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Stoichiometric Reductive C–N Bond Formation of Arylgold(III) Complexes with *N*-Nucleophiles

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Abstract: The reductive formation of substituted anilines from amines and three well-defined arylgold(III) complexes, i.e., dichloro(2,6-lutidine)phenylgold(III) (**2**), dichloro(2,6-lutidine)-*p*-tolylgold(III) (**3**), and chlorobis(triphenylphosphine)phenylgold(III) chloride (**4**) was studied. The reaction is stoichiometric in gold and represents a key step of a potential gold-catalyzed *intermolecular* amination reaction of arenes. It proceeds smoothly with a broad range of *N*-nucleophiles in the presence of sodium acetate (NaOAc) and enables the selective formation of *N*-substituted anilines in good yields. A mechanistic pathway is proposed and discussed as well.

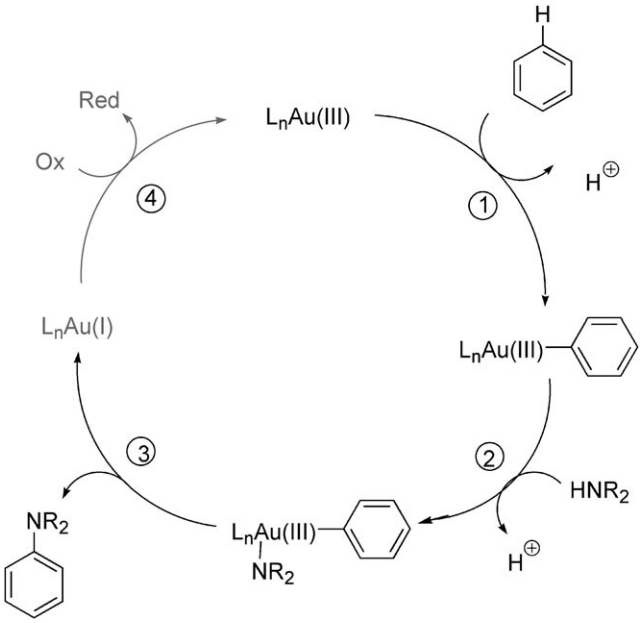
Keywords: amination; C–H activation; gold; homogeneous catalysis; reaction mechanisms

Introduction

In recent years gold-catalyzed transformations have substantially increased in scope and utility.[1] However, the synthetic versatility of the redox-couple Au(I)/Au(III)[2] (Scheme 1, step ④) drags behind that of the isoelectronic redox-couple Pt(II)/Pt(IV) and more over Pd(II)/Pd(0). On the other hand, the auration of simple arenes with Au(III) and Au(I) complexes (Scheme 1, step ①) occurs under much milder conditions than the corresponding platination or palladination.[3,4]

As early as in 1931 Kharasch et al. reported on the room temperature auration of unfuntionalized arenes such as benzene with $[AuCl_3]_2$ to form $[PhAuCl_2]_2$ (**1**-H).[5] This dimer is thermally labile and decomposes readily to chlorobenzene and AuCl.[6]

We took Kharash's finding as a stoichiometric model for the C–H activation in a potentially Au-catalyzed *intermolecular* amination of unfunctionalized arenes (Scheme 1). Such a transformation would enable the one-step synthesis of anilines from arenes and amines and could expand upon the scope of the palladium-catalyzed Hartwig–Buchwald amination,[7] which requires prefunctionalized haloarenes or phenols.



Scheme 1. Hypothetical catalytic cycle for the Au-catalyzed direct amination of benzene.

The adducts of Kharash's dimer **1**-R with ligands L such as 2,6-lutidine are stable. Such a ligand-stabilized monomer of the type $ArAuCl_2L$ (**2**-R) has first been reported by Fuchita et al.[8] They were also the first ones to report on a stoichiometric coupling of arenes and acetylenes based on **2**-R, which is a transformation complementary to the Sonogashira reaction, albeit not catalytic in metal.[8] Fuchita's mechanistic considerations remain elusive but point to the fact that ligand exchange and reductive elimination took place (Scheme 1, steps ② and ③).

The reductive elimination from Au(III) complexes is known,[9,10] but to the best of our knowledge there are only a few reports on the direct *intermolecular* reaction of arenes and *N*-nucleophiles.[11] Thus, a thorough study of reductive C–N bond formation with Fuchita's phenyllutidine Au(III) complex (**2**) and surrogates would serve as an excellent model to understand the elementary steps involved in this transformation.

Results and Discussion

Synthesis and Structural Characterization of Arylgold(III) Complexes 2 and 4

The reaction of benzene (R = H) or toluene (R = Me) with $[AuCl_3]_2$ in hexane is heterogeneous and proceeds smoothly to give regiospecifically, within 30 min, Kharash's intermediates **1**-R, which decompose rapidly in solution and in the solid state. Therefore, **1** was trapped with 2,6-lutidine without isolation as reported by Fuchita et al.[8] to give the stabilized arylgold(III) complex **2** in 29% (R = H) and **3** in 11% yield (R = Me), respectively (Scheme 2). Although the obtained yields are fairly low, it has to be considered that the maximum yield in this reaction is 50%, as liberated HCl consumes $[AuCl_3]_2$ to give tetrachloroauric acid. Surprisingly, the reaction of **1**-H with PPh_3 did not give $PhAuCl_2PPh_3$ as was expected based on early reports of Parkin et al.,[12] but yielded chlorobis(triphenylphosphine)phenylgold(III) chloride (**4**) in maximally 26% yield, which results from two-fold attack of PPh_3 on **1**-H.

Crystals of complexes **2** and **4** suitable for X-ray diffraction were grown from dichloromethane and the conformation of **2** was confirmed to be *trans*-dichloro(2,6-lutidine)phenylgold(III) (see Figure 1).[13]

The cationic complex **4** displays a slightly distorted square planar or even an elongated square pyramidal geometry, depending on how the second chloride atom is treated (see Figure 2, Table 1). The gold(III) center bears two triphenylphosphine ligands positioned *trans* to each other with similar P–Au bond distances (P1–Au1 = 2.37 Å and P2–Au1 = 2.36 Å). In contrast to Fuchita's lutidine complex **2**, the σ-coordinated phenyl ring in **4** is located *trans* to the basal chloride and *cis* to the two bulky phosphine ligands (C2–C1–Au1–P1 = 87.24°). The length of the carbon-gold bond in **4** is with 2.05 Å slightly elongated compared to 2.02 Å for **2**. The second chloride is weakly bound to the gold atom and is positioned at the apical position of an elongated square-pyramid. The

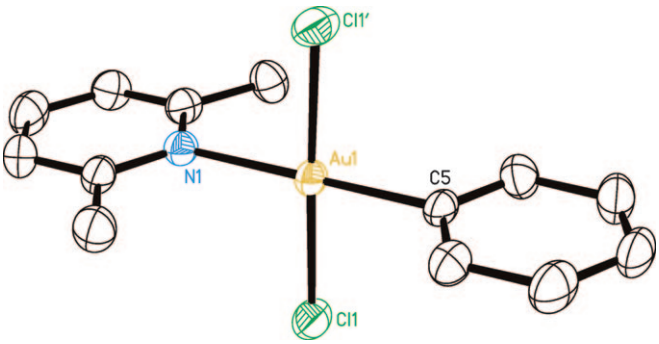
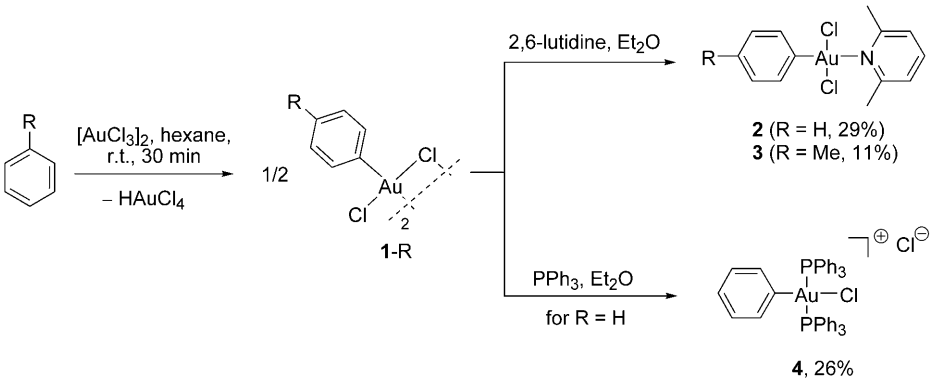


Figure 1. Molecular structure of **2** with thermal ellipsoids drawn at 50% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1–C5 2.017(6), Au1–N1 2.173(5), Au1–Cl1 2.276(1). Selected bond angles (°): N1–Au1–C5 180.0, Cl1–Au1–Cl1′ 177.85(5), N1–Au1–Cl1 91.08(3), C5–Au1–Cl1 88.92(3).



Scheme 2. Synthesis of arylgold(III)complexes **2**, **3**, and **4** by C–H activation of arenes with $[AuCl_3]_2$.

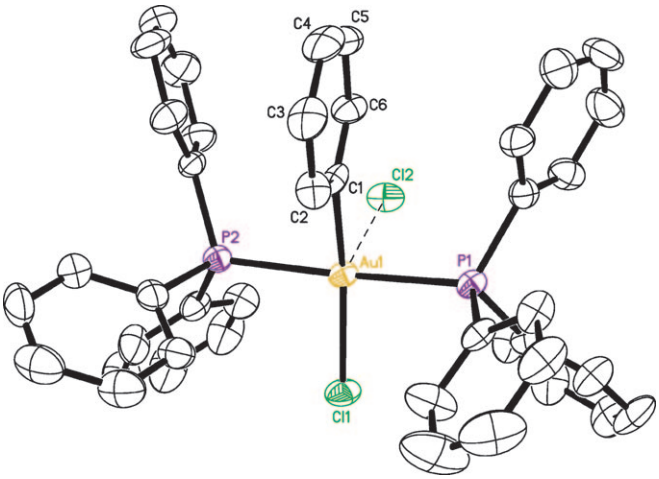


Figure 2. Molecular structure of **4** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1–P1 2.366(2), Au1–P2 2.361(2), Au1–C1 2.054(7), Au1–Cl1 2.383(2), Au1–Cl2 2.940(2). Selected bond angles (°): P1–Au1–P2 174.03(6), C1–Au1–Cl1 166.1(2), C1–Au1–P1 86.5(2), C1–Au1–P2 88.0(2), Cl1–Au1–P1 93.63(7), C1–Au1–P2 91.12(7). Selected torsion angle (°): C2–C1–Au1–P1 87.2(6).

Au1–Cl2 bond length is 2.94 Å, below the sum of the van-der-Waals radii (3.5 Å).

Reductive C–N Bond Formation by Reaction of Nucleophiles with Arylgold(III) Complexes 2, 3 and 4

In the absence of nucleophile and base the Fujita complex **2** is remarkably stable. Even after refluxing it for 24 h (0.01 M in THF, 70 °C) *ca.* 80% of the starting material was reisolated. The same is true for **3**, which did not show significant signs of decomposition by NMR in the presence of aniline ($pK_b = 9.42$), even after 5 d at room temperature in C_6D_6. Interestingly, when the same experiment was repeated with diethylamine as nucleophile ($pK_b = 3.07$), **3** decomposed readily at room temperature within 2 h to give 4-chlorotoluene in 92% yield. Such a P-ligand-induced *cis*-elimination has been reported by Fuchita et al. and others[14] for various cyclometallated Au(III) complexes.

When PPh_3 ($pK_b = 11.27$) was added to a solution of **3** in C_6D_6, chlorobenzene was isolated even after 5 min and in 95% yield. In this case, the reaction results in the clean formation of a by-product, which shows a diagnostic ^{31}P NMR signal at 45.9 ppm. This is close but not identical to the ^{31}P NMR signal of PPh_3AuCl ($\delta = 46.7$ ppm) as upon addition of commercially available PPh_3AuCl to the NMR sample an additional ^{31}P signal evolved.

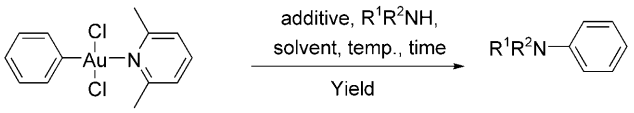
As acetate-containing Au(III) complexes are known to form gold(III) amides from aromatic amines,[15] we tried various acetate sources to enable a potential chlorine to acetate ligand exchange *in situ*. Indeed, addition of ammonium acetate to **2** and dibenzylamine yielded dibenzylphenylamine (**5b**), albeit in low yield (3%, Scheme 3, Table 2).

A change of the counterion from Cu^{2+} (41%) over Ag^+ (66%) to Me_4N^+ (78%) increased the yield in **5b** significantly. Although the fastest exchange from chloride to acetate was expected for AgOAc, finally, NaOAc turned out to be the optimal base giving **5b** in 88% yield. In turn, the yield in **5b** drastically decreas-

Table 1. Crystallographic data for **2**, **4** and **6**.

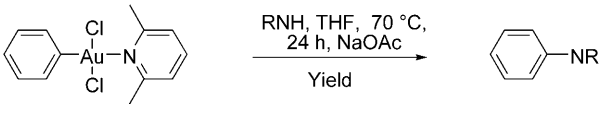
Compound	**2**	**4**	**6**
Emp. formula	$C_{13}H_{14}AuCl_2N$	$C_{42}H_{35}AuCl_2P_2 \cdot 1.5\,CH_2Cl_2$	$C_{10}H_{14}AuCl_2NO$
M [g mol^{-1}]	452.12	996.90	432.09
T [K]	200	200	200
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$
a [Å]	7.9966(3)	9.7810(1)	8.3597(17)
b [Å]	15.1581(5)	18.0733(1)	17.577(4)
c [Å]	11.6109(4)	26.8809(3)	8.5170(17)
α (°)	90	90	90
β (°)	94.7910(10)	99.242(1)	108.417(4)
γ (°)	90	90	90
V [Å^3]	1402.48(9)	4690.18(8)	1187.3(4)
Z	4	4	4
μ [mm^{-1}]	10.85	3.52	12.81
Refl. tot.	6961	38464	12392
Refl. unique/R_{int}	1610/0.0529	7997/0.0659	2954/0.0207
Parameters/restraints	81/0	506/60	136/0
$R^{[a]}/R_w^{[b]}$/GOF	0.0226/0.0551/1.020	0.043/0.124/1.17	0.015/0.037/1.05

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for all $I > 2\sigma(I)$.
[b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ for all $I > 2\sigma(I)$.



2 **5a** or **5b**

Scheme 3. Effect of base on the reaction of **2** with an *N*-nucleophile. For details, see Table 2.



2 **5a – j**

Scheme 4. Scope of C–N bond formation with complexes **2** and **5**. For details, see Table 3.

Table 2. Effect of base, solvent, temperature and time on the reaction of **2** with an *N*-nucleophile.

Additive	R^1, R^2	Solvent	Temp. [°C]	Time [h]	Yield **5a**, **b** [%][c]
None[a]	Bn, Bn	THF	70	24	–[d]
NH_4OAc[a]	Bn, Bn	THF	70	24	3
Me_4NOAc[a]	Bn, Bn	THF	70	24	78
NaO_2CCF_3[a]	Bn, Bn	THF	70	24	41
AgOAc[a]	Bn, Bn	THF	70	24	66
$Cu(OAc)_2$[a]	Bn, Bn	THF	70	24	41
Cs_2CO_3[a]	Bn, Bn	THF	70	24	45
K_2CO_3[a]	Bn, Bn	THF	70	24	84
NaOAc[a]	Bn, Bn	THF	70	24	88
NaOAc[a]	Bn, Bn	THF	70	3	28[e]
NaOAc[b]	H, Ph	THF	20	50	99
NaOAc[b]	H, Ph	THF	20	19	91
NaOAc[b]	H, Ph	THF	20	1.5	60
NaOAc[b]	H, Ph	C_6H_6	20	72	58
NaOAc[b]	H, Ph	CH_2Cl_2	20	72	70
NaOAc[b]	H, Ph	MeCN	20	72	85

[a] **2** (30 mg), additive (5 equiv.) and Bn_2NH (4 equiv.) in a stock solution of THF (6 mL, 10 mg of *n*-decane) in a sealed mininert™ vial.
[b] As above but 2 equiv. of aniline.
[c] GC yield calculated with *n*-decane as internal standard.
[d] Formation of biphenyl and chlorobenzene.
[e] 2 equiv. of Bn_2NH.

es upon reduction of the amount of nucleophile (28%), as well as on changing the basicity of the anion, as seen for the less basic trifluoroacetate counterion (41%). Interestingly, inorganic bases such as Cs_2CO_3 (45%) and especially K_2CO_3 gave **5b** in yields that are comparable to those obtained with NaOAc (84 *vs.* 88%).

In non-polar solvents such as benzene the reaction of **2** with aniline is slow and gives diphenylamine (**5a**) in 58% yield. More polar solvents such as dichloromethane and acetonitrile lead to better yields of 70 and 85%, respectively. Especially in THF the reaction proceeds rapidly to give **5a** in a virtually quantitative yield of 99%. Even after 19 (1.5 h) **5a** is obtained in 91 (60%) yield, respectively.

The scope of the reaction was subsequently evaluated using various amines under optimal reaction conditions, i.e., **2**, THF, 70 °C, NaOAc, 24 h (Scheme 4, Table 3). The reaction was broadly applicable and works with anilines to give **5a**, **d**, **e**, basic dialkylamines to give **5b**, **c**, **f**, sulfonamides to give **5g**, **h** and even with amides to give **5i**, **j**.

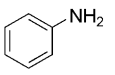
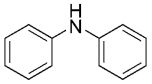
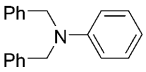
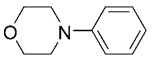
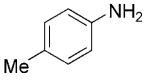
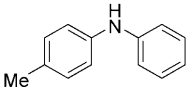
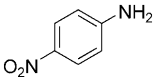
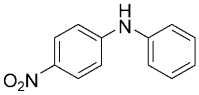
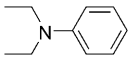
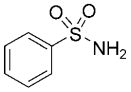
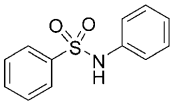
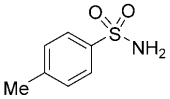
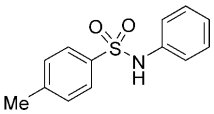
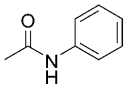
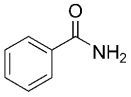
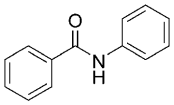
The yields obtained with complex **2** are similar or significantly higher if compared to **4** under otherwise identical conditions, as shown for the reaction with morpholine (59 *vs.* 99% yield), dibenzylamine (53 *vs.* 88%) and aniline (97 *vs.* 81%).

Mechanistic Studies for Complex 2

Based on literature precedents a chlorine to acetate exchange at the Au center as a first step into the reductive elimination is suggested[15] and this exchange has indeed been observed for acetate, and other nucleophiles such as methoxide and hydroxide.[4,9a] Despite this, we believe that the first mechanistic step (*cf.* Scheme 1, Scheme 5) is a ligand exchange from 2,6-lutidine to the *N*-nucleophile, as: a) upon addition of NaOAc as base but without nucleophile under otherwise identical conditions *via* ^{1}H NMR there are no signals assignable to acetate coordinated to gold, which are expected at $\delta = \sim 2.6$;[15] b) traces of free lutidine were detected by NMR; c) upon addition of PPh_3 as a strong σ-donating ligand, **2** (0.03 M in THF) was quantitatively converted within 1 h to a new complex (^{31}P NMR: signal shifted from $\delta = -5.3$ to ~33.7 ppm) even at room temperature and free lutidine was liberated as observed by ^{1}H NMR; d) this single new species is supposed to be $PhAuCl_2PPh_3$ (^{1}H NMR: two sets of aromatic signals in the ratio of 3:1), e) upon addition of 1 equivalent of morpholine to **2** at room temperature, in the absence or in the presence of NaOAc (after 1.5 h) all the starting complex was consumed and free lutidine and a new species formed which precipitated as colourless crystals from the reaction mixture. The precipitate turned out to be **6** by X-ray diffraction (Figure 3, Table 1).

The lengths of the Au–C and Au–N bonds in **6** and **2** do not change significantly [Au–C: 2.020(2) *vs.* 2.02, Au–N: 2.1734(19) *vs.* 2.17, Au–Cl 2.2845(6) *vs.* 2.27 Å]. The change in bond angles is more significant, i.e., with a glance at the N–Au–C angle, the Au atom in **6** significantly deviates from a linear arrangement [175.81(8) *vs.* 180.0°]. The ^{1}H NMR of **6** in THF-d_8 showed a broad singlet at 4.47, which we

Table 3. Scope of C–N bond formation with complexes **2** and **5**.

Entry	RNH	Amine **5a–j**	Yield of **5a–j** [%][a,b]
a			81 (97)[c]
b			88 (53)
c			99 (59)
d			94
e			85
f			53
g			83
h			69
i			91
j			42

[a] **2** (30 mg) and NaOAc (5 equiv.) in a stock solution of nucleophile (4 equiv.) in THF (6 mL, 10 mg of *n*-decane) in a sealed mininert vial.
[b] GC yields calculated using *n*-decane as internal standard.
[c] Numbers in brackets: **4** (5 mg) and NaOAc (5 equiv.) in a stock solution of nucleophile (2 equiv.) in THF (1.5 mL, 10 mg of *n*-decane) in a sealed mininert™ vial at 70 °C for 8 h.

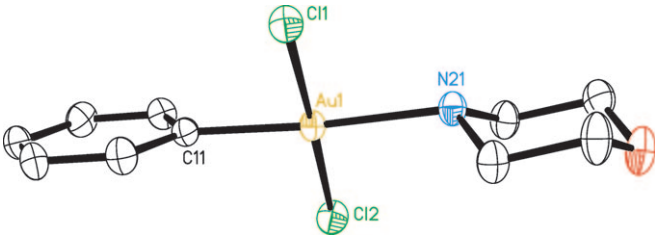
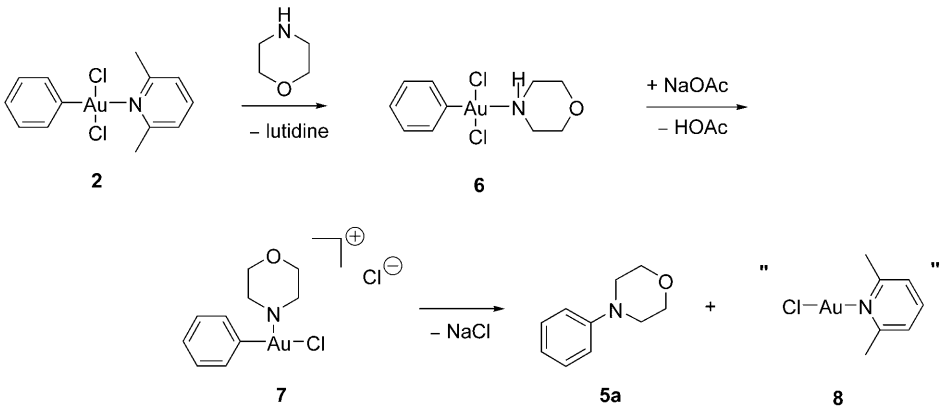


Figure 3. Molecular structure of **6** with thermal ellipsoids drawn at 30% probability. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å): Au1–C11 2.020(2), Au1–N21 2.173 (2), Au1–Cl1 2.2845(6). Selected bond angles (°): N21–Au1–C11 175.81(8), Cl1–Au1–C11 90.07(7), Cl1–Au1–N21 86.75(6), Cl2–Au1–C11 88.89(7), Cl2–Au1–N21 94.38(6).

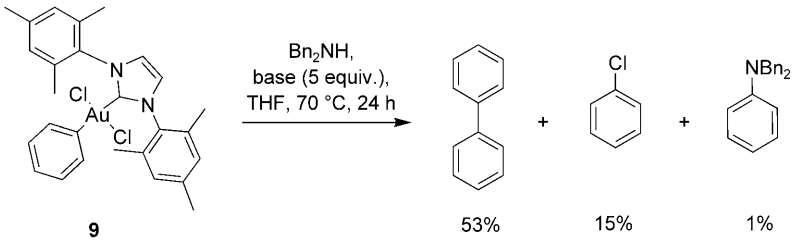
assign to the NH proton, 5 aromatic protons with $\delta =$ 6.96–7.08 ppm, and interestingly four diastereotopic methylene groups originating from morpholine (broad doublets at $\delta = 3.08$, 3.34, 3.67 and 3.87 ppm, *cf.* Supporting Information).

The coordination of aniline to the Au(III) center in **6** leads to a strong acidification of the NH proton,[16] and there is precedence that the formed Au(III)-amido complexes are easily generated in the presence of a mild base.[17] So is amidophenylgold(III) complex **6** subsequently deprotonated by NaOAc to give the putative T-shaped trigonal cationic species **7**, where amine and arene have the *cis*-conformation which is a prerequesite for reductive elimination.[9a,18] Thus, coupling product and the corresponding but not observed Au(I) species **8** are formed (Scheme 5).

As a final proof for the initial ligand exchange hypothesis, we chose the NHC complex $SIMesAuCl_2Ph$ (**9**),[19] which is not as easily liberated from **2** as is lutidine. Indeed, the reaction of **9** under standard reaction conditions gave only traces amounts of **5b** (1% yield), besides 53% of biphenyl and 15% of chlorobenzene as identified by GC-MS (Scheme 6). This finding supports the proposed mechanism.



Scheme 5. Proposed course of the Au(III)-mediated C–N bond formation.



Scheme 6. Attempted reductive amination with $IMesAuCl_2Ph$ and dibenzylamine.

Conclusions

In conclusion, we have shown that the lutidine ligand in well-defined arylgold(III) complexes, obtained by mild C–H activation of benzene with gold(III) chloride (**2** and **4**) is labile and easily exchanged to an *N*-nucleophile in the presence of acetate. Subsequent C–N bond formation occurs readily with amines, amides, sulfonamides, and even imides leading to arylated products in good to excellent yields. There is no indication that acetate acts as a ligand to gold. The mechanism of this amination is in accord with the general expectations on reductive eliminations from square planar d^8-complexes and a key intermediate in the mechanism has been characterized by X-ray crystallography. The development of a catalytic reductive amination based on the couple gold(I)/gold(III) existing out of C–H activation, C–N bond formation as presented here, and re-oxidation of Au(I) is the focus of our current research.

Experimental Section

All reactions were performed under an argon atmosphere using standard Schlenk techniques. Diethyl ether was dried by distillation from Na/Ph_2CO. Hexane and dichloromethane were dried with an MBraun solvent purification system. Methanol, diethyl ether, acetonitrile, tetrahydrofuran, dimethyl sulfoxide, 1,4-dioxane, and chloroform were purchased as anhydrous solvent purity. All solvents were saturated with argon prior to use. All deuterated solvents for NMR measurements were degassed *via* freeze-pump-thaw cycles and stored over molecular sieves (4 Å). Starting materials were purchased in reagent grade purity from Acros, Aldrich, Fluka, or Strem and used without further purification unless otherwise stated. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded at room temperature on a Bruker 250 spectrometer operating at 200, 50, and 81 MHz, respectively, with chemical shifts (δ, ppm) reported relative to the solvent peaks (^1H NMR, ^{13}C NMR). Data for X-ray crystal structure determination were obtained with a Bruker Smart CCD diffractometer (**2**, **4**) or a Bruker APEX diffractometer (**6**). Frames corresponding to a sphere of data were collected using 0.3° ω scans: radiation, Mo Kα; $\lambda = 0.71073$ Å. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied using the SADABS program[20] based on the Laue symmetry of the reciprocal space. Structure solution and refinement were carried out with the SHELXTL program system.[21] GC analyses were carried out on a Agilent 6890N modular GC base equipped with a split-mode capillary injection system and flame ionization detector using a standard HP-5 capillary column (30 m × 0.32 mm × 0.25 mm; He flow: 2.0 mL min^{-1}; program: 50 °C (1 min), 20 °C min^{-1} to 250 °C (10 min). The response factor ratios were determined by calibrations curves and the GC yields were calculated as reported (see Supporting Information).[22] Silica (60 Å, 63–200 mesh) for column chromatography was purchased from Chemie Brunschwig. Elemental analyses and mass spectra (ESI^+) were obtained from the chemistry department of the University of Heidelberg.

General Procedure for the Synthesis of Arylgold(III) Complexes 2 and 3

A hexane solution (10 mL) of arene (73.84 mmol) was added to a hexane suspension (20 mL) of $[AuCl_3]_2$ (1.12 g, 1.84 mmol) at room temperature. The initial red color of the solution rapidly changed to brown-orange. The solution was stirred for 30 min at room temperature and then diethyl ether was added at once (10 mL). The resulting suspension was filtered and the filtrate treated with a diethyl ether solution of 2,6-lutidine (393 mg, 3.29 mmol, 10 mL). The resulting yellow solution was stirred at room temperature for an additional hour and then volatiles were removed under vacuum. Purification of the residue *via* column chromatography (benzene/hexane = 2:3) yielded **2** and **3** as pale yellow solids.

Dichloro(2,6-lutidine)phenylgold(III) **(2):**[8] $R_f = 0.46$ (toluene); yield: 242 mg (29%). Crystals for X-ray analysis were obtained by slow evaporation of a dichloromethane solution. ^1H NMR ($CDCl_3$): $\delta = 3.08$ (s, 6H, CH_3), 7.31–7.13 (m, 7H, lut-*H* + Ar-*H*), 7.75 (t, 1H, $J = 6.0$ Hz, lut-*H*); ^{13}C NMR ($CDCl_3$): $\delta = 24.7$, 124.6, 127.1, 129.3, 130.1, 131.9, 139.9, 157.2; HR-MS (FAB): $m/z = 452.0201$, calcd. for $C_{13}H_{15}N^{35}Cl_2Au$ $(M+H)^+$: 452.0247; $m/z = 454.0274$, calcd. for $C_{13}H_{15}N^{35}Cl^{37}ClAu$ $(M+H)^+$: 454.0218.

Dichloro(2,6-lutidine)-p-tolylgold(III) **(3):**[8] Yield: 95 mg (11%) as a colorless solid. ^1H NMR ($CDCl_3$): $\delta = 2.34$ (s, 3H, CH_3), 3.07 (s, 6H, lut-CH_3), 6.98 (d, 2H, $J = 8.0$ Hz, Ar-*H*), 7.12 (d, 2H, $J = 8.0$ Hz, Ar-*H*), 7.29 (d, 2H, $J = 7.5$ Hz, lut-*H*), 7.75 (t, 1H, $J = 7.5$ Hz, lut-*H*); ^{13}C NMR ($CDCl_3$): $\delta = 20.6$, 24.7, 124.6, 128.2, 130.1, 131.4, 136.7, 139.9, 157.2; HR-MS (FAB): m/z = 466.0366, calcd. for $C_{14}H_{17}N^{35}Cl_2Au$ $(M+H)^+$: 466.0404; $m/z = 468.0338$, calcd. for $C_{14}H_{17}N^{35}Cl^{37}ClAu(M+H)^+$: 468.0374.

***Chlorobis(triphenylphosphine)phenylgold(III) chloride* (4):** A hexane solution (10 mL) of benzene (5.76 g, 73.84 mmol) was added to a hexane suspension (20 mL) of $[AuCl_3]_2$ (1.00 g, 1.64 mmol) at room temperature. The initial red color of the solution rapidly changed to brown-orange. The solution was stirred for 30 min at room temperature and then diethyl ether was added at once (10 mL). The resulting suspension was filtered and the solution treated with a diethyl ether solution of triphenylphosphine (95 mg, 3.62 mmol, 10 mL). The resulting yellow solution was stirred at room temperature for an additional hour and volatiles were then removed under vacuum. Recrystallization of the residue from dichloromethane/hexane, washing with diethyl ether and drying under vacuum afforded **4** as a colorless solid; yield: 0.39 g (26%). Crystals suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a dichloromethane solution of **4** at 4 °C. ^{1}H NMR ($CDCl_3$): $\delta = 6.51$ (bs, 2H, Ph-*H*), 6.74 (t, 1H, $J = 7.5$ Hz, Ph-*H*), 7.03 (d, 2H, $J = 7.5$ Hz, Ph-*H*), 7.3–7.9 (m, 30H, PPh_3-*H*); ^{13}C NMR ($CDCl_3$): $\delta = 125.6$, 128.6, 129.9, 131.6, 134.8; ^{31}P{^{1}H} NMR ($CDCl_3$): $\delta = 31.3$; HR-MS (ESI): $m/z =$ 833.1547, calcd. for $C_{42}H_{35}AuClP_2(M-Cl)^+$: 834.1568; anal. calcd. for $C_{42}H_{35}AuCl_2P_2 \cdot CH_2Cl_2$: C 54.11, H 3.91; found: C 54.16, H 3.93.

General Procedure for the Reaction of 2 with Various *N*-Nucleophiles to Yield 5a–j

To an oven-dried mininert™ vial were added **2** (30 mg, 67 μmol, 1 equiv.) and NaOAc (27 mg, 330 μmol, 5 equiv.). In cases where the *N*-nucleophile was a solid, the *N*-nucleophile was added to the mininert™ vial in solid form (266 μmol, 4 equiv.). The flask was then sealed under argon, and *n*-decane (10 mg) and THF (6 mL) were added to the reaction mixture *via* syringe. In cases where the *N*-nucleophile was a liquid, the *N*-nucleophile was added to the reaction flask *via* syringe (266 μmol, 4 equiv.). The vial was promptly placed in a 70 °C oil bath and stirred for 24 h. The yield of **5a–j** was determined by GC. For determination of response factors and calculation of GC yields, see Supporting Information.[22]

Reaction to Afford 4-Phenylmorpholine (5c) on a Preparative Scale

Under argon to an oven-dried Carius tube were added dichloro(2,6-lutidine)phenylgold(III) (**2**, 136 mg, 300 μmol), NaOAc (123 mg, 1.5 mmol) and THF (27 mL). Morpholine (105 μL, 1.2 mmol) was added to the reaction mixture *via* syringe. The vial was promptly placed in a pre-heated oil bath (70 °C) and stirred for 24 h. After filtration of the reaction mixture over celite and removal of volatiles under vacuum, the crude reaction mixture was purified by flash chromatography (pentane/diethyl ether = 7:3) to afford **5c**; yield: 45 mg (92%); ^{1}H NMR ($CDCl_3$):): $\delta = 3.17$ (t, $J = 4$ Hz, 4H), 3.88 (t, $J = 4$ Hz, 4H), 6.91 (m, 3H), 7.30 (t, $J = 8$ Hz, 2H).

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