Reductive C–C Coupling from Molecular Au(I) Hydrocarbyl Complexes: A Mechanistic Study

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ABSTRACT: Organometallic gold complexes are used in a range of catalytic reactions, and they often serve as catalyst precursors that mediate C–C bond formation. In this study, we investigate C–C coupling to form ethane from various phosphine-ligated gem-digold(I) methyl complexes including \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar})_2][\text{NTf}_2]\), \([\text{Au}_2(\mu-\text{C}_6\text{H}_2-2,4,6-\text{Me})_2(\text{XPhos})_2][\text{NTf}_2]\), and \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar})_2][\text{NTf}_2]\). Introducing the 

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Scheme 1. Proposed Pathways of C—C Bond Coupling Reactions Mediated by Molecular Gold Complexes7,14,31,36

(a) Reductive elimination

(b) Electrophile transfer

(c) Mixed-valent PhAr

(d) This work

![Diagram](https://example.com/scheme1.png)

centers, but these alkyl transfers appear to occur only in nonpolar solvents.23 Further, the putative binuclear Au intermediates responsible for alkyl transfer were not directly implicated in the C—C coupling reactions. From the starting complexes (Me)2Au(X)(L) (L = phosphine), it was proposed that larger phosphines facilitate ethane reductive elimination.30 Alternatively, Kochi has proposed that ethane formation could result from digold alkyl intermediates, but to our knowledge, such reactions were not directly observed.31,32 Other examples of ethane formation through bimolecular reductive elimination from M—CH3 species include NiII,33 CuI,34 and RuII.35 The formation of C—C bonds from (NHC)AuIII(R)(X)(R) intermediate, followed by competitive (a) C—C reductive elimination to form R—R and (b) intermolecular transfer of RX from a Au(III) intermediate to (NHC)AuI—R to yield (NHC)AuIII(R)2(X) followed by C—C reductive elimination to give the homocoupled product R—R. Related to these processes, the addition of F−-donors to Au(I) hydrocarbyl compounds also promotes C—C coupling reactions.36–39

Mixed-valent gold hydrocarbyl complexes have also been proposed as intermediates responsible for the C—C bond formation.17 For example, Toste and co-workers reported a fast bimetallic Au—Au bond reductive elimination from a mixed-valent bimetallic AuII/AuIII complex [ClAu]PNP[AuCl(C6H5-F)2] (PNP = Ph3P−N(CH3)−PPh3; Scheme 1c).17 In this study, the Au(I) complex [AuCl(C6H5-F)2]PNP[AuCl(C6H5-F)] is oxidized with PhICl to generate a symmetrical bimetallic Au(II) species, [ClAu(C6H5-F)2]PNP[AuCl(C6H5-F)2Cl]. The latter isomerizes to a mixed-valent AuII/AuIII complex, [ClAu]PNP[AuCl(C6H5-F)2], which undergoes reductive elimination to form a biaryl product. Similarly, O’Hair and co-workers reported a concerted redox couple mechanism from a reaction between allylic halides (CH2 = CHCH2X, X = Cl, Br, and I) and a gem-digold(I) compound, ([dppm]2Au)PH2 (dppm = bis(diphenylphosphino)methane, (Ph2P)2CH).45 It is hypothesized that the reductive coupling occurs from a AuII/AuIII complex, [ClAu]PNP[AuII(CH2—CHCH2)(Ph)]

Germane to these proposed binuclear Au precursors to C—C elimination, several gem-digold intermediates have been reported, including [Au2(σ,π-CH—CH=C6H4)(PPh3)2]-[NTf2]44 [Au2(μ-Ph)L2][NTf2]45 (L = PPh3 or NHCl), and [Au2(μ-R)(PMeAr)2][NTf2] (R = CH3, CH2 = CH2, C≡ CH, ArArop=2=C6H4-2,6-(CH2-2,6-Pr2)).46 The thermal stabilities of phosphine-ligated gem-digold hydrocarbyl complexes have been reported to depend on the steric properties of the ancillary ligands.46 Other related examples, including [Au2(μ-vinylP(Ph)3)][NTf2]14,15,44 and [Au2(μ-vinylP(Ph)3)][NTf2], readily decompose to the corresponding diene, [Au(PPh3)]2[NTf2], and colloidal gold byproducts. Nonetheless, a mechanistic understanding of these C—C coupling processes and, in general, of C—C formation from Au complexes is lacking.

Herein, we explore the formation of ethane from one of the simplest possible gold-based systems, namely, Au(CH3)(PPh3). To enable reliable mechanistic investigations, we extended our preliminary observations on triphenylphosphine-ligated systems to bulkier terphenyl and biaryl phosphines that provide kinetic stabilization of key digold intermediates. In particular, we have focused on C—C coupling reactions from gem-digold methyl complexes with a general formula [Au2(μ-CH3)(PMeAr)2][NTf2] and [Au2(μ-CH3)(XPhos)2][NTf2] (Figure 1). We studied the impact of the phosphine ligand on the stability of digold complexes, especially the influence on ethane elimination.

Figure 1. Phosphine-ligated gem-digold methyl complexes with the general formula [Au2(μ-CH3)(PR2Ar)(PTripp)][NTf2] investigated in this work (Xyl = 2,6-C6H3-Me2; Mes = 2,4,6-C6H3-Me3; Dipp = 2,6-C6H3-iPr2; Tripp = 2,4,6-C6H3-2,6-Pr2).

RESULTS AND DISCUSSION

Synthesis of Neutral Gold Complexes Based on Terphenyl and Biaryl Phosphines. Gold complexes with terphenyl phosphine (complexes 1a—1d in Scheme 2) and with biaryl “Buchwald phosphine” ligands (1e and 1f) were synthesized by methylation of Au(I) chloride precursors with MeMgX (X = Cl or Br) in 60–80% isolated yields.47 Formation of the new Au—C bonds is evidenced by the appearance of 1H NMR resonances in the range from 0.08 to 0.45 ppm with associated 13C{1H} signals at 3.4 to 8.3 ppm (ΔνPP = 100 Hz). Single crystals of 1a, 1e, and 1f were obtained by slow evaporation from a mixture of pentane and diethyl ether or pentane and dichloromethane solution from 5 to −25 °C (Figure 2). The solid-state structures of complexes 1e and 1f show a weak k+ type interaction (localized Au—n(arene) contact)48–50 between the Au(I) center and the ipso carbon of the arenes (C20, 1e; C16, 1f) with bond distances of 3.1748(17) and 3.180(4) Å, respectively. The distances

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Scheme 2. Synthesis of Phosphine-Ligated Gold Methyl Compounds with Terphenyl Phosphines (1a–1d) and Buchwald Phosphines (1e and 1f)

![Scheme 2](image)

Figure 2. ORTEPs of Au(CH3)(PMe2ArXyl2)(1a), Au(CH3)(XPhos)(1e), and Au(CH3)(BuXPhos)(1f) represented at 50% probability. (For If, one of the two chemically equivalent, but crystallographically distinct, structures is shown. For the second structure, see the Supporting Information.) Hydrogen atoms on the phosphine ligands are omitted for clarity. Selected bond lengths (Å): Au1−C1 = 2.123(2); P1−C2 = 1.825(3); P1−C3 = 1.823(3); P1−C4 = 1.852(2); Au1−C20 = 3.5023(18); Au1−C25 = 3.2510(18); Au1−C21 = 3.551(4); Au1−P1 = 2.2900(7). 1e, Au1−C1 = 2.1146(14); Au1−C20 = 3.1748(17); Au1−C25 = 3.5203(18); Au1−C21 = 3.409(4); Au1−P1 = 2.2900(7). 1f, Au1−C1 = 2.079(8); Au1−C20 = 3.180(4); Au1−C25 = 3.5023(18); Au1−C21 = 3.409(4); Au1−P1 = 2.2900(7). 1f, Au1−P1 = 2.3007(11). Selected bond angles (deg): C1−Au1−P1 = 179.6(3); Au1−C1−C2 = 115.9(7); C3−P1−Au1 = 111.5(3); C5−P1−Au1 = 115.6(3); C4−P1−Au1 = 112.3(3).

Figure 3. ORTEP of Au(C6H5)(PMe2ArXyl2)(2a) at 50% probability (one of the two crystallographically distinct structures, the other one being Au(C6H5)(PMe2ArMes2), see Figure S1). Hydrogen atoms on the phosphine ligands are omitted for clarity. Selected bond lengths (Å): Au1−C1 = 2.079(8); C1−C2 = 1.411(15). Selected bond angles (deg): C1−Au1−P1 = 178.6(3); Au1−C1−C2 = 115.0(7); C3−P1−Au1 = 111.5(3); C5−P1−Au1 = 115.6(3); C4−P1−Au1 = 112.2(3).

Figure 4. ORTEP of Au(C6H5)(PMe2ArMes2)(3a) at 50% probability. Hydrogen atoms on the phosphine ligands are omitted for clarity. Selected bond lengths (Å): Au1−C1 = 2.089(7); Au1−P1 = 2.302(2). Selected bond angles (deg): C1−Au1−P1 = 177.7(2); C8−P1−Au1 = 110.4(3); C7−P1−Au1 = 109.9(3); C9−P1−Au1 = 117.5(2).

by a similar procedure to their methyl analogues and characterized by spectroscopic techniques and single-crystal X-ray diffraction (Figures 3 and 4). The σ Au−C bond

between Au centers and arene ring centroids are 3.2659(10) Å (1e) and 3.449(2) Å (1f), also indicative of intramolecular Au−π(arene) interactions. Structure 1a does not exhibit this type of contact, in agreement with the preferred geometry adopted by the smaller phosphines of the terphenyl series.52 The Au−CH3 bond distances are 2.123(2) Å (1a), 2.1146(14) Å (1e), and 2.096(4) Å (1f).

Terminal ethyl and phenyl complexes Au(C6H5)(PMe2ArXyl2)(2a) and Au(C6H5)(PMe2ArMes2)(3a) were synthesized with the aim of exploring the possibility of C−C bond heterocoupling with different hydrocarbyl substituents bound to gold (see below). These compounds were prepared
(PPh₃) evolves ethane immediately at room temperature with complete consumption of Au(CH₃)(PPh₃) by the time of placing the sample in the NMR probe (<10 min; Scheme 3). The release of ethane is accompanied by clean formation of the homoleptic bisphosphine complex [Au(PPh₃)₂][NTf₂], along with Au(0), as evinced by the formation of black insoluble material. The nature of this solid was interrogated by transmission electron microscopy (TEM) analysis (Figure 5).

**Scheme 3. Ethane Elimination from Au(CH₃)(PPh₃) in the Presence of 1 equiv of Au(PPh₃)(NTf₂)**

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When a 1:1 molar mixture of Au(PPh₃)(NTf₂) and Au(CH₃)(PPh₃) was dissolved in dichloromethane at −70 °C, ethane formation was detected immediately by 1H NMR spectroscopy (Figure S9). Variable temperature ¹H and ³¹P{¹H} NMR analysis from −70 to 25 °C revealed the formation of an intermediate species characterized by a broad ¹H NMR resonance at 1.6 ppm associated with a ³¹P{¹H} NMR resonance at 37.5 ppm, which we attribute to the corresponding gem-digold methyl species [Au₂(μ-CH₃)(PMe₂Ar)₂][NTf₂] (Figure S8). However, this compound is only detectable at temperatures below −40 °C, and it rapidly evolves to the final products above this temperature.

**Scheme 4. General Synthesis of the gem-Digold Methyl Complexes with Terphenyl Phosphines (4a–4d) and Buchwald Phosphine-Ligated gem-Digold Methyl Complexes (4e and 4f)**

Compounds 4a–4f were characterized by multinuclear NMR spectroscopy, and their purity was confirmed by microanalysis. Distinctive ¹H NMR signals due to the methyl group, which are slightly shifted to higher frequencies (ca. 0.5–1.2 ppm) compared to their corresponding neutral precursors (1a–1f), are consistent with the formation of the gem-digold complexes. The presence of the bridging methyl ligand is further confirmed by ¹³C{¹H} NMR resonances shifted to lower frequencies by approximately 5 ppm compared to the parent compounds 1a–1f and characterized by a drastically reduced scalar-coupling to ³¹P (ca. 50 Hz; cf. ~100 Hz for 1a–1f). The compounds [Au₂(μ-CH₃)(XPhos)₂][NTf₂] (4e) and [Au₂(μ-CH₃)(BuXPhos)₂][NTf₂] (4f) were additionally authenticated by single-crystal X-ray diffraction (Figure 6; Table 1). The gold methyl bond distances in 4e and 4f are ~0.1 Å longer than in their corresponding neutral methyl complexes 1e and 1f. A characteristic Au–arene interaction is discernible for the two structures. While the structure of 4f exhibits a slightly shortened Au–arene distance (3.390(3) Å on average) than its neutral complex 1f (3.449(2) Å), compound 4e (3.432(2) Å on average) presents an apparently weaker Au–arene interaction than its neutral gold compound.
the phosphine ligand. Thus, the compound \([\text{Au}_2(\mu-\text{CH}_3)(\text{XPhos})]^{+}\) [NTf_2]^- (4e) and \([\text{Au}_2(\mu-\text{CH}_3)(\text{BuXPhos})]^{+}\) [NTf_2]^- (4f) at 50% probability (for 4e, only one of the three chemically equivalent, but crystallographically distinct, structures is represented). Hydrogen atoms on the phosphine ligands are omitted for clarity. Selected bond lengths (Å): 4e, Au1–C1 = 2.221(5); Au2–C1 = 2.235(5); Au1–Au2 = 2.7466(4); Au1–P1 = 2.2637(12); Au2–C1 = 2.204(9); Au2–C1 = 2.207(8); Au1–Au2 = 2.7763(7); Au1–P1 = 2.285(2); Au1–P2 = 2.2798(18). Selected bond angles (deg): 4e, C1–Au1–P1 = 168.41(14); C1–Au1–P2 = 172.39(13); Au1–C1–Au2 = 76.11(16); C1–Au1–Au2 = 52.17(13); C1–Au2–Au1 = 51.72(12). 4f, C1–Au1–P1 = 162.9(2); C1–Au2–P2 = 160.9(2); Au1–C1–Au2 = 78.0(3); C1–Au1–Au2 = 51.0(2); C1–Au2–Au1 = 50.9(2).

1e (3.2659(1) Å). The presence of intense aurophilic interactions is evinced by Au···Au distances in complexes 4e and 4f of 2.7466(6) and 2.7763(7) Å, respectively. These Au···Au distances are slightly longer than those reported for the related 4c (2.7120(8) Å) and ~0.1 Å shorter than the Au–Au distance in metallic gold (2.878 Å).

Ethane Elimination from gem-Digold Methyl Complexes. As anticipated, the stability of gem-digold methyl complexes largely depends on the steric shielding provided by the phosphine ligand. Thus, the compound \(\text{[Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{3b})]^{+}\) [NTf_2]^- (4a) is only stable in dichloromethane solution at ~50 °C or below. Above ~20 °C, 4a cleanly converts into \(\text{[Au}(\text{PMe}_2\text{Ar}^{3b})]^{+}\) [NTf_2]^- (5a), metallic gold, and ethane (Scheme 5). Complex \(\text{[Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{3b})]^{+}\) [NTf_2]^- (4b) reacts in a similar way, whereas bulkier phosphines provide enhanced stability. As such, complexes \(\text{[Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{3ppp})]^{+}\) [NTf_2]^- (4c) and \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{6ppp})]^{+}\) [NTf_2]^- (4d), in which the methyl substituents in the lateral aryl rings of the terphenyl moiety have been substituted by iso-propyl groups, are all stable at room temperature, while complexes 4e and 4f remain unaltered for hours even at temperatures up to 80 °C. Thus, the investigated Buchwald phosphines confer enhanced stability to gem-digold methyl species compared to terphenyl-based ligands, most likely as a result of the increased steric shielding provided by the cyclohexyl and tert-butyl groups directly bound to the phosphorus center in close proximity to the gold nuclei.

Overall, these observations indicate that kinetic analysis by ^1H and ^13C NMR spectroscopy monitoring is facilitated by larger phosphine ligands compared to PPh_3. For instance, heating complex 4e in dichloromethane at 90 °C enabled us to monitor by NMR spectroscopy its evolution to \(\text{[Au}(\text{XPhos})]^{+}\) [NTf_2]^- (5e) with concomitant release of ethane and formation of Au(0) (Figure S5). The thermolysis of 4e follows a second-order dependence on the digold complex with \(k_{\text{obs}} = 5.2(1) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}\) at 90 °C (Table 2), as previously observed for the PPh_3-based system. In the case of the more hindered complex 4f, this reaction does not take place at 100 °C, and intractable digold decomposition occurs at temperatures above 100 °C where the formation of methane, instead of ethane, was observed (Figure S14). This finding indicates that C–C coupling is likely not viable in the most sterically constrained digold system studied herein. This seems to be consistent with a second-order dependence on digold complex concentration during ethane formation, which might imply the need for more than two gold nuclei in close proximity along the reaction coordinate (see below for additional discussion).

Kinetic studies provide rates for ethane elimination from the more sterically hindered 4c and 4d of \(k_{\text{obs}} = 4.8(3) \times 10^{-3} \text{ and } 2.0(1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}\) at 50 °C, respectively. In contrast, the rates of ethane elimination from 4a and 4b had to be analyzed at lower temperatures (0 °C), resulting in rates of \(k_{\text{obs}} = 9.8(3) \times 10^{-2} \text{ and } 4.9(1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}\) at 0 °C, respectively. The corresponding half-life (\(t_{1/2}\)) values associated with these kinetic parameters at the working temperatures are approximately 260 (4a, 0 °C), 800 (4b, 0 °C), 5600 (4c, 50 °C), and 13,000 (4d, 50 °C) s.

Table 2 collects the corresponding activation barriers for C–C coupling from the methyl-bridged complexes 4a–4e, which

Table 1. Summary of Selected Bond Distances of the gem-Digold Methyl Complexes

| gem-digold methyl complexes | Au–arene* (Å) | Au–Au (Å) | Au–iso carbon of arene (Å) | Au–CH_3 (Å) |
|-----------------------------|--------------|-----------|--------------------------|------------|
| \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{3ppp})]^{+}\) [BAR_2]^- | 3.259(3) | 2.7120(8) | 3.027(3) | 2.210(5) |
| \([\text{Au}_2(\mu-\text{CH}_3)(\text{XPhos})]^{+}\) [NTf_2]^- | 3.321(3) | 2.7120(8) | 3.102(3) | 2.227(4) |
| \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{3ppp})]^{+}\) [NTf_2]^- | 3.400(2) | 2.7330(4) | 3.093(5) | 2.215(5) |
| \([\text{Au}_2(\mu-\text{CH}_3)(\text{PMe}_2\text{Ar}^{6ppp})]^{+}\) [NTf_2]^- | 3.465(2) | 2.7330(4) | 3.185(5) | 2.238(5) |

*Distance from Au to the centroid of the arene rings. aAverage over three independent molecules present in the asymmetric unit.
range from 17.2 kcal/mol at 0 °C for 4a to 26.4 kcal/mol at 90 °C for 4e. To complete these studies, we monitored the evolution of ethane from the gem-digold methyl [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a) in the temperature interval from −20 to 10 °C. An Eyring analysis provided activation parameters of $ ΔH^\ddagger = 20.5 ± 1.3 \text{kcal/mol}$ and $ ΔS^\ddagger = 11.9 ± 4.8 \text{e.u.}$ (Figure 7b), which correspond to $ ΔG^\ddagger_{298} = 16.9 ± 2.7 \text{kcal/mol}$.

To obtain a deeper insight into the nature of the Au species involved in C–C coupling processes, we first considered whether dissociation of complexes 4 into their monometallic components, namely, neutral methyl compounds 1 and triflimide species of type Au(PR₂Ar')(NTf₂), might be relevant. To check the viability of such equilibria, we explored exchange processes of the methyl bridge in compound 4a. In a first experiment, we examined the exchange between 1a and 4a at variable temperatures. For experimental convenience, we accessed an equimolar mixture of both species by adding 0.33 equiv of [Ph₃C][B(C₆F₅)₄] to 1a at −40 °C. Under these conditions, one-third of the neutral methyl compound is

displaced by the gem-digold methyl.

Table 2. Summary of Kinetic Data for Ethane Elimination from gem-Digold Complexes 4a–4e

| compound | T (°C) | k (M⁻¹ s⁻¹) | $ΔG^\ddagger$ (kcal/mol) |
|----------|--------|-------------|------------------------|
| [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a) | 0 | 9.8(3) × 10⁻² | 17.2(1) |
| [Au₂(μ-CH₃)(PMe₂ArMes₂)₂][NTf₂] (4b) | 0 | 4.9(1) × 10⁻² | 17.6(1) |
| [Au₂(μ-CH₃)(PMe₂ArDipp₂)₂][NTf₂] (4c) | 50 | 4.8(3) × 10⁻³ | 22.4(5) |
| [Au₂(μ-CH₃)(PMe₂ArTipp₂)₂][NTf₂] (4d) | 50 | 2.0(1) × 10⁻³ | 22.9(4) |
| [Au₂(μ-CH₃)(XPhos)₂][NTf₂] (4e) | 90 | 5.2(1) × 10⁻⁴ | 26.4(3) |
| [Au₂(μ-CH₃)(tBuXPhos)₂][NTf₂] (4f) | 100⁺ | N.A. | N.A. |

*Methane formation observed instead; N.A. (not available).

Figure 7. (a) Second-order kinetic representation for the consumption of 4a at −5 °C in CD₂Cl₂. (b) Eyring plot for ethane formation from gem-digold methyl [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a).

Scheme 6. (a) Dynamic Me/Me Exchange Equilibrium between [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a) and Au(CH₃)(PMe₂ArXyl₂) (1a) Species at −40 °C; (b) C–C Coupling and Product Distribution in the Reaction between Au(C₂H₅)(PMe₂ArXyl₂) (2a) and [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a); and (c) C–C Coupling and Product Distribution in the Reaction between Au(C₆H₅)(PMe₂ArXyl₂) (3a) and [Au₂(μ-CH₃)(PMe₂ArXyl₂)₂][NTf₂] (4a)
transformed by methyl abstraction into a cationic gold species that is immediately trapped by unreacted 1a to provide gem-digold 4a. Variable temperature $^1$H and $^{31}$P($^1$H) NMR spectroscopy analysis revealed dynamic behavior in solution (Figure S10), which we attribute to the exchange equilibrium depicted in Scheme 6a. It was possible to identify 4a by a $^{31}$P($^1$H) NMR resonance at 0.1 ppm recorded at −85 °C, whereas a broad signal at 21.1 ppm was assigned to 1a. These signals coalesce at approximately −40 °C, while the major component when reaching 25 °C is the homoleptic bisphosphine compound 5a that accompanies ethane formation. We further investigated this dynamic behavior by DFT methods (see the Supporting Information for details). Calculations indicate that dissociation of the dinuclear species [Au$_2$(μ-CH$_3$)(PMe$_2$ArXyl)$_2$][NTf$_2$] (4a) into the corresponding fragments, Au(CH$_3$)(PMe$_2$ArXyl) (1a) and Au-(PMe$_2$ArXyl)(NTf$_2$), is only slightly endergonic (ΔG = +0.5 kcal/mol), in agreement with our experimental results. The kinetic profile of ethane evolution in these equimolar mixtures is identical, within the experimental error, to that of pure 4a.

This suggests that, even if carbon–carbon coupling takes place from a trimetallic species involving the participation of compounds 1, the required dissociation of gem-digold methyl compounds 4 into compounds 1 and [Au(PR$_2$Ar)]$^+$ is not likely kinetically relevant.

Substituting methyl compound 1a by its related ethyl (2a) and phenyl (3a) derivatives showed the formation of cross-coupling products (Scheme 6b,c). In the case of 2a, the formation of propane and butane was apparent by $^1$H NMR spectroscopy, while in the reaction between 4a and 3a the formation of ethane, biphenyl, and toluene was detected in comparable amounts. GC-MS analysis of solution and gas headspace provided further evidence for cross coupling, since variable amounts of ethane, propane, and butane were measured from the reaction between 2a and 4a (Figure S21). In both cases, the main homogeneous gold-containing species when reaching room temperature is 5a.

To gather more information on the exchange between bridging and terminal hydrocarbyl substituents present in gem-digold and neutral compounds, we examined the reaction depicted in Scheme 6b at variable temperatures (Figure 8). A solid mixture of 2a and 4a in equimolar amounts was dissolved in CD$_2$Cl$_2$ at −40 °C to allow the exchange to take place and then cooled to −85 °C. At the latter temperature, the exchange process is halted, and a variety of gold-containing products are identified by $^{31}$P($^1$H) NMR. These include the neutral hydrocarbyl compounds 1a and 2a and their corresponding gem-digold species 4a and [Au$_2$(μ-CH$_3$)(PMe$_2$ArXyl)$_2$][NTf$_2$] (6a), whose broad resonances were recorded at 21.2, 21.9, 0.1, and 1.4 ppm, respectively. Also, sharp signals due to Au(PMe$_2$ArXyl)(NTf$_2$) and [Au(PMe$_2$ArXyl)$_2$][NTf$_2$] (5a) were identified at −4.2 and 10.8 ppm, respectively. The latter likely results from local solution warm-up during sample handling. Increasing the temperature to −40 °C results in coalescence of all prior resonances except for that of 5a, which is clearly not involved in the exchange process. Further raising the temperature to 25 °C leads to full consumption of gold precursors and quantitative formation of bisphosphine compound 5a along with the appearance of solid Au(0).

Having in mind that the above dynamic behavior reveals the presence of compounds 1, 4, and Au(PR$_2$Ar$^+$)(NTf$_2$) in solution, and also considering the fact that ethane evolution follows a second-order dependence on bridging methyl complexes 4, we considered three possible routes (Scheme 7). In the first, reductive coupling from two neutral gold methyl compounds of type 1 may take place, similar to prior work by Kochi and co-workers (Scheme 7a). However, it is important to highlight two distinctive features of our studies that contrast with those prior reports. First, reductive coupling from Au(CH$_3$)$_2$(PPh$_3$) only occurred at high temperatures (−100 °C), while C–C bond formation from bridging digold complexes 4 is more facile. In fact, the C–C coupling reaction readily proceeds at temperatures as low as −60 °C in the case of the PPh$_3$-based system (Figures S8 and S9). Second, whereas a first-order dependence on gold was demonstrated for reductive coupling from Au(CH$_3$)$_2$(PPh$_3$)$_3$, with phosphine dissociation toward “AuMe” as the rate-determining step, we have determined a second-order dependence on digold complexes 4 during ethane evolution. These observations suggest different operating mechanisms in the two cases, a notion that is further supported by DFT methods based on the PMe$_2$ArXyl$^{2-}$ system. In agreement with Kochi’s findings, the computed reaction free energy for the overall process (ΔG$_{298}^{\text{obs}}$ = 16.9 ± 2.7 kcal/mol, see above). Phosphine dissociation from 4a to yield [Au$_2$(μ-CH$_3$)$_2$](PMe$_2$ArXyl)$_2$[NTf$_2$]

Figure 8. Variable temperature of exchange processes between Au(CH$_3$)$_2$(PMe$_2$ArXyl)$_2$ (2a) and [Au$_2$(μ-CH$_3$)(PMe$_2$ArXyl)$_2$][NTf$_2$] (4a) monitored by $^{31}$P($^1$H) NMR spectroscopy.

Scheme 7. Potential Routes for Ethane Evolution with Regards to the Gold Coupling Partners

![Image](https://dx.doi.org/10.1021/jacslett12396)
reaction conditions (Figure S15). Similarly, CH$_3$ its precursors, rendering this pathway inaccessible under the reaction conditions (see above). These studies indicate that those pathways are unfeasible, both in the singlet and triplet state. We also evaluated the possibility of accessing the hypothetical Au(III) species [(CH$_3$)$_2$Au(PMe$_2$ArXyl$_2$)][NTf$_2$] from the above routes, since reductive coupling of ethane with such a complex should be accessible.\textsuperscript{18,29,30} In fact, we found a feasible barrier (+16.1 kcal/mol) for ethane formation from the hypothetical Au(III) complex [(CH$_3$)$_2$Au(PMe$_2$ArXyl$_2$)][NTf$_2$] (Figure S15). However, [(CH$_3$)$_2$Au(PMe$_2$ArXyl$_2$)][NTf$_2$] would be formed alongside the digold(0) species [Au$_2$(PMe$_2$ArXyl$_2$)$_2$], with these species being 42.1 kcal/mol higher in energy than the parent species [(CH$_3$)$_2$Au(PMe$_2$ArXyl$_2$)][NTf$_2$], though this excess of gold-trilimide did not have notable effects on the rate of ethane formation. This was, however, not surprising in line with our computational results, where the larger barrier originates after binding of [Au(PMe$_2$ArXyl$_2$)]\textsuperscript{+} to 4a. Nonetheless, even if Au-(PMe$_2$ArXyl$_2$)\textsuperscript{+} is required to facilitate phosphine

Figure 9. Free energy profile for [Au(PMe$_2$ArXyl$_2$)]\textsuperscript{+}-promoted phosphine migration and formation of masked “AuMe” from Au(CH$_3$)(PMe$_2$ArXyl$_2$) (1a, left) or [Au($\mu$-CH$_3$)(PMe$_2$ArXyl$_2$)$_2$]\textsuperscript{+} (4a, right) complexes; calculated at the oB97X-D/6-31G(d,p) level.
disassociation, its presence may also affect the observed rate of ethane evolution in an opposite manner by reducing the concentration of Au(CH₃)(PMe₂ArXyl₂) (1a) in solution, the latter species also being required for C–C coupling. This is because [Au₂(μ-CH₃)(PMe₂ArXyl₂)](NTf₂) (4a) is in dynamic equilibrium in solution with 1a and Au(PMe₂ArXyl₂)(NTf₂), as discussed above. To circumvent the influence of added Au(PMe₂ArXyl₂)(NTf₂) on that equilibrium, we investigated the effect of adding 5 equiv of BPh₃ as an alternative and less disruptive Lewis acid that could facilitate phosphine dissociation. While ethane evolution proceeded at a rate (t½ = 340 s) comparable to that of pure 4a (t½ = 260 s), we did observe a distinctive change in the kinetic profile. More precisely, this experiment revealed a first-order kinetic dependence on 4a (Figure S7), in contrast to the second-order profile observed when the consumption of the latter was monitored in pure form.

Next, we directed our efforts to examining, by computational means, the role of Au(PMe₂ArXyl₂)(NTf₂) on the pathways and energetics for the formation of ethane (Figure 9). Since we attribute a Lewis acidic role to this fragment, as supported by our experiments with BPh₃, we first studied BH₃ as a simplified Lewis acid. Thus, we examined the reaction between BH₃ and complex Au(CH₃)(PMe₂ArXyl₂) (1a). The formation of a Au–BH₃ adduct is slightly exergonic (ΔG = −0.9 kcal/mol), from which the transition state for the formation of a P–B bond (TS3) lies at +16.2 kcal/mol above the independently computed 1a and BH₃, giving the product at −7.4 kcal/mol (Figure S19). Encouraged by this result, we studied the analogous process with cation [Au(PMe₂ArXyl₂)]⁺ instead of BH₃ as the Lewis acid.63 A transition state for that process (TS4) was found at +29.3 kcal/mol, leading to the formation of a species of formula [(PMe₂ArXyl₂)₂AuAu(CH₃)]⁺, A in Figure 9, that lies at +18.5 kcal/mol and represents a form of masked “AuMe” stabilized by aurophilic and metal–arene interactions with the [Au(PMe₂ArXyl₂)]⁺ fragment. Nonetheless, the large barrier renders this process inaccessible from 4a, in agreement with the experimentally determined second-order dependence on its concentration.

To account for the second-order dependence on 4a, we considered its initial dissociation into 1a and Au(PMe₂ArXyl₂)(NTf₂) (4a), the latter providing 1 equiv of cation [Au(PMe₂ArXyl₂)]⁺ amenable to bind a second molecule of 4a. The resulting trigonal dicationic adduct [Au₂(μ-CH₃)(PMe₂ArXyl₂)]²⁺ (B) plus 1a are only 1.2 kcal/mol above two molecules of 4a (Figure 9). From trinuclear adduct B, the transition state for the formal transfer of a phosphine ligand between gold atoms was found at +21.3 kcal/mol (TS5), close enough to the experimentally determined value for the overall process of ethane evolution. This transition state gives trinuclear species C at +10.7 kcal/mol, from which dissociation of 5a is thermodynamically accessible (ΔG = +2.5 kcal/mol). This would render the bimetallic intermediate [Au₂(μ-CH₃)(PMe₂ArXyl₂)]²⁺ (Figure S20), which is reminiscent of the proposed highly reactive “AuMe” fragment proposed by Kochi.31,32 From such a reactive fragment, massed [Au₂(μ-CH₃)(PMe₂ArXyl₂)]⁺, it is expected that the approach of 1a would result in ethane elimination and formation of colloidal gold, not necessarily in that order.

Our combined experimental/computational approach led us to propose the mechanistic picture for C–C coupling at gem-digold compounds 4 depicted in Scheme 8. Compounds 4 readily dissociate in solution to form 1 and Au(PR₂Ar′)⁺(NTf₂), the latter functioning as a Lewis acid to favor phosphine migration from a second molecule of 4 by forming a trimetallic intermediate of type B.64 Following the release of diphasphine compounds 5, the resulting masked “AuMe” fragment reacts with 1a to liberate ethane with concomitant formation of elemental Au, eventually leading to the formation of Au nanoparticles. In this picture, phosphine migration from 4a constitutes the rate-limiting step of the overall process, in analogy to the previously proposed mechanism for reductive coupling from Au(CH₃)(PPh₃).31,32 In contrast, the remarkable acceleration observed for C–C coupling in compounds 4 compared to 1 seems to be the result of stabilization of key intermediates by the presence of aurophilic interactions combined with the Lewis acidic character of [Au(PR₂Ar′)]⁺ that enables phosphine migration, thus representing an example of rate acceleration by polymetallic entities compared to monometallic counterparts.65–67

**Scheme 8. Proposed Mechanism for the Reductive Coupling of Ethane from gem-Digold Compounds 4**

![Scheme 8](image-url)

**CONCLUSIONS**

Au-mediated C–C coupling processes have rapidly emerged as versatile and powerful strategies for organic synthesis. Despite numerous reports on the synthetic applicability of gold catalysts, mechanistic understanding has evolved at a slower pace. Previous studies have placed the Au(I)/Au(III) redox couple at the heart of all these transformations, while mechanistic investigations on C–C coupling processes without the apparent advent of Au(III) species is lacking. Herein, we have demonstrated that gem-digold methyl complexes [Au₂(μ-CH₃)(PR₂Ar′)]²⁺(NTf₂) (4) promote the homocoupling of the bridging methyl fragments to produce ethane at a remarkably higher rate than from its parent neutral species Au(CH₃)(PR₂Ar′) (1). We have also demonstrated that this approach permits the heterocoupling of the bridging methyl group with ethyl and phenyl fragments. The stability of compounds 4 toward reductive homocoupling is highly dependent on the steric bulk of the phosphine ligand. Whereas the system based on PPh₃ readily liberates ethane at −40 °C, those bearing terphenyl phosphines (PMe₂Ar′) exhibit considerably enhanced stability, which is further increased by the use of the more hindered XPhos and ‘BuXPhos, the latter being unable to mediate C–C coupling even at 90 °C. Our kinetic studies revealed second-order dependence on gem-digold methyl complexes 4 during ethane evolution, whereas a distinctive change toward a first-order dependence on the latter was ascertained in the presence of excess BPh₃ as an external Lewis acid. On the basis of our experimental studies combined with
DFT computational methods we have proposed a mechanism that involves rapid dissociation of a molecule of [Au(μ-CH3)(PMe2Ar)]2[NTf2] (4) toward Au(PMe2Ar)(NTf2) and Au(CH3)(PMe2Ar)⁺ (1). While Au(PMe2Ar)(NTf2) mediates phosphine migration from a second molecule of 4 via a trimetallic intermediate, compound 1 is proposed to react with the resulting highly reactive and masked “AuMe” fragment to effect the C–C coupling event, most likely by a multinuclear gold species. These studies highlight the relevance of multimetallic mechanisms in mediating uncommon transformations, herein also boosting the rate at which the C–C coupling transformation occurs.

### EXPERIMENTAL SECTION

**General Methods.** Unless otherwise noted, all reactions and manipulations were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques with dried and degassed solvents. All solvents were purchased from Sigma-Aldrich and used as received. Chemicals were degassed solvents. All solvents were purified by standard Schlenk techniques with dried and manipulations were performed under a nitrogen atmosphere in a glovebox or using standard Schlenk techniques with dried and degassed solvents.

**General Synthesis of Compounds 1.** A suspension of the corresponding gold chloride precursor AuCl(PR2Ar)2 (0.20 mmol) in toluene (10 mL) was cooled to −78 °C, and a solution of MeMgX (X = Cl or Br; 2.5 equiv) in toluene was added dropwise. The mixture was allowed to warm up slowly for 16 h. The volatiles were removed in vacuo, and the residue was extracted with benzene for 1a–1d or pentane for 1e–1f. Evaporation of the organic solvent led to compounds 1a–1f as white powders in around 60–80% yields. Isotopologue 1a-d was synthesized by the same procedure using freshly prepared CD3MgCl. Suitable crystals of compounds 1 can be obtained by slow solvent evaporation from pentane/Et2O or pentane/dichloromethane solutions.

**General Synthesis of Compounds 4.** A solid mixture of the corresponding gold chloride precursor AuCl(PR2Ar)2 (0.0175 mmol) and Au(CH3)(PMe2ArTripp2)(NTf2) have been authenticated by X-ray diffraction studies and their corresponding CIF files deposited in the Cambridge Crystallographic Data Centre with nos. 2024182–2024189.

### Spectroscopic Data

**NMR Assignments.** The NMR assignments are provided in the Supporting Information (SI). The assignments for all compounds are listed in the SI. The assignments for all compounds are listed in the SI. The assignments for all compounds are listed in the SI.

**Figure 10.** Labeling scheme used for 1H and 13C[1H] NMR assignments.
substances by precipitation with pentane at −20 °C (4c, 4d) or 25 °C (4e, 4f) in around 90% yields. Alternatively 4a–4f can be prepared in comparable by treating compounds 1a–1f with 1/2 equiv of [Ph3P][B(C6F5)4] in dichloromethane by an otherwise identical procedure. Spectroscopic and analytical data for selected compounds (others can be found in the SI). Compound 4b. 1H NMR (400 MHz, CDCl3, −30 °C): δ= 7.61 (t, 2 H, H2), 7.25 (s, 4 H, H4), 7.08 (m, 12 H, H8), 1.98 (s, 24 H, CH2(Xly)) , 1.16 (d, 12 H, 3JHH = 7.7 Hz, PMe6), 0.45 (br. s, 3 H, AuCH3−Au). All aromatic couplings are of ca. 7.5 Hz. 13C{1H} NMR (100 MHz, CDCl3, −30 °C): δ= 147.1 (d, 3JP = 11 Hz, C3), 141.1 (d, 3JP = 5 Hz, C5), 136.7 (C6), 133.3 (CH2), 131.8 (d, 3JC = 8 Hz, CH2), 129.0 (CH2), 128.2 (CH2), 127.8 (d, 3JP = 38 Hz, C1), 21.9 (CH3(Xly)), 16.9 (d, 3JP = 37 Hz, PMe6), 0.6 (AuCH3−Au). 31P{1H} NMR (162 MHz, CDCl3, −20 °C): δ= 1.1. Compound 4d. Anal. Calcld for M+, 1493.8; expt., 1493.8. Compound free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.0c11296.

Synthesis and characterization of new compounds, X-ray diffraction data, information on kinetic studies, variable temperature analysis and exchange experiments, DFT calculations, and MS and NMR spectra (PDF)

XYZ coordinates (XYZ)

Accession Codes

CCDC 2024182−2024189 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.
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