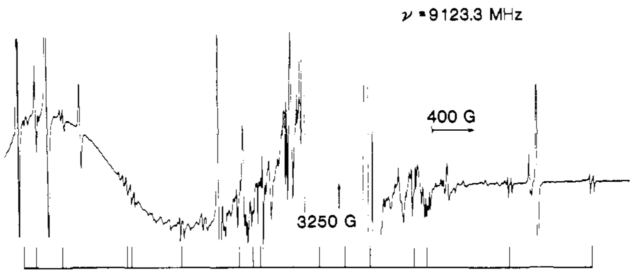

Figure 1. ESR spectrum of C_6D_6 containing ^{63}Cu and ^{107}Ag at 100 K. The stick diagram indicates the calculated line positions.

Table I. ESR Parameters for $^{107}Ag_3$, $^{63}Cu_3$, and $^{63}Cu^{107}Ag^{63}Cu$

trimer	*g* factor	a_M- (terminal), G	$\rho_M{}^a$	a_M- (central), G	$\rho_M{}^a$
Ag_3	1.9622	295	0.44	38.5	0.06
Cu_3	1.9925	625.5	0.29	55.6	0.026
CuAgCu	1.9621	880.5	0.41	35.5	0.054

^{a} Unpaired spin population on the metal atom M.

We report here the first positive ESR identification of a neutral mixed triatomic transition-metal cluster, CuAgCu, which has been produced at 77 K by cocondensing ^{63}Cu atoms ($I = {}^3/_2$), ^{107}Ag ($I = {}^1/_2$) atoms, and C_6D_6 on the cold surface of a rotating cryostat.[7,8] Isotopically pure silver (98.22% ^{107}Ag)[9] and copper (98.89% ^{63}Cu)[9] were chosen for these experiments because of the anticipated complexity of the spectra from natural copper and silver.

The EPR spectrum obtained by cocondensing the reactants in the order ^{63}Cu, ^{107}Ag, and C_6D_6 and annealing to 100 K is shown in Figure 1. It is dominated by almost isotropic features from $Cu(C_6D_6)$ and $Ag(C_6D_6)$[10] and a multitude of isotropic lines in the $g \sim 2$ region. In addition to these features there are a number of weaker doublets that occur at fields from ~300 to ~5650 G (ν 9123.3 MHz). These doublets are due to a single unpaired electron that shows equal, large isotropic hyperfine interactions with two equivalent nuclei with $I = {}^3/_2$ and a further, small interaction with a third nucleus with $I = {}^1/_2$. Of the 16 doublets expected for two equal, large hyperfine interactions, four were obscured by other features in the spectrum. The field centers of the remaining groups were used in conjunction with the Breit–Rabi equation[11] to obtain an exact solution of the isotropic spin Hamiltonian: $g_{iso} = 1.9621$, $a(2) = 880.5$ G. The average of the measured splittings of the doublets gave $a(1) = 35.5$ G. The large hyperfine interaction (hfi) is assigned to two terminal copper nuclei on the basis of two equivalent nuclei with $I = {}^3/_2$ and because the hfi of 880.5 G is much larger than the hfi for unit 5s spin population on a ^{107}Ag nucleus (653 G[12]). The small doublet can clearly be assigned to the central Ag nucleus of the mixed transition-metal trimer CuAgCu.

Using the one-electron parameters for ^{63}Cu (2150 G[12]) and ^{107}Ag, the value of $a_{63}(2) = 880.5$ G gives 4s unpaired spin populations of approximately 41% for each of the terminal copper atoms and the value of $a_{107}(1) = 35.5$ G gives a 5s unpaired spin population of approximately 5.4% for the central silver nucleus.

The ESR parameters for Ag_3, Cu_3, and CuAgCu are given in Table I. It is apparent from these data that ρ for the terminal Cu nuclei of CuAgCu is much larger than the corresponding ρ for Cu_3 and approaches ρ for the terminal nuclei of Ag_3. The negative ρ for the silver nucleus of CuAgCu is also closer to the negative ρ for the central Ag nucleus of $^{107}Ag_3$ rather than the central Cu nucleus of $^{63}Cu_3$, which is consistent with the difference in the unpaired spin populations on the terminal nuclei of $^{107}Ag_3$ and $^{63}Cu_3$.

We conclude from the similarities of the unpaired spin populations and *g* factors for $^{107}Ag_3$ and $^{63}Cu^{107}Ag^{63}Cu$ that these two triatomic clusters have similar structures. That is, CuAgCu is slightly bent with a $^2B_2$ electronic ground state in C_{2v} symmetry. The difference in ρ' s for Cu_3 and CuAgCu suggests a difference in the obtuse angle of the isosceles triangle for these species and is perhaps good evidence for a nonlinear structure.

There is evidence in the ESR spectrum produced by cocondensing Cu and Ag for the other triatomic clusters, i.e., CuCuAg, AgAgCu, and AgCuAg. These species, however, do not cover as large as field range as CuAgCu, which in conjunction with spectral overlap makes them difficult to positively identify.

Experiments similar to the ones described in this communication have been performed with ^{197}Au and ^{107}Ag, and we have tentatively identified triatomic clusters in this system. These species have, however, not yet been fully analyzed and will be the subject of a future publication.

Registry No. $AgCu_2$, 52373-99-6.

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(7) Bennett, J. E.; Thomas, A. *Proc. R. Soc. London, Ser. A* **1964**, *280*, 123–138.

(8) Bennett, J. E.; Mile, B.; Thomas, A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1–77.

(9) ^{107}Ag and ^{63}CuO were obtained from Oak Ridge National Laboratory, TN. ^{63}CuO was reduced to ^{63}Cu with H_2 at 500 °C.

(10) Buck, A.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.*, in press.

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(12) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577–582.

Free-Radical Rearrangement of a Silyl Radical via Net 1,2-Migration of an Acetoxy Group

James W. Wilt* and Steven M. Keller

Department of Chemistry, Loyola University of Chicago
Chicago, Illinois 60626

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Among the outstanding differences between the rearrangement of carbon and silicon radicals is the scarcity of vicinal 1,2-shifts observed with the latter.[1] A notable example is the vicinal migration of chlorine, a well-known process for carbon radicals[2] but not for silicon radicals.[3] Of present interest is the vicinal migration of the acetoxy group in a carbon radical.[4,5] Although the exact nature of the rearrangement is still somewhat problematical, it is a radical-chain sequence that exchanges the oxygen atoms of the acetoxy group.[6]

We report that this vicinal rearrangement (or at least its net effect) is also exemplified by the silicon radical analogue. (Acetoxymethyl)dimethylsilane (**1**) was synthesized by reductive cleavage[7] of the disiloxane **2**[8] as shown in eq 1. Acetate **1** is a

$$\underset{\mathbf{2}}{(\mathrm{AcOCH_2SiMe_2})_2\mathrm{O}} \xrightarrow[\text{ether, }\Delta]{\mathrm{LiAlH_4}} \xrightarrow{\mathrm{Ac_2O}} \underset{\mathbf{1}\ (40\text{–}45\%)}{\mathrm{AcOCH_2SiHMe_2}} \qquad (1)$$

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(1) For reviews, cf.: Jackson, R. A. *Adv. Free-Radical Chem.* **1969**, *3*, 278. Brook, A. G.; Bassindale, A. R. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 2, pp 172–173. Wilt, J. W. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Publishing: New York, 1983; Vol. 3, pp 159–174.

(2) Cf.: Wilt, J. W. "Free Radicals"; Kochi, J., Ed.; Wiley: New York, 1973; Vol. 1, pp 362–267.

(3) The seemingly analogous process with silicon radicals actually involves no vicinal shift but rather is the result of two consecutive chain processes; Jung, I. N.; Weber, W. P. *J. Org. Chem.* **1976**, *41*, 946.

(4) Surzur, J.-M.; Teissier, P. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1967**, *264*, 1981; *Bull. Soc. Chim. Fr.* **1970**, 3060. Tanner, D. D.; Law, F. C. P. *J. Am. Chem. Soc.* **1969**, *91*, 7535.

(5) For a recent study with additional references, cf.: Barclay, L. R. C.; Griller, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1982**, *104*, 4399.

(6) Beckwith, A. L. J.; Tindal, P. K., *Aust. J. Chem.* **1971**, *24*, 2099. Beckwith, A. L. J.; Thomas, C. B. *J. Chem. Soc., Perkin Trans. 2* **1973**, 861.

(7) For such cleavages of disiloxanes, cf.: Schumb, W. C.; Robinson, D. W. *J. Am. Chem. Soc.* **1955**, *77*, 5294. Harvey, M. C.; Nebergall, W. H.; Peake, J. S. *Ibid.* **1957**, *79*, 1437.

(8) Speier, J. L.; Daubert, B. F.; McGregor, R. R. *J. Am. Chem. Soc.* **1949**, *71*, 1474.

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colorless mobile liquid with a powerful banana oil odor, air-stable but exceedingly sensitive to acids; bp 120–122 °C; ^{1}H NMR (CCl_4, Me_4Si) δ 3.83 (1 H, m, SiH), 3.70 (2 H, d, $J = 3$ Hz, CH_2), 1.93 (3 H, s, $OCOCH_3$), 0.10 (6 H, d, $J = 4$ Hz, CH_3Si); IR (neat) ν 2180 (SiH), 1730 (C=O), 1260, 845 (CH_3SiCH_3) cm^{-1}. Anal. Calcd for $C_5H_{12}O_2Si$:C, 45.41; H, 9.15. Found: C, 44.91; H, 9.11. When **1** was irradiated[9] in a quartz NMR tube at 254 nm in hexadecane solvent containing carbon tetrachloride in varying concentrations,[10] decane (internal standard), and a 0.1 mol equiv of di-*tert*-butyl peroxide (DTBP) as initiator, the formation of the rearranged and principal product (chloromethyl)dimethylacetoxysilane (**3**) was rapid (eq 2) and readily

$$\mathbf{1} \xrightarrow[\text{decane, } h\nu]{\text{DTBP, CCl}_4} \underset{\mathbf{3}}{ClCH_2SiMe_2OAc} + \underset{\mathbf{4}}{ClSiMe_2CH_2OAc} \qquad (2)$$

followed by the development of its CH_2Cl singlet resonance at δ 2.87. The concentration of 1 M **1** dropped to ca. 0.05 M within 3 h. Reaction in Pyrex at 366 nm[9] was similar but considerably slower. A sample of **3** collected on an SE-30 column at 100 °C was shown to be identical with material synthesized independently.[11] (Acetoxymethyl)dimethylchlorosilane (**4**) and *tert*-butyl alcohol were also observed.[12] The preponderance of **3** over **4** was maintained even as the concentration of carbon tetrachloride was increased from 1 to 5 mol equiv.[13] A detailed analysis of the effect of the relative concentrations of **1** and carbon tetrachloride upon the amounts of **3** and **4** is incomplete, but it is probable that no single-chain sequence is operative. One likely partial chain sequence is shown in eq 3–7. No evidence is available as yet upon

$$\text{DTBP} \xrightarrow{h\nu} t\text{-BuO}\cdot \qquad (3)$$

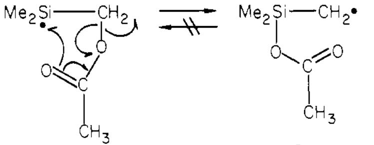
$$\mathbf{1} + t\text{-BuO}\cdot \rightarrow \underset{\mathbf{1}\cdot}{\cdot SiMe_2CH_2OAc} + t\text{-BuOH} \qquad (4)$$

$$\mathbf{1}\cdot \xrightarrow{\overset{k_5}{\Omega}} \underset{\mathbf{3}\cdot}{AcOSiMe_2CH_2\cdot} \qquad (5)$$

$$\mathbf{3}\cdot + CCl_4 \rightarrow \mathbf{3} + \cdot CCl_3 \qquad (6)$$

$$\mathbf{1}\cdot + CCl_4 \xrightarrow{k_7} \mathbf{4} + \cdot CCl_3 \qquad (7)$$

the possible chain-termination steps or upon the exact nature of the rearrangement step (eq 5). The high bond strength of the Si–O bond formed makes the provisional path in eq 8 attractive.



1· **3**· (8)

Both oxygen-18 and "mixing" studies are planned to establish the mechanism more definitively. In any case, the acetoxy shift is apparently not reversible. Treatment of **3** with tri-*n*-butyltin hydride (TBTH) led only to acetoxytrimethylsilane (**5**, identical with commercial material) as shown in eq 9, even at low concentrations of TBTH.[15]

$$\mathbf{3} \xrightarrow[\text{AIBN, hexadecane, 366 nm}]{\text{TBTH}} \underset{\mathbf{5}}{Me_3SiOAc} \qquad (9)$$

Complicating the chain sequence given above is the hidden fact that **1** itself can compete with carbon tetrachloride as a chain transfer agent. To simplify the situation, a second rearrangement study was undertaken. When **1** was irradiated at 366 nm in Pyrex as before but with *no* added carbon tetrachloride, rearranged silane **5** formed. For example, 1 M **1** so treated for 3 h was consumed to the extent of 39% as **5** was formed to the extent of 26% (a 67% yield). Addition of **3** to this reaction left **3** unaffected, showing that its reduction to **5** by **1** was not an additional complication in the first rearrangement study.[16] On the other hand, addition of 0.05 M galvinoxyl inhibited the reaction of 1 M **1**, essentially halving its rate.[17] Moreover, control studies showed (a) no reaction occurred at 40 °C (the temperature reached in the apparatus[9]) without irradiation, (b) no reaction occurred at 366 nm in the absence of DTBP, and (c) **5** itself was stable under the reaction conditions used. From these results another radical-chain sequence may therefore be postulated as shown in eq 10–13. The

$$\text{DTBP} \xrightarrow{h\nu} t\text{-BuO}\cdot \qquad (10)$$

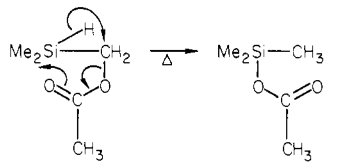
$$\mathbf{1} + t\text{-BuO}\cdot \rightarrow \mathbf{1}\cdot + t\text{-BuOH} \qquad (11)$$

$$\mathbf{1}\cdot \xrightarrow{\Omega} \mathbf{3}\cdot \qquad (12)$$

$$\mathbf{1} + \mathbf{3}\cdot \rightarrow \mathbf{5} + \mathbf{1}\cdot \qquad (13)$$

ability of **1** to serve as a chain transfer agent (eq 13) undoubtedly competes with eq 6 of the earlier sequence and complicates the product vs. concentration relationship expected for each chain.

A final factor in this rearrangement is the thermal "dyotropic" rearrangement[18] of **1** to **5** (eq 14). With 1 M solutions of **1** this



1 **5** (14)

rearrangement became significant at ca. 130 °C. With higher concentrations it was observed to a slight extent even at 100 °C.[19] In no way, however, could this process account for the clearly radical rearrangement found under the present conditions.

Ongoing work is aimed at the clarification of the mechanistic features of this radical rearrangement as well as a search for others of this exceedingly rare breed.

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(9) A small dual lamp irradiator (Bradford Scientific, Epping, NH) was used for these reactions. The 254-nm lamp was a low-wattage germicidal bulb (GE G4T4). The 366-nm lamp was a coated GE F 4T4-BL tube.

(10) Specifically, studies were carried out on 1 M solutions of **1** that were 0.2, 1, and 5 M in carbon tetrachloride together with the other components listed.

(11) Jakoubková, M.; Reich, P.; Papoušková; Novák, P.; Pola, J.; Chvalovský, V. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3471.

(12) The structure of **4** is provisional and is based upon assumed spectral characteristics. Its independent synthesis has not yet been accomplished.

(13) Clearly CCl_4 is not an effective transfer agent. Others are under investigation. As $k_7 \sim 4.6 \times 10^9$ M^{-1} s^{-1},[14] it is clear that k_5 will be quite large because [**3**] > [**4**] even in excess CCl_4. Continuing work hopefully will provide precise values for this and other rate constants.

(14) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5123.

(15) Extensive results on the reduction of α-halosilanes with organostannanes may be found in the following: Belmonte, F. G. Ph.D. Dissertation, Loyola, 1981. Zieske, P. A. M.S. Thesis, Loyola, 1981. The work is being readied for publication.

(16) Silicon hydrides are considerably less effective than their tin hydride congeners in such reductions.[15] Nevertheless, reduction by silicon hydrides can occur under more vigorous conditions than those used here. Cf.: Wilt, J. W.; Chwang, W. K.; Dockus, C. F.; Tomiuk, N. M. *J. Am. Chem. Soc.* **1978**, *100*, 5534.

(17) Preliminary results indicate a chain length of ca. 10 for the conversion of **1** to **5** under the conditions used.

(18) Cf.: Brook, A. G.; Bassindale, A. R., ref 1, pp 151–161. Much of the work on such processes has been done by Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 129; *Tetrahedron* **1973**, *29*, 2189.

(19) All chromatographic studies were corrected for the small extent of dyotropic rearrangement that occurred during such analyses.