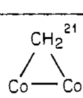
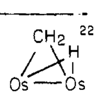
Table II. Mode Assignments for Methylene on Ru(001) (with Isotopic Shift Ratios) Compared to Those of CH_2I_2 and Relevant Organometallic Complexes

mode	$>CH_2$ on Ru(001)[a]	$\nu(CH_2/CD_2)$	CH_2I_2[23]	 [21]	 [22]
ν_s(MCM)	460 (m)	1.0		467	
δ(MCM)	550 (w)	*b*		566	
ν_a(MCM)	650 (w)	1.04	484	635	660
CH_2 rock	775 (sh)	*b*	716	774	811
CH_2 twist	900 (s)	1.33	1031	906	869
CH_2 wag	1135 (s)	1.35	1105	1127	961
CH_2 scissors	1450 (s)	1.20	1350	1360	1428
$\nu_s(CH_2)$	2940 (s)	1.33	2967	2918	2935
$\nu_a(CH_2)$	3050 (m)	1.33	3047	2981	2984

[a] $>CH_2$ from both C_2H_4 and CH_2N_2. [b] Not resolved.

An energy loss spectrum for a coverage of approximately 10^{15} methylenes/cm^2, corresponding to an exposure of 0.8 L (1 L $\equiv$ 10^{-6} torr s), on Ru(001) at 80 K is shown in Figure 1a. For comparison, a similar spectrum corresponding to an exposure of 0.1 L of diazomethane on Ru(001) is shown in Figure 1b. All pressures reported are uncorrected ionization gauge readings. The electron energy loss measurements of Figure 1 were made in the specular direction with an incident energy of approximately 4 eV and a resolution of approximately 60 cm^{-1} (fwhm of the elastically scattered beam).

At surface coverages below one monolayer (cf. Figure 1, a and b), the ethylene and diazomethane spectra are identical. Adsorbing successively increasing coverages of both ethylene and diazomethane results in multilayer formation as judged by the fact that the electron energy loss spectra agree well with IR spectra of the molecular species (cf. Table I).[19,20] In addition, complementary thermal desorption mass spectra show that molecular ethylene desorbs only below 115 K from a condensed multilayer. Spectra similar to Figure 1, a and b, are obtained on annealing these multilayers between 120 and 180 K. The first layer, which adsorbs dissociatively to $>CH_2$ at 80 K, decomposes to yield surface carbon and hydrogen. This hydrogen desorbs at 345 K, independent of coverage. No hydrogen associated with the ruthenium substrate is observed unless H_2 is either preadsorbed or postadsorbed with the ethylene. When approximately $^1/_4$ monolayer of H_2 is adsorbed prior to an exposure of 1 L of C_2D_4, complete isotopic mixing occurs, and two thermal desorption peaks are observed, one reaction-limited, at 345 K, the other desorption-limited, at 400 K.

Interpretation of the electron energy loss spectra of the dissociated fragments was facilitated by a comparison with high-resolution FT IR spectra of $(\mu\text{-}CH_2)[CpCo(CO)]_2$ and $(\mu\text{-}CD_2)[CpCo(CO)]_2$ in KBr,[21] kindly provided by Theopold and Bergman, and recent vibrational spectra of metal cluster complexes published by Oxton et al.[22] The assignment of bridging methylene on Ru(001) was made by comparing the energy loss spectra with these IR data together with those of CH_2I_2,[23] as summarized in Table II.[24] The presence of terminal methylenes was ruled out on the basis of observed ν_s(RuCRu) and ν_a(RuCRu) modes. Formation of ethylene from possible surface diffusion of $>CH_2$ on Ru after dissociation is both not expected at 80 K and not observed in the spectra at this temperature.

On warming the surface to 180 K, the $>CH_2$ scissors mode decreases in intensity, and a peak at 1373 cm^{-1} emerges. This can be attributed to the formation of CH_3 groups.[25] By 280 K, the energy loss spectra indicate a combination of CH_2, CH, CH_3, and C species of which the hydrocarbon fragments decompose below 500 K. At 700 K, only carbon remains on the Ru, as evidenced by peaks at 820 and 600 cm^{-1}. On the basis of reactions with O_2 and CO, we tentatively assign the 820-cm^{-1} peak to a C–C stretch while assigning the 600-cm^{-1} peak to a C–Ru stretch.

Further experiments are currently underway to examine the reactions of this bridging methylene with reagents of catalytic interest.

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Registry No. $(\mu\text{-}CH_2)[CpCo(CO)]_2$, 74656-87-4; $(\mu\text{-}CD_2)[CpCo(CO)]_2$, 84623-10-9; carbon monoxide, 630-08-0; ruthenium, 7440-18-8; diazomethane, 334-88-3; ethylene, 74-85-1; methylene, 2465-56-7; methyl, 2229-07-4; methylidyne, 3315-37-5; diiodomethane, 75-11-6.

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(24) In some cases, peak positions have been identified from spectra with better resolution than those shown in Figure 1.

(25) Cf. IR spectra of CH_3X (X = Cl, Br, I), ref 19, pp 51–53.

ESR Spectrum of Matrix-Isolated CuAgCu[1]

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A small number of triatomic clusters have been identified by electron spin resonance spectroscopy since Lindsay et al.[2] first detected Na_3. K_3 has been observed by Thompson and Lindsay[3] while we have recently prepared Ag_3[4] and Cu_3.[5] ESR spectra indicate that these four trimers are chemically bound, with singly occupied molecular orbitals that have predominantly s character. Na_3, K_3, and Ag_3 have >90% of the s unpaired spin population (ρ) residing on the two terminal atoms with a small amount of negative unpaired spin population on the unique atom. Cu_3 is somewhat different in that 60% of ρ_{4s} resides on the terminal atoms with correspondingly smaller negative ρ_{4s} on the central Cu atom. All four species show a negative *g* shift ranging from −0.0011 for Na_3 to −0.04 for Ag_3. This has been taken as evidence for an "obtuse angled" isosceles triangular geometry with ground-state C_{2v} symmetry in the $^2B_2$ representation.

There are little or no experimental data for mixed metal trimers although the structures of mixed alkali metal trimers have been calculated in the diatomics in molecules (DIM) approximation using empirically evaluated integrals.[6]

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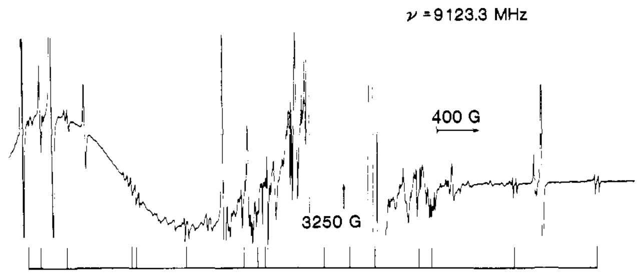

Figure 1. ESR spectrum of C_6D_6 containing ^{63}Cu and ^{107}Ag at 100 K. The stick diagram indicates the calculated line positions.

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	ρ_M[a]	a_M (central), G	ρ_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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Free-Radical Rearrangement of a Silyl Radical via Net 1,2-Migration of an Acetoxy Group

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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

$$\underset{\mathbf{2}}{(AcOCH_2SiMe_2)_2O} \xrightarrow[\text{ether, }\Delta]{LiAlH_4} \xrightarrow{Ac_2O} \underset{\mathbf{1}\ (40\text{–}45\%)}{AcOCH_2SiHMe_2} \qquad (1)$$

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