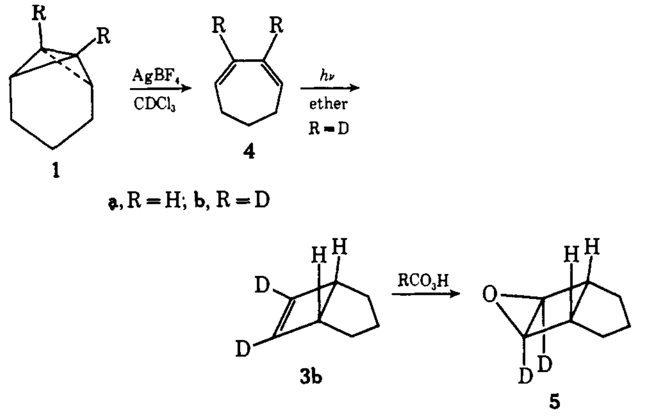
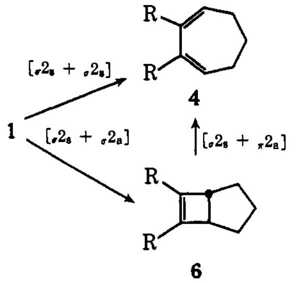
exclusively as in **3b** (absence of vinyl absorption at δ 5.86 in $CDCl_3$).[8]

In dramatic contrast, exposure of dilute $CDCl_3$ solutions of **1a** to catalytic amounts of silver fluoroborate at nmr probe temperatures (~40°) results within minutes in quantitative conversion to *cis,cis*-1,3-cycloheptadiene (**4a**). Bicyclic hydrocarbon **3a** was readily dismissed as a possible intermediate, since it is stable to the reaction conditions for long periods of time. Additionally, the intervention of **2a** was shown to be unlikely on the basis of the observation that *cis,trans*-1,3-cyclooctadiene is not subject to trans → cis isomerization under entirely comparable circumstances, but rather is deposited as a stable complex.[9] No complex formation is visible during the Ag^+-catalyzed rearrangement of **1**.

When **1b** was rearranged in this manner, *cis,cis*-1,3-cycloheptadiene-d_2 was similarly produced in high yield. However, because the four vinyl protons of **4a** appear as a pseudosinglet at δ 5.74 in $CDCl_3$, the deuterium substitution pattern had to be deduced indirectly. To this end, this diene was photolyzed in ether solution.[11] The isolated **3** was shown to be labeled exclusively as **3b**, thus unequivocally identifying the diene as **4b**. Further confirmation of the assignment was derived by epoxidation of the **3b** so produced. As anticipated, the resulting epoxide (**5**) was devoid of >C*H*O- absorption at δ 3.47 ($CDCl_3$).[12]



In view of these data, *it is clear that the rearrangement of* **1** *under conditions of* Ag^+ *catalysis is not governed by the same electronic considerations which control its thermal isomerization.* Rather, the conversion of **1** to **4**, if concerted, is required to be the formal result either of a direct symmetry disallowed $[_{\sigma}2_s + {}_{\sigma}2_s]$ bond reorganization, or of a two-step process involving initial thermally allowed $[_{\sigma}2_s + {}_{\sigma}2_a]$ rearrangement to *trans*-bicyclo[3.2.0]hept-6-ene (**6**) and subsequent $[_{\sigma}2_s + {}_{\pi}2_a]$ ring opening. The first alternative is very attractive for, in addition to being eminently feasible in the thermodynamic sense, it invokes a role for Ag^+ very similar to that observed in the rearrangements of cubyl systems.[1,3] The first step of the second alternative constitutes an example of a long recognized, but previously unrealized, thermally allowed rebonding pathway for bicyclobutanes.[4a,13] Unfortunately, thermodynamic analysis of this step is not possible in the present instance because of the unavailability of **6**. The purely thermal conversion of severely twisted **6** to **4** under very mild conditions would not be unexpected.



The capability of deciding between these alternatives exists and is presently under active investigation. Although the ultimate resolution of this question is of considerable direct importance to an understanding of the mechanistic role played by Ag^+ in this and other[14] bicyclobutane rearrangements, it is now evident that the observed dramatic lowering of transition-state energies is associated not only with relief of strain but also in a very fundamental way with interaction between the strained σ bonds and the atomic orbitals of the noble metal ion.

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[8] In addition, the ratio of bridgehead allylic protons to methylene hydrogens was precisely 1:3.

[9] The stability of the silver nitrate complexes of *cis,trans*-1,3-cyclooctadiene[10a] and *cis,trans*-1,3-cyclononadiene[10b] has previously been recognized. The corresponding cis,cis isomers do not give rise to such complexes.

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[12] The preparation of nonlabeled **5** has been reported: L. A. Paquette, A. A. Youssef, and M. L. Wise, *ibid.*, **89**, 5246 (1967).

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[14] G. R. Allen, Jr., unpublished observations.

[15] (a) Senior Education Awardee, American Cyanamid Company, 1969-1970; (b) National Science Foundation Graduate Trainee, 1970-1971.

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Organosilicon Compounds Containing Monovalent Gold

Sir:

The current interest in the coordination chemistry of gold in its lower valency state[1,2] and of organogold species[3-7] prompts us to report some recent results on the organosilicon chemistry of gold.[8] The findings in

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[8] H. Schmidbaur and M. Bergfeld, *Inorg. Chem.*, **5**, 2069 (1966); M. Bergfeld and H. Schmidbaur, *Chem. Ber.*, **102**, 2408 (1969).

earlier work on siloxy compounds of mercury, thallium, and lead in their higher and lower oxidation states[9,10] had suggested experiments attempting the synthesis of complexes containing gold(I) as part of the moieties Au–O–Si, Au–N–Si, and Au–C–Si, which had not been previously described in the literature.

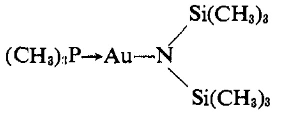
Trimethylphosphinegold(I) chloride has been found to react with equimolar amounts of sodium trimethylsilanolate in diethyl ether at room temperature to yield trimethylphosphinegold(I) trimethylsilanolate (**1**) as a colorless crystalline product (from petroleum ether (50–70°), 80%), mp 79–80°.[11]

$$(CH_3)_3P\rightarrow AuCl + (CH_3)_3SiONa \longrightarrow NaCl + (CH_3)_3P\rightarrow Au{-}O{-}Si(CH_3)_3$$

1

Cryoscopic measurements and mass spectrometry have invariably shown the compound to be a monomer in benzene solution and in the vapor state, respectively. The mass spectral fragmentation pattern (with 1^+ (1) → $Me_3PAuOSiMe_2^+$ (88) → Me_3PAu^+ (53) → Me_3P^+ (100), $Me_3SiOSiMe_2^+$ (54) at 70 eV) further confirms the composition implied by the formula **1**. Benzene solutions exhibit the expected two proton nmr resonances of equal intensity, $\tau(Me_3Si)$ at 10.08 ppm being a singlet accompanied by satellites with $^2J(^1HC^{29}Si)$ = 5.9 Hz, and $\tau(Me_3P)$ at 9.47 ppm being a doublet with $^2J(^1HC^{31}P)$ = 11.6 Hz.[12] The complex is sufficiently volatile to be sublimed *in vacuo* and it is not until 190° that it decomposes with precipitation of a gold mirror and formation of hexamethyldisiloxane, trimethylphosphine oxide, and trimethylphosphine. The infrared spectrum of a Nujol mull shows the stretching vibrations of the inorganic skeleton at 745 and 682 cm^{-1} (PC_3), at 668 and 612 cm^{-1} (SiC_3), at 933 cm^{-1} (SiO), and at 488 cm^{-1} (AuO). ν(AuP) is expected below 350 cm^{-1}.

Tri*phenyl*phosphinegold(I) trimethylsilanolate (**2**), as prepared by the same procedure (75%, mp 145–147°), has very similar characteristics. The *arsenic* analog $(C_6H_5)_3As\rightarrow Au{-}O{-}Si(CH_3)_3$ (**3**), mp 140–143° dec, is of more limited thermal stability. Its solutions are particularly labile and are rapidly decomposed even when kept below room temperature, although the pure crystalline material is less sensitive and may be stored unchanged over a period of several days, if protected against light. Yields are therefore considerably lower (20%).



$$(CH_3)_3P\rightarrow Au{-}N\begin{smallmatrix}Si(CH_3)_3\\ \\ Si(CH_3)_3\end{smallmatrix}$$

4

Trimethylphosphinegold(I) chloride reacts with sodium bis(trimethylsilyl)amide to yield trimethylphosphinegold(I) bis(trimethylsilyl)amide (**4**). This interesting first Au–N–Si species is a soft crystalline solid, mp 35–37°, very soluble in nonpolar organic solvents, which distills as a colorless liquid at 81° under reduced pressure (0.2 mm). Mass spectra again are consistent with a monomeric formula of the proposed composition, as are the ^1H nmr data: $\tau(Me_3P)$ 9.93 ppm (doublet, 9 H, $^2J(^1HC^{31}P)$ = 10.2 Hz), $\tau(Me_3Si)$ 10.03 ppm (singlet, 18 H, $^2J(^1HC^{29}Si)$ = 6.4 Hz), in benzene solution. A tri*phenyl*phosphine analog, $(C_6H_5)_3P\rightarrow Au{-}N[Si(CH_3)_3]_2$ (**5**), mp 120–123°, is not volatile, but molecular weights found in benzene solution again correspond to the monomer.[9] The silicon–nitrogen stretching vibrations for **4** and **5** appear at 1005 cm^{-1}. The ν(Au–N) and ν(Au–P) bands have not yet been located and are expected below 350 cm^{-1}. $(C_6H_5)_3As\rightarrow Au{-}N[Si(CH_3)_3]_2$ (**6**), mp 41–43°, resembles **4** and **5**, though being somewhat less stable.

Triphenylphosphine(trimethylsilylmethyl)gold(I) (**7**) was obtained in small to moderate yields from triphenylphosphinegold(I) chloride and trimethylsilylmethyllithium in diethyl ether at temperatures between −30 and −20°. Compound **7**, a white crystalline solid, mp 111–112.5°, was identified by its proton nmr spectrum which showed the crucial vicinal $^1H{-}C{-}Au{-}^{31}P$ coupling for the methylene protons (τ 9.82 ppm, doublet, $^3J(^1H_2CAu^{31}P)$ = 10 Hz), along with the Me_3Si singlet (τ 10.07 ppm, $^2J(^1H_3C^{29}Si)$ = 6.5 Hz), and a phenyl multiplet (τ 3.0 ppm, in dioxane). Compound **7** is the prototype of an organogold–phosphine complex bearing a silicon substituent in the α-carbon position, which clearly lowers the overall thermal stability of the compounds. This is immediately obvious from its general behavior, if compared with that of the nonsilylated alkylgold species.[13] The solid and its solutions decompose readily upon standing. Attempts to prepare the corresponding tri*methyl*phosphine or triphenyl*arsine* complexes met with no success.

$$(C_6H_5)_3P\rightarrow Au{-}Cl + (CH_3)_3SiCH_2Li \longrightarrow LiCl + (C_6H_5)_3P\rightarrow AuCH_2Si(CH_3)_3$$

7

The structures of the compounds **1**–**7** are assumed to be linear at sp-hybridized gold atoms. In the absence of a phosphine or arsine donor, which is essential for the completion of the valency configuration of the metal, the above types of organosilicon derivatives of gold are not stable. The corresponding gold(III) derivatives can reach a stable configuration in the absence of a suitable donor molecule by an intermolecular coordination interaction.[8] No such coordination phenomenon has been detected with gold(I) analogs, though some phosphine*copper*(I) aryloxides are known to be associated *via* metal–oxygen bridges.[14] Work on organosilicon derivatives of the lighter coinage metals is now in progress.

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