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Bidentate (P^N) Au(III)–azide complexes: synthesis and reductive elimination studies†

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Herein, we report the synthesis and characterization of novel (P^N) aryl Au(III)–azide complexes. The reductive elimination from these Au(III) complexes to forge C(sp^2)–N_3 bonds has also been demonstrated. Considering the feasibility of C(sp^2)–N_3 reductive elimination in Au(III)–azide complexes, the gold-catalyzed C(sp^2)–N_3 cross-coupling reaction has been achieved. Furthermore, it is shown that the Au(III)–azide complexes undergo facile azide exchange with cyano and alkyne nucleophiles, facilitating C(sp^2)–C(sp) cross-coupling.

Gold(III) complexes are of significant interest due to their redox activity and potential applications in catalysis,[1] medicinal chemistry[2] and materials science.[3] In recent years, Au(III) complexes have been largely explored as key intermediates in gold-catalyzed cross-coupling reactions. Due to the high redox potential of the Au(I)/Au(III) redox couple, the Au(III) complexes are prone to undergo reduction to Au(I) (E^0_{red} Au(III)/Au(I) = +1.41 V *vs.* SHE) or Au(0) (E^0_{red} Au(III)/Au(0) = + 1.52 V *vs.* SHE).[4] This tendency renders the synthesis of stable Au(III) complexes difficult.

Traditionally, chelating bidentate and pincer tridentate ligands play a crucial role in stabilizing Au(III) complexes by modulating redox potentials (Scheme 1a).[5] Bidentate (C^N) ligands have been widely employed for the synthesis of stable Au(III) complexes, with their properties and catalytic performance thoroughly investigated.[6] In recent years, the bidentate (P^N) ligands have emerged as powerful ligands for enabling redox gold catalysis.[7] Such bidentate (P^N) ligands also proved to be effective in stabilizing the resultant Au(III) complexes enabling their isolation, characterization and their further catalytic applications. For instance, the group of Maynard and Spokoyny utilized (P^N) ligands to develop organometallic Au(III) bioconjugation reagents for the chemoselective cysteine arylation of unprotected peptides and proteins.[8] Furthermore, Houk, Maynard and Spokoyny demonstrated the application of a hemilabile (P^N) ligand "MeDalPhos" in achieving the ultrafast organometallic abiotic cysteine bioconjugation.[9] In 2021, Nevado and co-workers reported the synthesis of DalPhos based (P^N) aryl Au(III) fluoride complexes and explored their reactivity in transmetalation reactions (Scheme 1b).[10] Subsequently, in 2024, Bourissou and co-workers reported the synthesis of (P^N) aryl Au(III) fluorides *via* ligand-enabled oxidative fluorination of Au(I) and demonstrated their reductive elimination to obtain aryl fluorides (Scheme 1c).[11]

The oxidative addition of Au(I) has long been considered the key challenge, driving the design and development of various ligands to facilitate the oxidation process.[12] In contrast, due to the limited number of stable Au(III) complexes, the study of reductive elimination from Au(III) remains relatively underexplored. Clearly, the stability of gold(III) complexes depends on the ligand system and the nature of the donor atoms.[5] We envisioned that azide being a nucleophilic ligand could effectively stabilize the (P^N) ligated gold(III) intermediates. The early report on an Au(III)–azide complex by Uson and co-workers involved the synthesis of $[(N_3)Au(C_6F_5)_2PPh_3]$ from the $[O_3ClOAu(C_6F_5)_2PPh_3]$ precursor.[13] Later, Gade and co-workers synthesized an (N^N^N)Au(III)–azide complex featuring a bis(2-pyridylimino)isoindolato (BPI) ligand.[14] Recently, Au(III)-azide complexes such as $[PPh_4][(CF_3)_3Au(N_3)]$,[15] *trans*-$[AuF_2(N_3)(SIMes)]$,[16] and $[Au(N_3)(dpb)]$[17] (dpb = 1,3-di(2-pyridyl)phenide) were isolated and characterized. Additionally, bis, tris, and tetra-azido gold(III) complexes have been reported.[18] Interestingly, the reactivity of the Au(III)–azide complexes has never been reported. Motivated by the exceptional activity of bidentate (P^N) ligands,[7] we envisaged that the (P^N) ligand could provide access to stable Au(III)–azide complexes. Here, we present the synthesis and characterization of (P^N) aryl Au(III)–azide complexes, along with their reductive elimination studies to forge C(sp^2)–N_3 bonds (Scheme 1d). Based on the gathered knowledge, we have also shown the feasibility of obtaining azidoarenes from a ligand-enabled gold-catalyzed C(sp^2)–N_3 cross-coupling reaction. Furthermore, we showed

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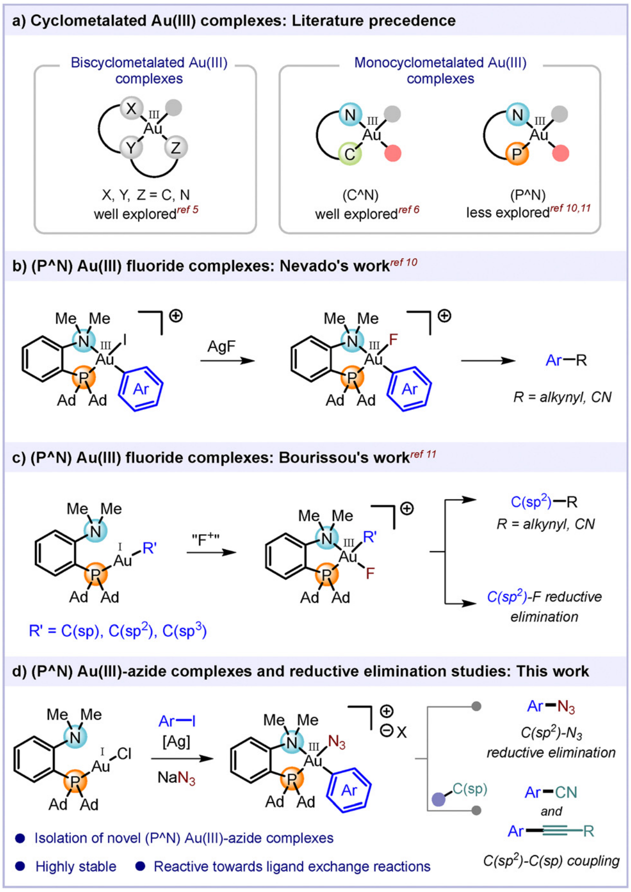
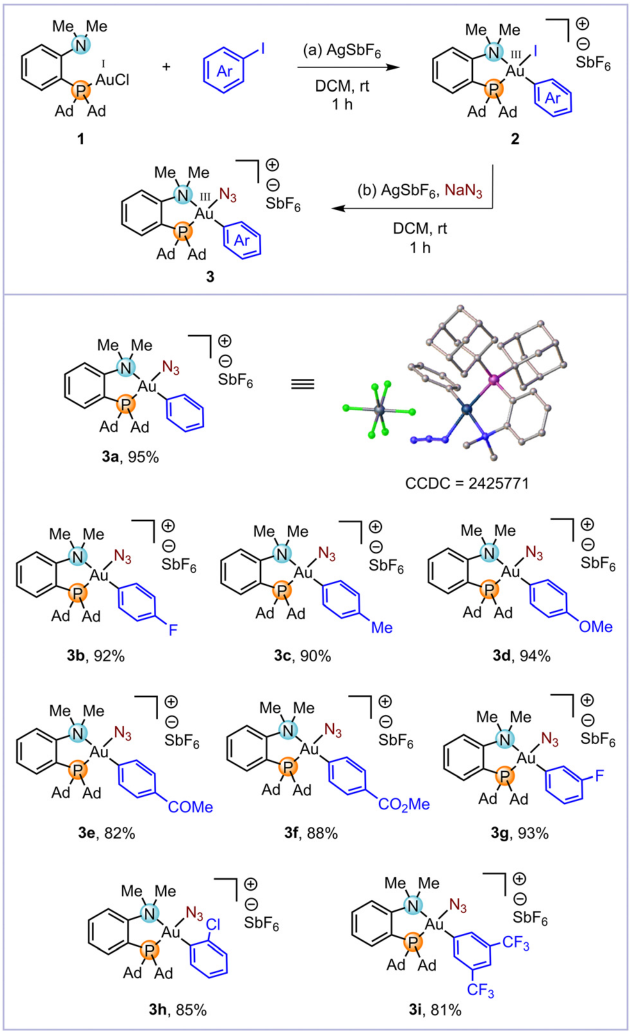


Scheme 1 Gold(III) complexes – literature background and present work.



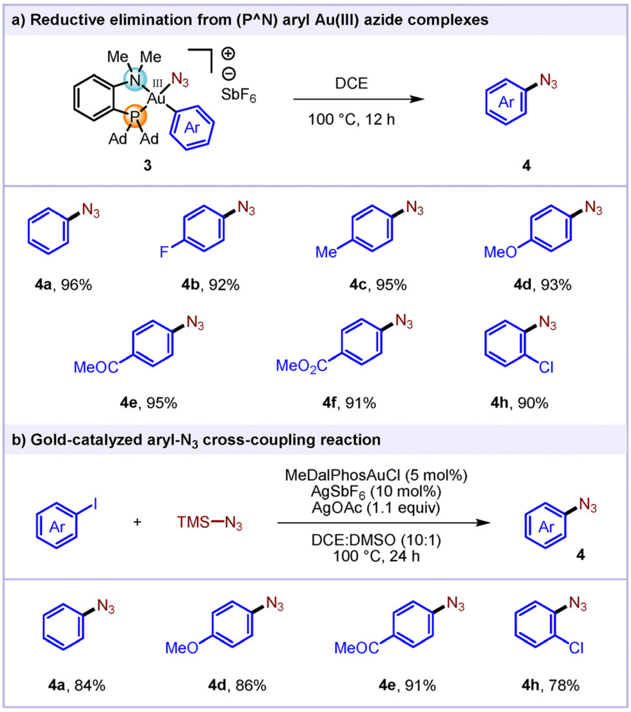
Scheme 2 Synthesis of (P^N) ligated Au(III)–azide complexes.[a] [a] Reaction conditions: (a) 0.20 mmol **1**, 0.40 mmol Ar–I, 1 equiv. $AgSbF_6$, DCM, rt, 1 h. (b) 1 equiv. $AgSbF_6$, 2 equiv. NaN_3, DCM, rt, 1 h. [b] Isolated yields. [c] Ellipsoids are shown at 50% probability level.

that the (P^N) aryl Au(III)–azide complexes can undergo facile ligand exchange followed by reductive elimination to forge a $C(sp^2)$–C(sp) bond.

At first, the synthesis of (P^N) ligated Au(III)–azide complexes was achieved by following a two-step procedure (Scheme 2). Firstly, the (P^N) gold chloride **1** was treated with aryl iodides in the presence of $AgSbF_6$ in dichloromethane at room temperature to generate the aryl Au(III) complex **2**. This complex was further treated with $AgSbF_6$ and sodium azide to obtain the aryl Au(III)–azide complex **3**. Crystals could be obtained by vapor diffusion of *n*-hexane into a concentrated CH_2Cl_2 solution of the gold complex **3a** at room temperature. The structure of **3a** was unambiguously confirmed by NMR spectroscopy and X-ray diffraction analysis. The Au(III)–azide complex **3a** features a square planar geometry with the azide group positioned *trans* to the phosphine ligand. The bond length of the Au–N bond *trans* to the phosphorus atom is 2.052 Å and that of the Au–C bond *trans* to the nitrogen atom is 1.965 Å. The terminal N–N bond length (1.121 Å) is shorter than the internal N–N bond length (1.187 Å), which is consistent with the bond length values observed for the (C^N) cyclometalated Au(III)–diazide complex.[18e] The C–Au–N bond angle in **3a** is 89.995° as determined from the X-ray structure. As shown in Scheme 2, (P^N) ligated aryl Au(III)–azide complexes bearing various electron-rich (–Me and –OMe), electron-deficient (–COMe, $–CO_2Me$, and $–CF_3$) and halogen groups (–F and –Cl) at the ortho, meta and para positions (**3a–3i**) were synthesized in good to excellent yields (81–95%). Notably, the Au(III)–azide complexes demonstrated remarkable stability, regardless of the electronic nature of the aryl group at the Au(III) center.

With Au(III)–azide complexes in hand, we sought to explore their reactivity towards transmetalation and reductive elimination processes. We initially investigated the $C(sp^2)–N_3$ reductive elimination under thermal conditions (Scheme 3a). To our delight, when complex **3a** was subjected to heating at 100 °C, the $C(sp^2)–N_3$ reductive elimination occurred to deliver the aryl azide **4a** in 96% yield. Similarly, the gold(III)–azide complexes (**3a–3f**, and **3h**) were found to undergo reductive elimination to afford the corresponding aryl azides in excellent yields (90–96%) (Scheme 3a).

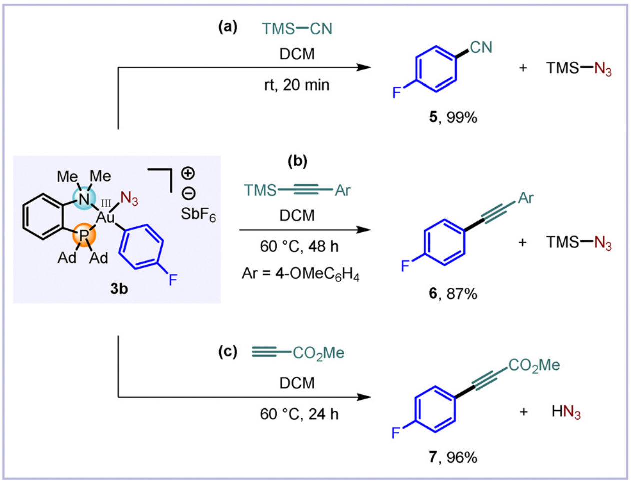
Owing to the potential of (P^N) ligands in facilitating several C–C,[19] C–N,[20] C–O[21] and C–S/Se[22] cross-coupling reactions, we investigated the gold-catalyzed aryl-N_3 cross-coupling reaction.[23]



Scheme 3 (a) $C(sp^2)-N_3$ reductive elimination from (P^N) aryl Au(III)–azide complexes.[a] [a] Conditions: 0.40 mmol **3**, DCE (0.1 M), 100 °C, 12 h. (b) Gold-catalyzed aryl-N_3 cross-coupling reaction.[b] [b] Conditions: 0.2 mmol iodoarene, 0.2 mmol $TMSN_3$, 5 mol% MeDalPhosAuCl, 10 mol% $AgSbF_6$, 1.1 equiv. AgOAc, DCE : DMSO (10 : 1), 100 °C, 24 h. [c] Isolated yields.

Motivated by the successful reductive elimination of $C(sp^2)-N_3$ under stoichiometric conditions, we performed the reaction of iodobenzene with NaN_3 in the presence of 5 mol% MeDalPhosAuCl, 1.1 equiv. of AgOAc and 10 mol% $AgSbF_6$ in DCE : DMSO (10 : 1) at 100 °C for 24 h.[24] The reaction resulted in the formation of a trace amount of azidobenzene **4a** as the product. Interestingly, using trimethylsilyl azide as the cross-coupling partner, we were pleased to observe the formation of **4a** in 84% yield (Scheme 3b). Furthermore, a range of electronically diverse aryl iodides were evaluated, yielding the desired products in good to excellent yields in nearly all cases (*cf.* **4d**, **4e** and **4h**). As compared to previously reported C–N cross-coupling reactions of iodoarenes with amines,[20] the $C(sp^2)-N_3$ coupling requires an elevated temperature of 100 °C. This may be attributed to the strong binding of azide to the Au(III) center, which makes the reductive elimination difficult at lower temperatures.

Furthermore, we investigated the reactivity of Au(III)–azide complexes towards ligand exchange reactions utilizing complex **3b** as the model substrate (Scheme 4).[10,11] Delightfully, complex **3b** reacted efficiently with trimethylsilyl cyanide at room temperature to afford 4-fluorobenzonitrile **5** in 99% yield. Next, the reaction of **3b** with ((4-methoxyphenyl)ethynyl)trimethylsilane delivered the $C(sp^2)-C(sp)$ cross-coupled product **6** in 87% yield. Interestingly, methyl propiolate could also be used as a cross-coupling partner to obtain the product **7** in 96% yield. Taken together, the work highlights the stable yet reactive nature of Au(III)–azide complexes, making them valuable intermediates in organic synthesis.



Scheme 4 Reactivity of (P^N) aryl Au(III)–azide complex towards ligand exchange and reductive elimination processes.[a] (a) Reaction with TMSCN. Conditions: 0.20 mmol **3b**, 1.0 mmol TMSCN, DCM (0.1 M), rt, 20 min. (b) Reaction with TMS-alkyne. Conditions: 0.20 mmol **3b**, 1.0 mmol TMS-alkyne, DCM (0.1 M), 60 °C, 48 h. (c) Reaction with terminal alkyne. Conditions: 0.20 mmol **3b**, 1.0 mmol methyl propiolate, DCM (0.1 M), 60 °C, 24 h. [a] Isolated yields.

In conclusion, the synthesis of (P^N) aryl gold(III)–azide complexes has been successfully achieved. The MeDalPhos-ligated Au(III)-azide complexes, featuring a broad range of electronically diverse aryl groups, demonstrate high stability, facilitating their isolation and characterization. The gold(III)–azide complexes readily undergo $C(sp^2)-N_3$ reductive elimination under thermal conditions, a finding that has enabled the development of a catalytic aryl-N_3 cross-coupling reaction. Furthermore, we showed that the Au(III)–azide complex undergoes ligand exchange with various C(sp) nucleophiles leading to $C(sp^2)-C(sp)$ cross-coupling products.

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Data availability

The data supporting this article, including synthetic procedures, spectral data, and crystallographic data have been included as part of the ESI.† Crystallographic data have been deposited at the CCDC under identification number 2425771.†

Conflicts of interest

There are no conflicts to declare.

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