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# Reactivity of [2,6-Bis((dimethylamino)methyl)phenyl]gold(I), an Unusual Intermolecularly Stabilized Bis(amino)aryl−Gold(I) Dimer, toward Alkyl Halides. X-ray Crystal Structures of Its Iodomethane and Methylene Diiodide Adducts[†]

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Novel [2,6-bis((dimethylamino)methyl)phenyl]gold(I) dimer (**4**) was prepared in 60% yield from [AuCl(tht)] (tht = tetrahydrothiophene) and [2,6-bis((dimethylamino)methyl)phenyl]-lithium. Compound **4** is a rare example of a dimeric organogold(I) species involving intermolecular gold(I)−N(sp$^3$) coordination. Variable-temperature NMR points to the formation of a 10-membered ring and provides evidence for the occurrence of a boat−chair ring conformation equilibrium. Reaction of **4** with MeI affords the unexpected heteroaurate(I) [Au(C$_6$H$_3${CH$_2$NMe$_3$}$_2$-2,6)I]I (**5**) by Me transfer to the nitrogen atom of the *ortho* amino ligand. The molecular structure of **5** was elucidated by means of X-ray analysis. Conversely, the reaction of **4** with CH$_2$I$_2$ afforded the organogold(III) complex [Au(C$_6$H$_3${CH$_2$NMe$_2$}-2-{CH$_2$N(Me)$_2$CH$_2$}-6)I]I (**6**), containing a methylene fragment bridging a Au(III) center and a quaternary N center, as confirmed by a single-crystal X-ray diffraction study. A mechanistic pathway involving prior coordination of the alkyl halide to gold(I) followed by oxidative addition and alkyl transfer is proposed to account for the formation of both **5** and **6**.

## Introduction

Organogold(I) chemistry is dominated by the formation of coordinatively unsaturated 14-electron complexes [AuRL] that have generally linear geometry. These compounds are usually obtained by coordination of a monanionic alkyl or aryl group R and a neutral ligand L (e.g., a tertiary phosphine or arsine, isonitrile, tetrahydrothiophene, or more rarely alkylamine) which was initially present in the inorganic gold(I) precursor. However, examples of three- and four-coordinate gold(I) compounds have been reported recently.[1] Gold(I) is also known to form three-center−two-electron bonds, and examples of aryl− and alkyl−gold(I) derivatives (homo- and heteronuclear complexes usually displaying metal−metal bonds and nonlinear geometries) have been described.[2]

Alkyl or aryl groups carrying the donor functionality L can react with gold(I) precursors of the generic type [AuXL′], in which X = halide, displacing X as well as the neutral ligand L′, thus forming cyclic di- or oligogold compounds. Relevant examples include complexes such as [Ph$_2$P(CH$_2$)$_3$Au]$_2$,[3] [{2-C(TMS)$_2$(C$_5$H$_4$N)}Au]$_2$,[4] [Au$_2${C$_6$H$_4$(PPh$_2$)-2}$_2$],[5,6] [Au$_2$(C$_6$H$_4${CH$_2$NMe$_2$}-2)$_2$],[7] or [Au$_2$(Fc{CH$_2$NMe$_2$}-2)$_2$] (Fc = ferrocenyl ligand).[8] The compounds with difunctional phosphines undergo two-center oxidative addition reactions with dihalogens and pseudo-halogens reminiscent of those described for structurally related gold(I) ylide complexes.[9]

Amine complexes of gold(I) are generally regarded as relatively unstable. Several compounds containing ha-

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[†] This contribution is dedicated to Professor Martin A. Bennett on the occasion of his 65th birthday.

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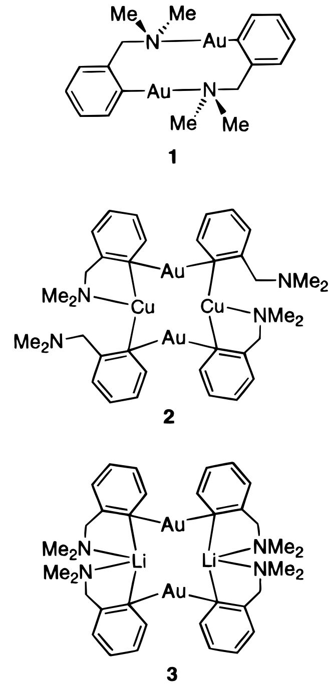
**Chart 1. Structures of Compounds 1−3**



**1**

**2**

**3**

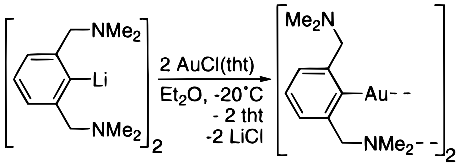
lides and aliphatic amines have been reported recently;[10] the stability of the latter compounds can be attributed partly to the formation of hydrogen bonds involving the N−H functions and partly to aurophilic interactions. To the best of our knowledge, only a few organogold(I) amine compounds have been reported.[11,12] Our group prepared several years ago the complexes $[Au_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_2]$ (**1**),[7] $[Au_2Cu_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$ (**2**),[7] and $[Au_2Li_2(C_6H_4\{CH_2NMe_2\}\text{-}2)_4]$ (**3**).[13] In these compounds the amine function displays different coordination modes, i.e. Au−N bonding in **1**, weak Cu−N interactions in **2**, and Li−N bonding in **3** (Chart 1). The crystal structures of the heteronuclear compounds (**2** and **3**) were confirmed by single-crystal X-ray studies, whereas the structure of **1** was proposed on the basis of spectroscopic and mass spectrometry data.

Since the adopted structures depend to a large extent on both the chelating properties and the number of coordinating groups, we decided to prepare organogold compounds with a second (dimethylamino)methyl group in the *ortho* position of the aromatic ring: i.e., gold(I) compounds derived from the monoanionic pincer ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$, abbreviated as NCN. This second amino group should have an effect on the structural and bonding features of the corresponding organogold complexes as well as on their reactivity. Furthermore, the presence of amino groups in close proximity to the gold(I) center might assist oxidation steps and stabilize the resulting species by *ortho* chelation. The resulting $\eta^3$(N,C,N) coordination of the NCN ligand provides enhanced nucleophilicity on the gold center and achieves a square-planar geometry, which is expected for 16-electron organogold(III) species. Therefore, NCN−Au complexes are anticipated to be good candidates for the study of oxidative addition reactions of gold(I) compounds with dihalides and halogenated compounds. There have been several reports on the preparation of stable gold(III) compounds with the NC ligand $[C_6H_4(CH_2NMe_2)\text{-}2]^-$ [14−20] and their antitumor and antimicrobial activity,[21] while Parish et al. reported on the synthesis and characterization of $[AuCl(NCN)][Hg_2Cl_6]$.[22] However, these NC and NCN complexes were obtained from gold(III) precursors and organomercury reagents.

Here we report on the synthesis, spectroscopic characterization, and behavior in solution of the novel NCN−Au$^I$ complex $[Au(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]_2$ (**4**) as well as its reactivity toward alkyl iodides, which afforded new, unexpected aurate type derivatives.

## Results and Discussion

**Synthesis and Dynamic Behavior of $[Au(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]_2$ (4).** Compound **4** was prepared in reasonable yield by reacting [AuCl(tht)] with 1 equiv of $[Li(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ in diethyl ether at − 20 °C (eq 1).



(1)

The organogold(I) compound **4** is extremely light sensitive when dissolved in benzene, toluene, or $Et_2O$ and moderately light sensitive in the solid state, turning yellow or even gray within a few hours. Compound **4** is very soluble in toluene and benzene and slightly soluble in pentane, whereas it decomposes in halogenated solvents. Solutions of **4** have to be handled below 0 °C to avoid autocatalytic decomposition to metallic gold (which at room temperature occurs within a few minutes). This compound which is dimeric according to FAB mass spectrometry shows a temperature-dependent $^1$H NMR spectrum (Table 1). The observation that over the whole temperature range the aromatic protons remain unchanged excludes dynamic processes involving the aromatic rings. However, the $^{13}C\{^1H\}$ NMR data at +25 °C provides evidence for the asymmetry of the aromatic ring, since five distinct resonances appear in the aro-

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**Table 1. $^1$H NMR Data of $XC_6H_3(CH_2NMe_2R)_2$-2,6 Compounds and Gold Derivatives[a]**

| | | | δ, ppm | | | |
|---|---|---|---|---|---|---|
| X | R | solvent | aromatic | | −$CH_2$− | −$NMe_2$ |
| Br | none | $CDCl_3$ | 7.10−7.30 | | 3.49 | 2.24 |
| H | Me | $D_2O$ | 7.55−0.83 | | 4.62 | 3.10 |
| Au (**4**) | none[b] | $C_6D_5CD_3$ | 7.17 | 6.99 | 3.92 | 2.59 |
| | | | | 7.68 | | 2.30 |
| | none[c] | $C_6D_5CD_3$ | 7.00 | 6.85 | 3.72 | 2.52 |
| | | | | 7.43 | 3.97 | 2.14 |
| AuI (**5**) | Me | $CD_3CN$ | 7.43 | 7.74 | 4.95 | 3.23 |
| AuI (**6**) | $R_1$ = none | $CD_3CN$ | 7.09 | 7.35 | 4.40 | 3.15 |
| | $R_2$ = $CH_2$[d] | | | | 4.50[e] | 3.17 |
| | | $CD_2Cl_2$ | 7.25 | 7.40 | 4.40 | 3.24 |
| | | | | | 4.85[f] | 3.39 |

[a] Chemical shifts are given relative to TMS. [b] Measured at 25 °C. [c] Measured at 100 °C. [d] Measured at 25 °C. [e] Broad signal. At 40 °C it splits into two signals at 4.52 and 4.49 ppm (one of them due to the inserted $CH_2$ group). [f] Measured at 25 °C. Signal of the inserted $CH_2$ group at 4.52 (s) ppm.

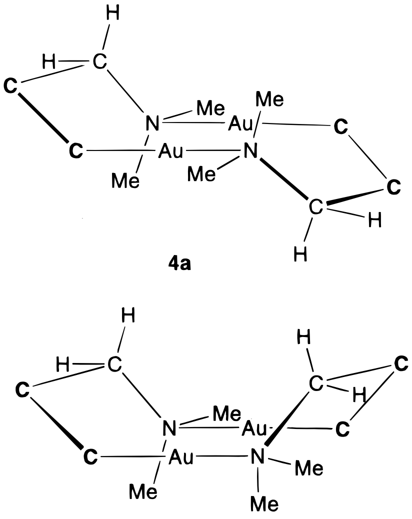


**Figure 1.** Schematic representation of the two possible conformations of the 10-membered chelate ring in **4**.

matic region ($C_{ipso}$ could not be detected). The $^1$H NMR spectrum, at −60 °C, shows one AB and one AX spin system (perfectly resolved) for the methylene protons at $\delta_A$ 3.98, $\delta_B$ 3.85, $\delta_{A'}$ 4.68, and $\delta_X$ 2.98 ppm. These observations are attributed to rigid Au−N coordination over the whole temperature range: i.e., to the presence of a 10-membered ring formed by intermolecular Au−N coordination (see Figure 1 for a schematic structure). One $CH_2NMe_2$ substituent remains uncoordinated (homotopic $NMe_2$ methyl groups, whereas the methylene protons are diastereotopic). The $CH_2$ protons and $NMe_2$ methyl groups of the second, coordinated, $CH_2NMe_2$ substituents are diastereotopic; i.e., the methylene C and the amino N centers are not residing in a molecular symmetry plane. When the temperature was raised from −60 to + 90 °C for both the $CH_2$ and the $NMe_2$ methyl protons, coalescence was observed at ca. +15 °C. At +90 °C the $CH_2$ protons (δ 3.97 and 3.72 ppm) and the $CH_3$ groups (δ 2.53 and 2.14 ppm) appear as two sets of two singlets. Also in the $^{13}C\{^1H\}$ NMR spectra of **4** at +25 °C the $CH_2$ and $CH_3$ groups appear as two sets of two singlets (see Table 2). Together, the $^1$H and $^{13}$C chemical shift patterns point to the inequivalence of the $CH_2NMe_2$ substituents, which indicated that one of the amine substituents remains coordinated even at +90 °C while the other is free.

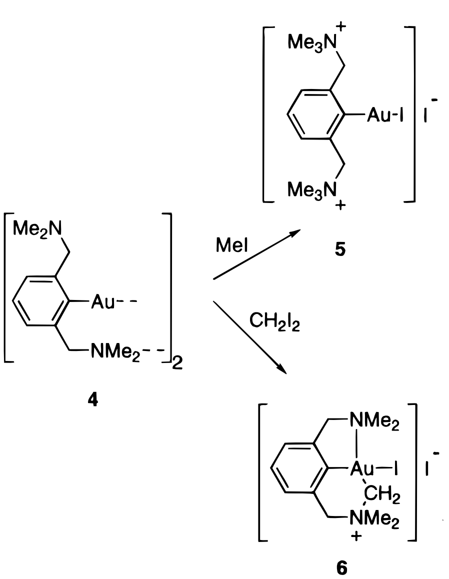
**Table 2. $^{13}C\{^1H\}$ NMR Data of $XC_6H_3(CH_2NMe_2R)_2$-2,6 Compounds and Gold Derivatives[a,b]**

| | | | δ, ppm | | | | |
|---|---|---|---|---|---|---|---|
| X | R | solvent | *o*-$C_6H_3$ | *m*-$C_6H_3$ | *p*-$C_6H_3$ | $CH_2$ | Me C |
| Br | none | $CDCl_3$ | 138.57 | 129.42 | 126.61 | 63.96 | 45.60 |
| H | Me | $D_2O$ | 127.92 | 134.56 | 127.91 | 67.04 | 52.08[c] |
| Au (**4**) | none | $C_6D_6$ | 146.86 | 124.18 | 140.59 | 71.38 | 45.83 |
| | | | 160.61 | 129.84 | | 76.24 | 49.80[c] |
| AuI (**5**) | Me | $CD_3CN$ | 137.20 | 135.51 | 126.15 | 76.56 | 54.63 |
| AuI (**6**) | $R_1$ = none | $CD_3CN$ | 148.43 | 129.91 | 125.65 | 71.56 | 52.87 |
| | $R_2$ = $CH_2$ | | 128.59 | 129.17 | | 71.27 | 54.90[d] |

[a] Measured at 25 °C. [b] In all spectra $C_{ipso}$ could not be observed. [c] Broad. [d] $CH_2$ resonance at 56.27 ppm.

Keeping in mind that **4** (see Figure 1) is a dimeric species and taking into account the preference of gold(I) to adopt linear stereochemistries, the coordination of the amino group must be intermolecular, thus forming a 10-membered ring as shown in Figure 1. Only two conformations, a boatlike and a chairlike one, are possible due to the rigid, linear $C_{ipso}$−Au−N arrangement. From molecular modeling studies (see the Experimental Section)[23] we can infer that one of the conformations (boat, **4b**) is favored energetically and, most probably, represents the only NMR pattern of **4** at low temperature. However, it must be noted that owing to the lack of symmetry in both conformations, **4a** and **4b**, the benzylic protons and the methyl groups of the coordinated *ortho* amino substituent are diastereotopic. The methylene groups of the free $NMe_2$ function remain homotopic, since rapid pyramidal inversion occurs at the nitrogen center. When the temperature is raised, a boat−chair conformational equilibrium becomes fast on the NMR time scale, which renders the proton resonances of the free and coordinated $CH_2$ moieties as well as those of the coordinated $NMe_2$ groups isochronous.

**Reactions with Methyl Iodide and Diiodomethane.** Addition of methyl iodide to a solution of **4** in benzene resulted in quantitative precipitation of the gold(I)−ammonium salt **5** (eq 2).



(2)

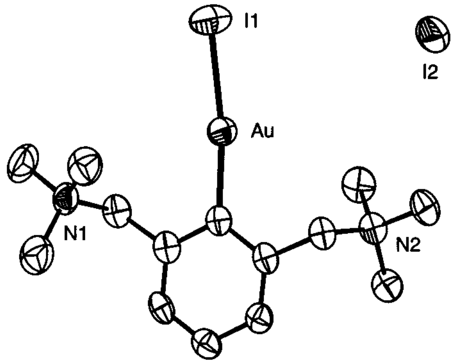


**Figure 2.** Structure of **5**.

Complex **5** is stable to air, light and heat. It is sparingly soluble in polar solvents such as water, ethanol, and acetonitrile but insoluble in benzene, toluene, chloroform, and diethyl ether. The presence of only one signal for the $NMe_3$ moiety in the $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **5** (see Tables 1 and 2) shows that all methyl groups are equivalent, while the downfield chemical shift with respect to free $NMe_2$ in, for example, **4** is as expected for ammonium methyl groups. These observations point to the formation of a symmetrical species with quaternized *ortho* amino substituents. This feature, together with the insolubility of **5**, could only be rationalized by assuming that **5** is actually an ammonium salt, which was confirmed by an X-ray single-crystal structure determination (vide infra).

Reaction of **4** with excess $CH_2I_2$ (eq 2) afforded the gold(III) ammonium species **6**, which, according to its $^1H$ and $^{13}C\{^1H\}$ NMR spectra in $CD_2Cl_2$ and $CD_3CN$, respectively (25 °C), contained three different methylene groups in a 1/1/1 ratio. The presence of five distinct aromatic $^{13}C$ resonances in the $^{13}C\{^1H\}$ NMR spectra at 25 °C points to the formation of an unsymmetrical species, possessing two different type of *ortho* aminomethyl substituents. Furthermore, two broad NMe signals in the $^{13}C\{^1H\}$ NMR spectrum pointed to the occurrence of a dynamic process. which was confirmed by low-temperature $^1H$ NMR measurements. Thus, the four Me groups (coordinated to the two N atoms), which appear as two singlets at 25 °C, finally give rise to four broad signals at − 80 °C, while the three methylene singlets present at 25 °C split to afford three broad sets of AB spin systems. The fact that the methylene groups remained inequivalent over the whole temperature range as well as the observed upfield chemical shifts of one of the $CH_2$ groups suggests that one $CH_2$ fragment is actually bonded to the gold center. The molecular structure of **6** was likewise established using single-crystal X-ray diffraction methods.

**Molecular Structure of the Diiodomethane Adduct 5.** Figure 2 shows the zwitterionic molecular structure and the adopted numbering scheme. Crystallographic data and selected bond distances and angles are given in Tables 3 and 4, respectively.

**Table 3. Crystal Data and Structure Refinement for 5 and 6**

| | **5** | **6** |
|---|---|---|
| | Crystal Data | |
| empirical formula | $C_{14}H_{25}N_2AuI_2 \cdot H_2O$ | $C_{13}H_{21}AuI_2N_2 \cdot CH_3CN$ |
| fw | 690.15 | 697.14 |
| cryst size (mm) | 0.20 × 0.23 × 0.38 | 0.14 × 0.14 × 0.50 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) |
| $a$ (Å) | 9.6280(6) | 13.7685(7) |
| $b$ (Å) | 22.9164(9) | 7.3762(5) |
| $c$ (Å) | 9.0688(5) | 21.8875(11) |
| $\beta$ (deg) | 98.850(10) | 118.352(3) |
| $V$ (Å$^3$) | 1977.11(19) | 1956.2(2) |
| $Z$ | 4 | 4 |
| $D_{calcd}$ (Mg m$^{-3}$) | 2.319 | 2.367 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 10.8 | 10.7 |
| $F$(000), e | 1272 | 1280.0 |
| | Data Collection | |
| $T$ (K) | 293 | 150 |
| $\theta_{min}$, $\theta_{max}$ (deg) | 1.8, 27.5 | 1.7, 27.5 |
| wavelength (Mo Kα), Å | 0.710 73 (graphite monochromated) | |
| data set | −12 to +12; −29 to 0; 0−11 | −17 to +17; −9 to 0; −28 to +21 |
| total no. of data | 4899 | 9347 |
| total no. of unique data | 4517 | 4493 |
| no. of obsd data ($I > 2.0\sigma(I)$) | 3190 | 3758 |
| $R_{int}$ | 0.045 | 0.034 |
| | Refinement | |
| $N_{ref}$, $N_{par}$ | 4517, 187 | 4493, 195 |
| $(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$ | 0.02, 0.00 | 0.00, 0.00 |
| R1, wR2, $S$ | 0.0484, 0.1247, 1.03[a] | 0.0281, 0.0605, 1.01[b] |
| min, max $\Delta\rho$ (e/Å$^3$) | −1.90, 1.48 | −0.95, 1.07 |

[a] $w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 8.458P]$, where $P = (F_o^2 + 2F_c^2)/3$.
[b] $w = 1/[\sigma^2(F_o^2) + (0.027P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

**Table 4. Selected Bond Lengths (Å) and Angles (deg) for $[Au(C_6H_3\{CH_2NMe_3\}_2\text{-}2,6)I]I$ (5)**

| | | | |
|---|---|---|---|
| Au(1)−I(1) | 2.5746(9) | N(1)−C(10) | 1.498(16) |
| Au(1)−C(1) | 2.034(9) | N(2)−C(11) | 1.521(11) |
| N(1)−C(7) | 1.552(13) | N(2)−C(12) | 1.499(13) |
| N(1)−C(8) | 1.481(15) | N(2)−C(13) | 1.486(12) |
| N(1)−C(9) | 1.493 (15) | N(2)−C(14) | 1.493(13) |
| I(1)−Au(1)−C(1) | 171.7(3) | C(11)−N(2)−C(13) | 108.3(7) |
| C(7)−N(1)−C(8) | 112.4(8) | C(11)−N(2)−C(14) | 111.8(7) |
| C(7)−N(1)−C(9) | 105.1(8) | Au(1)−C(1)−C(2) | 118.8(7) |
| C(7)−N(1)−C(10) | 110.6(8) | Au(1)−C(1)−C(6) | 123.9(7) |
| C(11)−N(2)−C(12) | 110.3(7) | | |

Compound **5** is an example of a structurally characterized organogold(I) compound possessing a close to linear trans C−Au−halogen arrangement (C−Au−I = 171.7(3)°). Although several organoaurates(I) of the type Q[AuRX] are known,[8,11,24] only a few have been structurally characterized.[25−27] Examples of neutral [AuRX][28] and cationic [AuRX]X[29] compounds (with R = ylide) have also been reported. However, to the best of our knowledge **5** is the first example of an aurate(I) compound (in which the RAuX arrangement has an overall cationic charge) to be structurally characterized. The Au−C distance (2.034(9) Å) is close to that reported for

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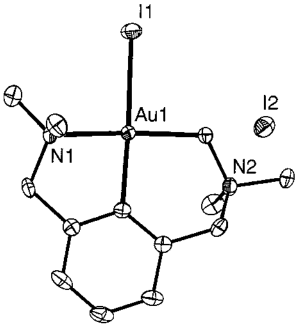

**Figure 3.** Structure of **6**.

**Table 5. Selected Bond Lengths (Å) and Angles (deg) for [Au($C_6H_3${$CH_2NMe_2$}-2-{$CH_2N(Me)_2CH_2$}-6)I]I (6)**

| | | | |
|---|---|---|---|
| Au(1)−I(1) | 2.6600(5) | N(1)−C(9) | 1.498(7) |
| Au(1)−N(1) | 2.158(4) | N(2)−C(10) | 1.505(8) |
| Au(1)−C(1) | 2.019(6) | N(1)−C(11) | 1.498(7) |
| Au(1)−C(13) | 2.037(6) | N(2)−C(12) | 1.507(8) |
| N(1)−C(7) | 1.497(7) | N(2)−C(13) | 1.497(7) |
| N(1)−C(8) | 1.473(7) | | |

| | | | |
|---|---|---|---|
| I(1)−Au(1)−N(1) | 96.73(12) | C(1)−Au(1)−C(13) | 94.3(2) |
| I(1)−Au(1)−C(1) | 176.74(17) | Au(1)−N(1)−C(7) | 106.9(3) |
| I(1)−Au(1)−C(13) | 87.83(16) | Au(1)−N(1)−C(8) | 117.5(4) |
| N(1)−Au(1)−C(1) | 81.5(2) | Au(1)−N(1)−C(9) | 104.5(3) |
| N(1)−Au(1)−C(13) | 171.11(19) | Au(1)−C(13)−N(2) | 119.2(4) |

related gold(I) derivatives [$BnPPh_3$][Au($C_6F_5$)Cl][25] (2.054(17) and 2.042(15) Å), [$NEt_4$][Au(mes)Cl][26] (2.018(7) Å), and [$N(PPh_3)_2$][{Au(mes)}$_2$($\mu$-CN)][26] (2.035(11) Å) or the most recently characterized [$MePPh_3$][Au($C_6F_5$)Br][27] (2.009 Å).

The Au−I distance (2.5746(9) Å) is similar to those found in the isonitrile−gold(I) complexes [(PhNC)AuI] (2.524(1) and 2.523(1) Å) and [(MeOC(O)$CH_2$NC)AuI] (2.538(1) Å), which were the first examples containing a C−Au−I arrangement to be structurally characterized.[30]

**Molecular Structure of the Methylene Iodide Adduct 6.** A view of the molecular geometry of the complex **6**, which crystallizes with one molecule of acetonitrile, is shown in Figure 3.

Selected bond lengths and angles are given in Table 5. The four-coordinate gold(III) center has a square-planar coordination geometry achieved by the newly formed dianionic terdentate N,C,C′ ligand and the iodine atom. The six-membered $AuC_3NC$ and the five-membered $AuC_3N$ chelate rings are distinctly puckered. The C(1)−Au−I angle is 176.74(17)°, indicating an almost perfectly linear arrangement. The Au−C(1) and Au−C(13) distances are 2.019(6) and 2.037(6) Å, respectively, and are slightly longer than the distance found for the only known NCN−gold(III) complex, [Au($C_6H_3${$CH_2NMe_2$}$_2$-2,6}Cl][$Hg_2Cl_6$],[22] of 1.96(2) Å. These Au−C distances are within the range of those found for the NC−organogold(III) compounds [Au(NC)(py)$_2$]$^{2+}$ (2.028(11) Å),[15] [Au(NC)Cl(Ph)] (1.947−2.011 Å),[17] [Au(NC)(phen)($PPh_3$)][$BF_4$] (2.033(11) Å),[18] [Au(NC)($H_2NC_6H_4S$)]$ClO_4$ (2.014(5)) Å),[18] [Au(NC)($C_6F_5$)Cl]$^+$ (2.022(10) Å),[19] [Au(NC)($Et_2NCS_2$)] (2.04(2) Å),[21] [Au(NC)($Me_2NCS_2$)]$^+$ (2.03(2) Å),[21] and [Au(NC)(SCH($CO_2$)$CH_2CO_2$] (2.04(5) Å),[21] in which NC is [$C_6H_4$($CH_2NMe_2$)-2]$^-$. The Au−I(1) distance of 2.6600(5) Å is very similar to that found in **5**.

**Reaction Pathway of the Alkyl Halide Addition.** Prior to the discussion of the reaction pathways to the alkyl halide reaction products **5** and **6** it is important to note that the related platinum(II) and rhodium(I) compounds [Pt($C_6H_3${$CH_2NMe_3$}$_2$-2,6)($H_2O$)]($CF_3SO_3$)[31−33] (**7**) and [[Rh($C_6H_3${$CH_2NMe_2$}$_2$-2,6)(COD)][33,34] (**9**), respectively, react with methyl iodide in a completely different fashion (Scheme 1).

Reaction of **7** with MeI affords the unexpected arenium[35,36] species **8**, formed via an oxidative addition step to afford a $Pt^{IV}$ intermediate (**7′**) followed by 1,2-migration of the methyl group (Scheme 1). This reaction has been found to be reversible.[32] Similar reactions have been observed for related terdentate PCP−metal compounds.[37,38] On the other hand, reaction of the Rh(I) compound **9** with MeI gave only the Rh(III) oxidative addition product [[Rh($C_6H_3${$CH_2NMe_2$}$_2$-2,6)(Me)(I)] (**10**), which showed high stability toward reductive elimination of the C−C-coupled product. Furthermore, although in **9** the NCN ligand displays only $\eta^2$(N,C) chelate bonding, i.e., having a noncoordinating *o*-$CH_2NMe_2$ substituent, a situation similar to that encountered in **4**, the initially free $Me_2NCH_2$ substituent did not react with MeI (even when an excess was used). This fact suggests that the Rh(I) center is a far better Lewis base than the nitrogen center of the free $Me_2NCH_2$ substituent. Thus, in light of these observations and the reported reactivity of organogold(I) species toward alkyl halides (vide infra), the formation of **5** was unexpected. For example, dinuclear gold(I) bis(ylide) complexes react with alkyl halides RX (X = Br, I) to give asymmetrically substituted bicyclic digold(II) compounds. This is a reversible process when R bears electron-withdrawing substituents.[9] Accordingly, the question arose whether formation of **5** proceeds via an oxidative addition step to give a gold(III) intermediate, from which the methyl is transferred to the free N center, or by direct nucleophilic attack of the free amine function of **4** on MeI assisted by the neighboring gold(I) center. It was found that the free arene ligand HNCN itself reacts with MeI but that this reaction was much slower than quaternization of the free amines in **4**. A similar increase in the alkylation rate of trialkylamine (i.e., $NEt_3$) was observed by Crabtree et al. when using the iodomethane complex [$IrH_2$(IMe)$_2$($PPh_3$)$_2$]$^+$.[39] This rate enhancement ($10^4$−$10^5$) was interpreted as resulting from electrophilic activation of the C−I bond by prior coordination to an

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[35] The term "arenium" is preferred to "arenonium", as used by us previously.[33,34] For a discussion of this nomenclature, see: Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808.

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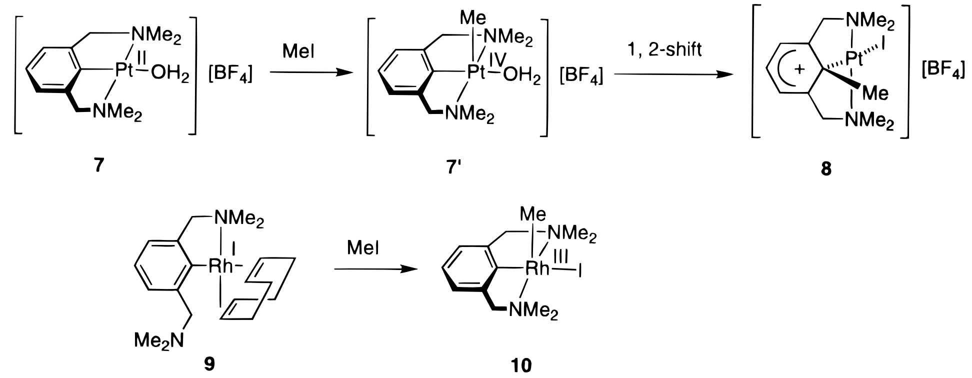
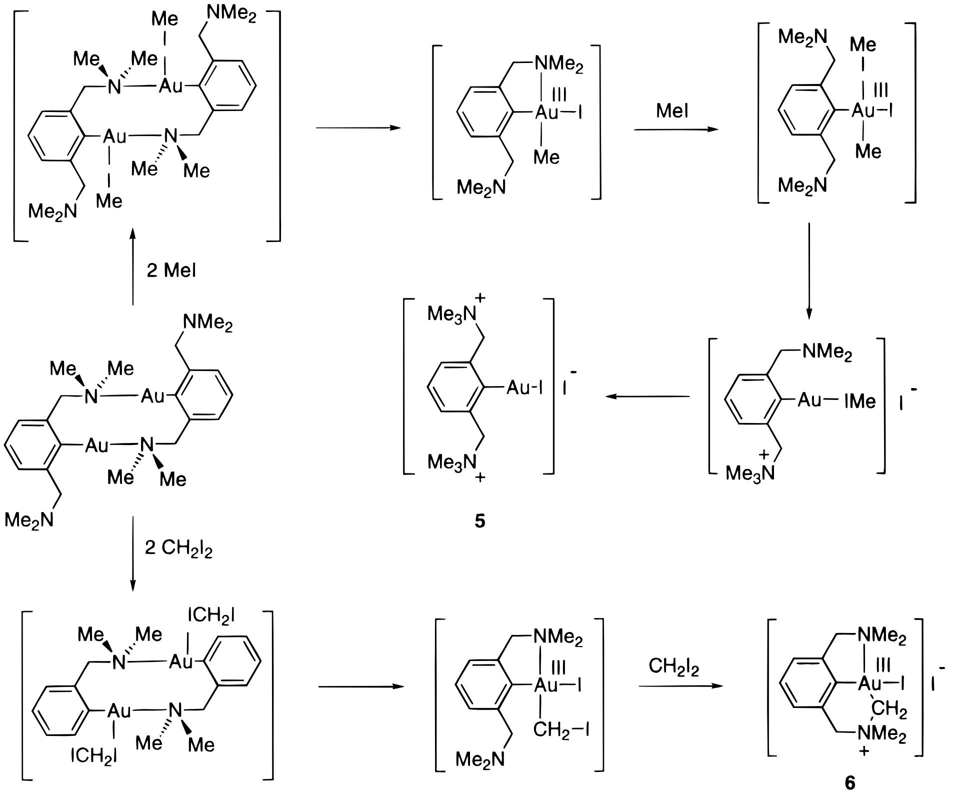
**Scheme 1. Additions of MeI to Pt(II)[32,33,36] and Rh(I)[33,34] NCN Complexes**



**Scheme 2**



iridium(III) center. Similarly, ruthenium and rhenium iodomethane complexes have been reported to be very efficient alkylating agents.[40] In our case, this alkylation can occur intramolecularly because of the close proximity of the nucleophilic amine. Unfortunately, attempts to follow the reaction by NMR spectroscopy (in order to get a quantitative idea of the reaction rate acceleration or to observe such an intermediate) were not conclusive due to the precipitation of **5** in the NMR tube. This also hampers the isolation or characterization of the proposed intermediate gold−iodomethane complex (Scheme 2).

Attempts to stabilize intermediates related to the reaction of **4** with MeI were carried out using the more electrophilic methylene diiodide instead of iodomethane. A priori, several isomers might be formed in this reaction (Chart 2).

However, only isomer **6** could be isolated from the reaction mixture. This seems to indicate that (i) formation of **6′** is not favored, since it might react further to afford species such as **11** and **12**, and (ii) the I−C bond cleavage activates the formed $CH_2I$ intermediate in such a way that subsequent intramolecular rearrangement occurs prior to any other transformation. Furthermore, with methylene dihalides $CH_2X_2$ (X = Cl, Br, I), dimeric gold(I) ylide complexes can undergo a two-center−four-electron oxidative addition reaction to give gold(III) A-frame complexes in which a methylene group bridges two gold centers. While no dinuclear gold(II) halogenoalkyl halide complexes are isolated from the reactions of symmetrical methylene dihalides, the intermediacy of such species is documented for asymmetric substrates (cf. Chart 3).[9]

In the present case the steric requirements of the amino ligands cannot hold the gold atoms in a close proximity (stabilizing a plausible gold(II)−gold(II) in-

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[40] Winter, C. H.; Arif, A.; Gladysz, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 7560.

**Chart 2. Plausible Products of the Addition of $CH_2I_2$ to 4**

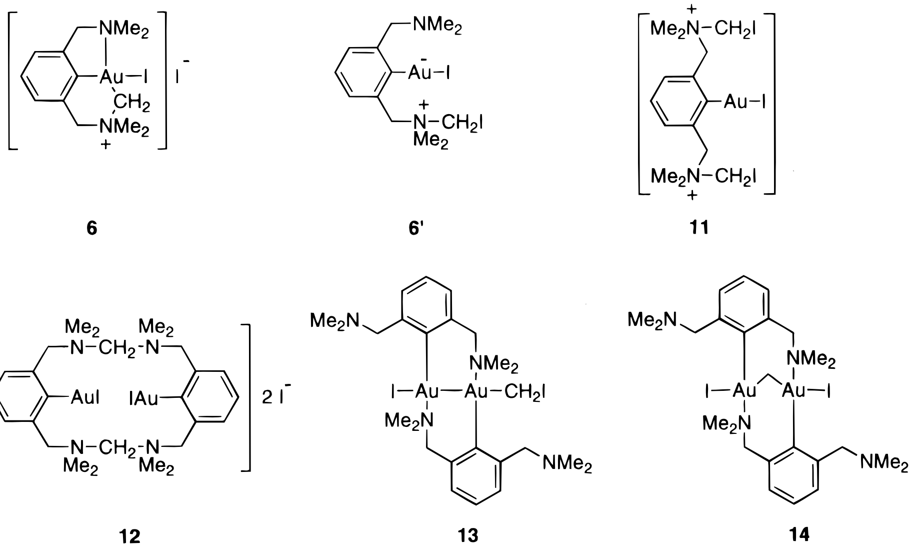
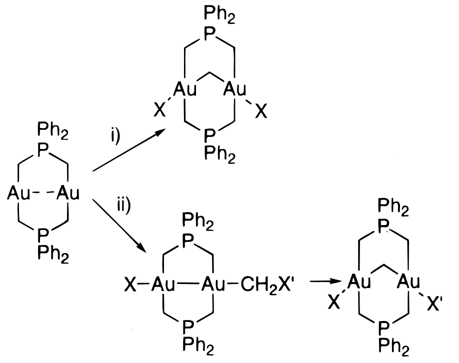


**Chart 3**



termediate), thus preventing formation of dimeric organogold(II) and -(III) compounds such as **13** and **14**. Furthermore, preliminary experiments suggest that dihalogens add oxidatively to **4**. However, the expected cationic gold(III) compounds could not be isolated in a pure state. Such reactions are likely, since the presence of the coordinated amine in **4** enhances the nucleophilicity of the gold atom. All these observations favor a route involving oxidation of **4** to a gold(III) species rather than direct nucleophilic attack of the nitrogen to coordinated $CH_2I_2$ (see Scheme 2).

**Conclusion.** Although a large variety of bridged dimeric gold compounds (not only phosphorus bis(ylide) complexes[9] but also compounds with alkyl or aryl groups carrying the donor functionality $L^{3-8}$) have been prepared, **4** represents a rare example of a dimeric organogold(I) species stabilized by intermolecular coordination of amines. However, these ligands cannot provide **4** with a rigid environment in which the gold(I) atoms are held together; therefore, the reaction of **4** with MeI or $CH_2I_2$ leads to a completely different outcome. In **4** the nitrogen atoms behave as nucleophiles toward MeI and formation of the ammonium groups provides, by charge localization, stabilization of the product **5**. In this respect **5** and **6** are unique examples of organometallic species that possess such localized charges. Furthermore, the different reaction products of related platinum and rhodium complexes possessing the terdentate NCN ligand with MeI clearly illustrate how the nature of the metal tunes the reactivity of their complexes.[33]

## Experimental Section

**General Procedures.** All sensitive organometallic syntheses were performed under a dry and deoxygenated dinitrogen atmosphere using standard Schlenk techniques unless otherwise stated. All solvents were carefully dried and distilled prior to use. Solutions of **4** were handled below 0° C and *protected from light*. All standard chemicals were purchased from Acros Chimica or Aldrich and used without further purification. [AuCl(tht)],[41] the NCN ligand [$m$-$C_6H_4\{CH_2NMe_2\}_2$],[42] and its lithiated derivative [$Li(C_6H_3\{CH_2NMe_2\}_2)$-2,6}][42] were prepared as described in the literature. Proton (200 or 300 MHz) and $^{13}C$ (50 or 75 MHz) NMR spectra were recorded on a Varian Inova 200/300 MHz spectrometer. Chemical shifts are given in ppm using TMS as an external standard. Elemental analyses were performed by Doris and Kolbe, Mikroanalytisches Laboratorium, Mülheim a.d. Ruhr, Germany. Mass spectra (FAB+, nitrobenzyl alcohol as matrix) were obtained from the Analytical Chemical Department of the University of Utrecht.

**[$Au(C_6H_3\{CH_2NMe_2\}_2$-2,6)]$_2$ (4).** *The whole procedure should be carried out below 0 °C, and the glassware has to be protected from exposure to light.* To a stirred suspension of [AuCl(tht)] (0.48 g, 1.5 mmol) in $Et_2O$ (30 mL) was added, at −20° C, a solution of [$Li\{C_6H_3(CH_2NMe_2)_2$-2,6}] (0.33 g, 1.7 mmol) in $n$-pentane (15 mL). The resulting solution was stirred for 1 h at this temperature, followed by removal of the solvent in vacuo. Compound **4** was then extracted with cold toluene. Addition of $n$-hexane and cooling at −20 °C afforded a white microcrystalline powder (0.37 g, 60% yield). $^1H$ NMR ($C_6D_6$, 25 °C): $\delta$ 2.18 (s, 6H, $NMe_2$), 2.40 (s, 6H, $NMe_2$), 3.85 (s, 2H, $CH_2$), 6.88 (d, 1H, $m$-CH), 7.12 (t, 1H, $p$-CH) and 7.64 (d, 1H, $o$-CH) [$^2J_{H-H}$ = 7.8 Hz]. $^{13}C\{^1H\}$ NMR ($C_6D_6$, 25 °C): $\delta$ 45.83 ($CH_3$) and 49.80 (br, $CH_3$), 71.38 and 76.24 ($CH_2$), 124.18 and 129.84 ($m$-CH), 140.59 ($p$-CH), 146.86 and 160.61 ($o$-CH), $C_{ipso}$ not observable. FAB mass spectroscopy: [M] ($m/z$ 389, 13%); [M]$_2$ ($m/z$ 777, 76%). Anal. Calcd for $C_{24}H_{38}N_4Au_2$: C, 37.11; H, 4.93; N, 7.22. Found: C, 37.15; H, 5.07; N, 7.17.

**Molecular Mechanics Calculations.** Molecular modeling studies were carried out using the SPARTAN 5.1 software package with the MMFF set[23] as supplied with the program. Idealized $C_2$-symmetrical models **4a** and **4b** (Figure 1) were

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[41] Usón, R.; Laguna, A.; Laguna, M. *Inorg. Synth.* **1989**, *26*, 85.

[42] Steenwinkel, P.; Jastrzebski, J. T. B. H.; Deelman, B. J.; Grove, D. M.; Kooijman, H.; Veldman, N.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, *16*, 5486.

constructed and then minimized: $E(\mathbf{4a}) = 180.18$ kcal mol$^{-1}$; $E(\mathbf{4b}) = 147.05$ kcal mol$^{-1}$.

**[Au($C_6H_3${$CH_2NMe_3$}$_2$-2,6)I]I (5).** To a stirred solution of **4** (0.062 g, 0.08 mmol) in $C_6H_6$ was added methyl iodide (0.12 mL, 0.2 mmol) via syringe. A white precipitate formed readily, which was collected, washed with *n*-pentane, and then dried (0.051 g, 48% yield). $^1$H NMR ($CD_3CN$, 25 °C): $\delta$ 3.23 (s, 18H, $NMe_3$), 4.95 (s, 4H, $CH_2$), 7.43 (t, 1H, *p*-CH) and 7.74 (d, 2H, *m*-CH) [$^2J_{H-H} = 7.8$ Hz]. $^{13}$C{$^1$H} NMR ($CD_3CN$, 25 °C): $\delta$ 54.63 ($CH_3$), 76.56 ($CH_2$), 126.15 (*m*-CH), 135.51 (*p*-CH) and 137.20 (*o*-CH), $C_{ipso}$ not observable. FAB mass spectroscopy: $M^+$ (*m*/*z* 545), 87%. Anal. Calcd for $C_{14}H_{25}N_2AuI_2$: C, 25.02; H, 3.75; N, 4.17. Found: C, 25.32; H, 3.84; N, 4.05.

**[Au($C_6H_3${$CH_2NMe_2$}-2-{$CH_2N(Me)_2CH_2$}-6)I]I (6).** To a stirred solution of **4** (0.07 g, 0.09 mmol) in $C_6H_6$ was added methylene iodide (0.20 mL, 0.25 mmol) via syringe. A white precipitate formed after 20 min of stirring at room temperature; it was collected, washed with *n*-pentane, and dried (0.077 g, 67% yield). $^1$H NMR ($CD_3CN$): $\delta$ 3.15 (s, 12H, $NMe_3$), 3.17 (s, 12H, $NMe_3$), 4.40 (s, 2H, $CH_2$), 4.50 (br, 4H, $CH_2$), 7.09 (t, 1H, *p*-CH) and 7.35 (d, 2H, *m*-CH) [$^2J_{H-H} = 7.8$ Hz]. $^{13}$C{$^1$H} NMR ($CD_3CN$): $\delta$ 52.87 and 54.90 ($CH_3$), 56.27 ($CH_2$), 71.56 and 71.27 ($CH_2$), 125.65 (*m*-CH), 129.91 and 129.17 (*p*-CH), 128.59 and 148.43 (*o*-CH), $C_{ipso}$ not observable. FAB mass spectroscopy: $M^+$ (*m*/*z* 529), 100%. Anal. Calcd for $C_{13}H_{21}N_2AuI_2$: C, 23.80; H, 3.23; N, 4.27. Found: C, 23.50; H, 3.10; N, 4.15.

**X-ray Structure Determination of complexes 5 and 6.** X-ray data were collected at 293 K (**5**) and at 150 K (**6**) on an Enraf-Nonius CAD4T rotating-anode diffractometer for colorless crystals glued on a Lindemann glass capillary. Numerical details have been collected in Table 3. Unit cell dimensions were derived from the SET4 setting angles[43] of 25 reflections in the ranges 13° < $\theta$ < 17° (**5**) and 10° < $\theta$ < 14° (**6**).The space groups were uniquely determined from the observed systematic extinctions. An empirical correction for absorption was done with PLATON/DELABS.[44]

The structures were solved with Patterson techniques using DIRDIF96[45] and refined on $F^2$ by full-matrix least squares using SHELXL97.[46] Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. A final difference map showed no significant residual features. All other calculations (including ORTEP illustrations) were done with PLATON.[44]

**Acknowledgment.** This work was supported in part (A.L.S.) by The Netherlands Foundation for Chemical Sciences (C.W.) with financial aid from The Netherlands Organization for Scientific Research (N.W.O.).

**Supporting Information Available:** Tables of crystal data, fractional coordinates of the non-hydrogen atoms, anisotropic thermal parameters, fractional coordinates of the hydrogen atoms, bond distances and angles of the non-hydrogen atoms, and bond distances and angles of the hydrogen atoms for **5** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM991043V

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[46] Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.