phosphonium salt **4** can be accessible through the reaction of **1b** with HOTf (Figure 2).[8] The positive charge of the phosphonium in **4** strengthens the $[LAu]^+$ nature with the apparent contribution from the resonance structure **4'**. Indeed, stirring a THF solution of **4** and Ad_2PH in a 1:1 molar ratio at room temperature for 12 hours led to Ph_2PH and **5** (^{31}P NMR: 50.5 ppm, d, $^1J_{P-H}$ = 358.2 Hz). Compound **5** was obtained as an off-white solid in 85% yield after workup. In a similar manner, **4** reacted with **1b** in THF yielded Ph_2PH and a diaurophosphonium salt **6** (^{31}NMR: 23.8 ppm) within 5 min. The formation of **5** and **6** suggests that the Au−P bond of **4** can be easily cleaved via demetallation with a base stronger than Ph_2PH. Compound **6** represents an extremely rare example of a diaurophosphonium salt. Of note, these results consist with the proposed reaction mechanism for Pd- or Ru-catalyzed phosphination, in which a metal-substituted phosphonium was formed initially and then replaced with a secondary phosphine.[18] The direct σ-metathesis of $[M]-PR_2$ (M = Pd, Ru) with the corresponding aryl or alkyl halide is highly impossible.

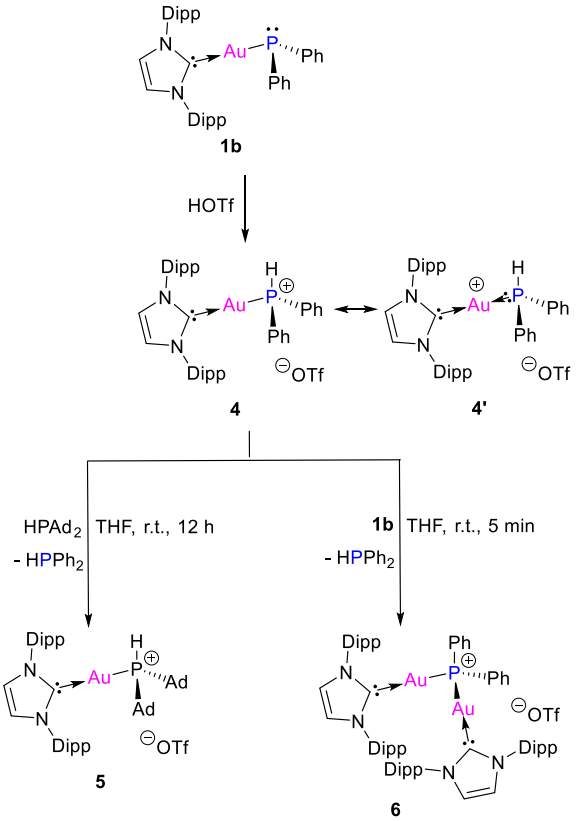


Figure 2. Synthesis of **4**-**6**.

Phosphines are well known to be oxidized with elemental chalcogen. We therefore envisioned the possibility of breaking the Au−P in an oxidative fashion (Figure 3). To this end, we treated **1a** with S_8 (1/8 equiv.) at room temperature. The reaction ended up with a complicated mixture, and no identified product was isolated. Nevertheless, when 2 equivalents of Se powders were employed, **1a** was converted into **7a** (^{31}P NMR: 21.2 ppm; ^{77}Se NMR: 100.3 ppm). The one-bond phosphorus-selenium coupling constant was observed to be 579.8 Hz. Control experiments showed that the reaction with an equal equivalent of Se gave **7a** as well along with the unchanged **1a**. Single crystals of **7a** suitable for X-ray diffraction were obtained by slow evaporation a saturated Et_2O solution at room temperature. As illustrated in

Figure 3b, two structural isomers of **7a** were observed in the solid state. Note that only a set of product resonances was seen in the NMR spectra of **7a**, indicating the P−Se bond of **7a** rotates rapidly in solution. The Au−Se bond lengths of the two isomers are similar (2.4082(6) and 2.4178(6) Å), falling into the range of the reported Au−Se bond length of LAuSeCN (2.4142(8) Å) (L = 1,3-di-tert-butylimidazol-2-ylidine). The terminal P−Se bonds (P(1)−Se(2): 2.1073(13) Å; P(2)−Se(4): 2.0963(14) Å) are shorter compared with the bridging P−Se bonds (P(1)−Se(1): 2.2131(12); P(2)−Se(3): 2.2246(14) Å). In a similar vein, the reaction of **1b** with Se yielded **7b** (^{31}P NMR: 19.5 ppm; ^{77}Se NMR: 115.4 ppm), and X-ray showed that the unit cell contains a sole **7b** molecule (Figure S18).

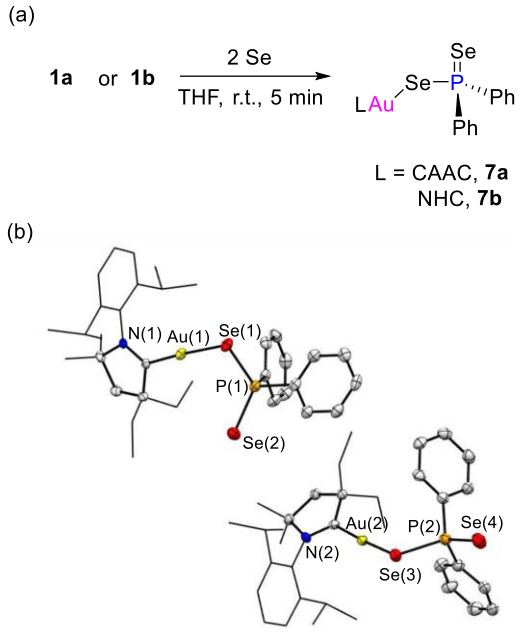


Figure 3. (a) Synthesis of **7**. (b) Solid-state structure of **7a**. Thermal ellipsoids are set at the 40% probability level.

To shed light on the possible pathway for the formation of **7b**, we conducted DFT modeling at the M06-2X/def2-SVP//M06-2X/def2-TZVP level of theory. The results indicate that the reactions involve three steps (Figure 4). Initial oxidation of **1b** gave rise to **IN1** (94.5 kcal mol^{-1}). A subsequent [LAu] migration via **TS1** (-78.5 kcal mol^{-1}) with the activation barrier of 16 kcal mol^{-1} furnishes **IN2** (-95.2 kcal mol^{-1}). Final exergonic oxidation results in **7b** with the energy release of 90.6 kcal mol^{-1}

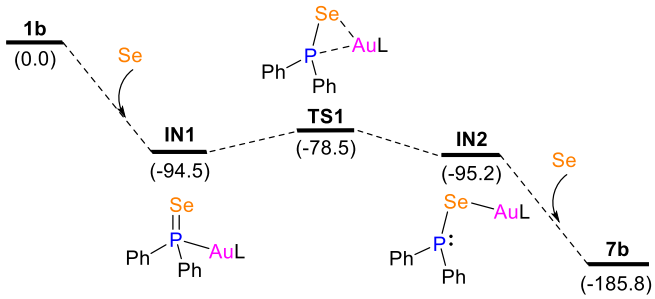


Figure 4. Free energy profile for the formation of **7b**. Energies are given in kcal mol^{-1}. L = IDipp.

Conclusions

Although the Au−P bond in AuPhos is much less reactive in comparison to M−P bonds in many TM-phosphido complexes, we have documented three methods that effect the scission of the Au−P bond, leading to a variety of Au-substituted species **2**, **3**, **5**, **6**, **7a** and **7b**. Importantly, the formation of the protonated phosphonium **4** can promote the ensuing demetallation with a neutral phosphine, which provides mechanistic insights into TM-catalyzed phosphination reactions. The utilization of AuPhos for construction of other unusual Au-containing species via the Au−P bond cleavage is under active investigation in our lab

Experimental Section

1. General Considerations

All manipulations were carried out under an atmosphere of argon using standard Schlenk line or in a N_2-filled glovebox. Solvents were dried over $LiAlH_4$ or Na metal, stored with 4Å molecular sieves before use. NMR spectra were recorded with Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) or 600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) spectrometer at 298 K. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad signal), integration, coupling constants *J* in hertz (Hz). High resolution mass spectrometry (HRMS) was performed with a Thermo Fisher Scientific Q-Exactive MS System with electrospray ionization (ESI) method. Crystal data were collected on a Bruker D8 Venture diffractometer with graphite monochromated Cu Kα (λ =1.54178). Data reduction, scaling and absorption corrections were performed using SAINT (Bruker, V8.38A, 2013). The structure was solved with the XT structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. Data were corrected for absorption effects using the empirical multiscan method (SADABS). The model was refined with the ShelXL program using Least Squares minimization. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions.
Commercial reagents were purchased from Energy Chemical, *J*&K, or TCI Chemical Co. and used as received. Compounds **1** and **4** were synthesized according to our recent work.[8]

2. Synthesis Procedure

Synthesis of 2: AuPhos **1a** (30 mg, 0.04 mmol) was dissolved in THF (1 mL) and added dropwise to a solution of $KP(TMS)_2$ (8.6 mg, 0.04 mmol) in THF (1 mL). After stirring for 5 min, the solvent was removed under vacuum. The residue was extracted with 1 mL *n*-pentane and stored at -30 °C. After overnight, colorless crystals of **2** suitable for single crystal diffraction were obtained (12 mg, 41%).
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) 7.15 (t, *J* = 7.8 Hz, 1H, ^{Dipp}Ar-*H*), 7.00 (d, *J* = 7.8 Hz, 2H, ^{Dipp}Ar-*H*), 2.76 (sept, *J* = 6.7 Hz, 2H, ^{Dipp}C*H*$(CH_3)_2$), 1.79 (m, 4H, C*H*$_2$CH$_3$), 1.56 (d, *J* = 6.7 Hz, 6H, ^{Dipp}C*H*$_3$), 1.43 (s, 2H, C*H*$_2$), 1.10 (d, *J* = 6.7 Hz, 6H, ^{Dipp}C*H*$_3$), 0.91 (t, *J* = 7.4 Hz, 6H, CH$_2$C*H*$_3$), 0.87 (s, 6H, C*H*$_3$), 0.48 (d, *J* = 4.1 Hz, 18 H, Si*H*$_3$).
^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ (ppm) 260.6 (d, $^2J_{P\text{-}C}$ = 48.9 Hz, $C_{carbene}$), 145.4, 135.1, 129.7, 125.0, 79.8, 63.1, 42.2, 31.8, 29.4, 28.7, 27.7, 22.8, 9.6, 6.9 (d, $^2J_{P\text{-}C}$ = 11.2 Hz).
^{31}P NMR (243 MHz, C_6D_6) δ (ppm) = -233.1(s).
HRMS(ESI) $[M+H]^+$ $C_{28}H_{54}NAuPSi_2^+$: calc. 688.3192, found. 688.3190 m/z.

Synthesis of 3: A precooled THF solution of **1a** (1 mL, 30 mg, 0.04 mmol) was added dropwise to a precooled THF solution (1 mL) of LiC(N_2)TMS (8 mg, 0.067 mmol) at -45 °C. After stirring for 12 hours, the solvent was removed under vacuum and the residue was extracted with 2 mL *n*-pentane. After concentrated to 0.5 mL, the solution was stored at -30 °C. Colorless crystals suitable for diffraction of **3** were obtained after 12 h (11 mg, 43% yield).
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) 7.13 (t, *J* = 7.8 Hz, 1H, ^{Dipp}Ar-*H*), 7.00 (d, *J* = 7.8 Hz, 2H, ^{Dipp}Ar-*H*), 2.75 (sept, *J* = 6.7 Hz, 2H, ^{Dipp}C*H*(CH_3)$_2$), 1.66 (m, 4H, CH_2CH$_3$), 1.52 (d, *J* = 6.7 Hz, 6H, ^{Dipp}CH_3), 1.43 (s, 2H, CH_2), 1.09 (d, *J* = 6.7 Hz, 6H, ^{Dipp}CH_3), 0.97 (t, *J* = 7.5 Hz, 6H, CH$_2$CH_3), 0.86 (s, 6H, CH_3), 0.17 (s, 9H, SiH_3).
^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ (ppm) 251.9, 145.4, 135.2, 129.8, 125.1, 79.5, 62.6, 42.3, 35.7, 31.8, 29.4, 28.7, 27.1, 22.9, 9.5, 0.9
HRMS (ESI) [M+H]$^+$ $C_{28}H_{54}NAuPSi_2^+$: calc. 624.3043, found. 624.3041 m/z.
IR (ATR, neat): 2970, 2950, 2877, 1988 (CNN stretch), 1533, 1461, 1265, 1240, 1140, 867, 835, 749, 625, 529 cm^{-1}.

Synthesis of 5: $HPAd_2$ (12 mg, 0.04 mmol) was dissolved in THF (0.5 mL) and added to a THF solution of compound **4** (37 mg, 0.04 mmol) (1.5 mL). After stirring for 12 hours at room temperature, the solution was concentrated to 0.5 mL and layered with *n*-pentane (2 mL) and kept at -30 °C for 12 hours. After this time, large colorless crystals formed in the vessel. The supernatant was decanted and the solid was washed with 1 mL *n*-pentane, then dried *in vacuo* gave **5** as an off-white solid (35 mg, 85%).
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) 7.58 (s, 2H, C*H*=C*H*), 7.48 (t, *J* = 7.7 Hz, 2H, ^{Dipp}Ar-*H*), 7.30 (d, *J* = 7.7 Hz, 4H, ^{Dipp}Ar-*H*), 4.26 (d, *J* = 358.2 Hz, 1H, P*H*), 2.52 (sept, *J* = 6.9 Hz, 4H, ^{Dipp}CH), 1.84 (m, 6H, cod-*H*), 1.65 (m, 6H, cod-*H*), 1.52 (m, 18H, cod-*H*), 1.28 (d, *J* = 6.9 Hz, 12H, ^{Dipp}CH$_3$), 1.26 (d, *J* = 6.9 Hz, 12H, ^{Dipp}CH$_3$).
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ (ppm) 191.5 (d, $^2J_{P\text{-}C}$ = 113.8 Hz, $C_{carbene}$), 146.1, 133.6, 131.0, 125.1, 124.3, 42.1, 38.0 (d, $^2J_{P\text{-}C}$ = 25.6 Hz), 35.7, 29.0, 28.1 (d, $^3J_{P\text{-}C}$ = 10.0 Hz), 25.0, 24.3.
^{31}P NMR (243 MHz, $CDCl_3$) δ (ppm) = 50.5 (d, $^1J_{P\text{-}C}$ =358.2 Hz).
^{19}F NMR (565 MHz, $CDCl_3$) δ (ppm) = -81.0 (s).
HRMS (ESI) [M-OTf]$^+$ $C_{47}H_{67}N_2AuP^+$: calc. 887.4702, found. 887.4704 m/z.

Synthesis of 6: AuPhos **1b** (19 mg, 0.025 mmol) and compound **4** (18.5 mg, 0.02 mmol) were charged in a vessel and then 2 mL THF was added. After stirring for 5 min, the solvent was removed under vacuum. The residue was washed with 2 mL Et_2O and then dried under vacuum affording **6** as a gray powder. (24 mg, 81%). The NMR of **6** fitted well with the reported values.[8]

Synthesis of 7a: Selenium powder (3.2 mg, 0.04 mmol) was added into a THF solution (1 mL) of **1a** (15 mg, 0.02 mmol) at room temperature. After stirring for 5 min, the solvent was removed under vacuum. The residue was washed with 0.5 mL cold *n*-pentane and dried under vacuum affording **7a** as a white powder (15 mg, 81%).
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) 8.48 (m, 4H, Ph-*H*), 7.04 (t, *J* = 7.7 Hz, 1H, ^{Dipp}Ar-H), 7.02 (m, 4H, Ph-*H*), 6.94 (m, 4H, ^{Dipp}Ar-*H*/Ph-*H*), 2.71 (sept, *J* = 6.8 Hz, 2H, ^{Dipp}CH), 1.89 (sept, *J* = 7.1 Hz, 2H, CH_2CH$_3$), 1.79 (sept, *J* = 7.1 Hz, 2H, CH_2CH$_3$), 1.45 (d, *J* = 6.8 Hz, 6H, ^{Dipp}CH_3), 1.42 (s, 2H, CH_2), 1.06 (d, *J* = 6.8 Hz, 6H, ^{Dipp}CH_3), 0.85 (t, *J* = 7.1 Hz, 6H, CH$_2$CH_3), 0.81 (s, 6H, CH_3).
^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ (ppm) 247.1 (d, $^2J_{P\text{-}C}$ = 3.1 Hz, $C_{carbene}$), 145.3, 141.9 (d, $^1J_{P\text{-}C}$ = 62.2 Hz), 134.6, 132.1 (d, $^2J_{P\text{-}C}$ = 11.5 Hz), 130.0, 129.8 (d, $^3J_{P\text{-}C}$ = 3.1 Hz), 125.0, 80.0, 63.1, 41.5, 31.6, 29.4, 28.7, 27.3, 22.7, 9.7.
^{31}P NMR (243 MHz, C_6D_6) δ (ppm) = 21.2 (s) satellite (d, $^1J_{P\text{-}Se}$ = 579.8 Hz).
^{77}Se NMR (115 MHz, C_6D_6) δ (ppm) = 100.3 (d, $^1J_{P\text{-}Se}$ = 579.8 Hz).
HRMS (ESI) [M+H]$^+$ $C_{34}H_{46}NAuPSe^+$: calc. 776.2193, found. 776.2190 m/z.

Synthesis of 7b: With a similar procedure, selenium powder (3.2 mg, 0.04 mmol) was added into a THF solution (1 mL) of **1b** (15.5 mg, 0.02 mmol) at room temperature. After stirring for 5 min, the solvent was removed under vacuum. The residue was washed with 0.5 mL cold *n*-pentane and dried under vacuum affording **7b** as a white powder (12 mg, 63%).
^{1}H NMR (600 MHz, C_6D_6) δ (ppm) 8.22 (m, 4H, Ph-*H*), 7.24 (t, *J* = 7.8 Hz, 2H, ^{Dipp}Ar-*H*), 6.94 (m, 6H, Ph-*H*), 6.28 (s, 2H, C*H*=C*H*), 2.57 (sept, *J* = 6.8 Hz, 4H, ^{Dipp}C*H*), 1.42 (d, *J* = 6.8 Hz, ^{Dipp}CH$_3$), 1.05 (d, *J* = 6.8 Hz, ^{Dipp}CH$_3$).
^{13}C{^{1}H} NMR (151 MHz, C_6D_6) δ (ppm) 186.5 (d, $^2J_{P\text{-}C}$ = 3.8 Hz, $C_{carbene}$), 145.6, 141.7 (d, $^1J_{P\text{-}C}$ = 61.8 Hz), 134.6, 131.8 (d, $^2J_{P\text{-}C}$ = 11.5 Hz), 130.9, 129.5 (d, $^3J_{P\text{-}C}$ = 3.0 Hz), 127.6, 127.5, 124.5, 122.7, 29.1, 24.8, 24.1.
^{31}P NMR (243 MHz, C_6D_6) δ (ppm) = 19.5, (s), satellite (d, $^1J_{P\text{-}Se}$ = 581.0 Hz).
^{77}Se NMR (115 MHz, C_6D_6) δ (ppm) = 115.4 (d, $^1J_{P\text{-}Se}$ = 581.0 Hz)
HRMS (ESI) [M+H]$^+$ $C_{39}H_{47}N_2AuPSe^+$ calc. 851.2302, found. 851.2293 m/z.

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Keywords: Au-P bond • phosphines • cleavage • Au-substituted species• mechanism

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