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Cryochemical Studies. 3. ESR Studies of the Reaction of Group 1B Metal Atoms with Acetylene and Phenylacetylene in a Rotating Cryostat[1]

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Abstract: The paramagnetic products of the reaction of copper, silver, and gold atoms with acetylene and phenylacetylene at 77 K in a rotating cryostat have been examined by ESR spectroscopy. Cu and C_2H_2 give the mono- and bis(acetylene) π complexes, $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$, Ag and C_2H_2 give the vinyl $AgCH{=}\dot{C}H$, and Au and C_2H_2 give the vinyls $AuCH{=}\dot{C}H$ and $CH_2{=}\dot{C}Au$. All three metal atoms react with phenylacetylene to give β-substituted α-styryls, with Cu and Ag giving one radical and Au giving two isomeric radicals. The stability of the β-substituted vinyls increases in the order $AuCH{=}\dot{C}H < AgCH{=}\dot{C}H$, and $CH_2{=}\dot{C}Au$ is more stable than $AuCH{=}\dot{C}H$. Interestingly $Cu(C_2H_2)_2$ is more long-lived than the organometallic vinyls.

Kasai, McLeod, and Watanabe[2] have studied the paramagnetic products of the reaction of copper and silver atoms with solid acetylene in argon at 4 K by ESR spectroscopy and have concluded that copper reacts to give copper–acetylene complexes with one or two acetylene ligands, i.e., $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$, while silver reacts to give pseudocomplexes with one, two, three, and more than three ligands, i.e., Ag .... (C_2H_2), Ag .... $(C_2H_2)_2$, and Ag .... $(C_2H_2)_{n\geq 3}$. In addition they found that if Ag atoms are allowed to react with acetylene in the vapor phase the β-substituted vinyl radical, $AgCH{=}\dot{C}H$ is produced.

In this paper, we present the results of a study of the reaction of group 1B metal atoms with acetylene and phenylacetylene in a rotating cryostat at 77 K. We find that under our experimental conditions Cu reacts with acetylene to give the π complexes $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$ whereas Ag and Au give σ-bonded vinyls. All three groups 1B metal atoms react with phenylacetylene to give β-substituted α-styryls, and while Cu and Ag give one radical, it would appear that Au gives two stereoisomeric α-styryls. In addition to providing ESR spectroscopic parameters and structural information, this study also gives some qualitative data on the relative stabilities of organometallic vinyls and Cu–acetylene complexes.

Experimental Section

Materials. Acetylene (Matheson), phenylacetylene, cyclohexane, adamantane (Aldrich), $^{13}C_2H_2$, enriched to 90% in ^{13}C, $^{13}C_2D_2$, enriched to 90% in ^{13}C and 98% in ^2H, C_2D_2, enriched to 99% in ^2H, and C_6H_5-$C{\equiv}CD$, enriched to 99% in ^2H (Merck, Sharpe, and Dohme, Canada, Ltd.), were used after thorough degassing and distillation. ^{107}Ag and ^{63}CuO were obtained from Oak Ridge National Laboratory, TN. ^{63}CuO was reduced to ^{63}Cu with hydrogen at 500 °C. Pure Au and natural Ag and Cu were kindly provided by Dr. C. M. Hurd (N.R.C., Ottawa).

Cryostat. The rotating cryostat and the method used to vaporize group 1B metals and investigate their reaction with organic compounds in an inert matrix at 77 K have been described elsewhere.[3]

Results

Acetylene–Cu. The ESR spectrum obtained when ^{63}Cu atoms, acetylene, and adamantane are condensed in a rotating cryostat in the sequence adamantane, copper, and acetylene is shown in Figure 1a. The spectrum consists principally of an intense central feature, shown at lower gain and in expanded scale in Figure 1b, and several almost isotropic transitions in the range 0–6000 G. The isotropic features are most readily assigned from the transitions in the region 4500–5500G. These have been labeled I, II, II′, II″, and II‴ in Figure 1a. The line at 5553 G, labeled I, can be assigned to the ESR transition $M_S = \pm 1$, $M_I = -{}^3/_2$ from isolated ^{63}Cu atoms.[4] Calculation of the hyperfine interaction (hfi) from the Breit–Rabi equation assuming $g = 2.0023$ gives $a_{63} = 2050$ G. The program used to calculate this coupling constant predicts that the only other transition that can be seen in the spectrum is the NMR transition $M_S = -{}^1/_2$, $M_I = -{}^3/_2 \leftrightarrow -{}^1/_2$ at 1290 G.

The transitions occurring at 5030, 4983.5, 4919, and 4761 G labeled II, II′, II″, and II‴, in Figure 1a, are assigned to $^{63}Cu(C_2H_2)$ in four magnetically nonequivalent sites.[2] The coupling constants estimated from these $M_I = -{}^3/_2$ transitions are $a_{63}(\mathrm{II}) = 1479$ G, $a_{63}(\mathrm{II'}) = 1434$ G, $a_{63}(\mathrm{II''}) = 1368$ G, and $a_{63}(\mathrm{II'''}) = 1218$ G, and the other lines are predicted to occur in the range 2300–2600 G, 750–1170 G, and 340–930 G. These coupling constants are very close to the value of 1460 G reported by Kasai, McLeod, and Watanabe[2] for $Cu(C_2H_2)$ in a single trapping site in an argon matrix.

The anisotropic spectrum shown in Figure 1b is identical, although somewhat better resolved, to the spectrum assigned by Kasai, McLeod, and Watanabe[2] to $Cu(C_2H_2)_2$ at 4 K. The spectral pattern is an overlapping quartet of quintets which is consistent with a Cu atom associated with four equivalent protons. The ESR parameters for this species, calculated by the method of computer simulation are $g_{\parallel} = g_{\perp} = 2.0019 \pm 0.002$, $A_{\parallel}(\mathrm{Cu}) \sim 0$ G, $A_{\perp}(\mathrm{Cu}) = 67 \pm 5$ G, $A_{\parallel}(\mathrm{H}) = A_{\perp}(\mathrm{H}) = 29 \pm 3$ G, values which are similar to those reported by Kasai, McLeod, and Watanabe.[2] There was no evidence for transitions which could be assigned to the Cu–acetylene adduct $CuCH{=}\dot{C}H$.

Warm-up experiments indicated that $Cu(C_2H_2)$ in adamantane decayed rapidly at 100 K whereas $Cu(C_2H_2)_2$ in adamantane decayed very slowly at temperatures in the range 120–160 K and was present in substantial concentrations even at 170 K.

Ozin, McIntosh, Power, and Messmer[5] have studied the products of the reaction of Cu atoms with acetylene in pure acetylene and acetylene diluted with argon at 10–12 K by visible and infrared spectroscopy and have confirmed the formation of $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$. These complexes are less stable in these matrices and $Cu(C_2H_2)_2$, for example, decayed completely when the sample was warmed to 80 K. This apparent difference in stability in the various matrices is probably a result of the temperature at which appreciable diffusion in the host matrix becomes important.[6]

The Dewar–Chatt–Duncanson bonding picture has been proposed for $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$[5] with minimal π delocalization of charge from the metal atom to ligand for $Cu(C_2H_2)$.

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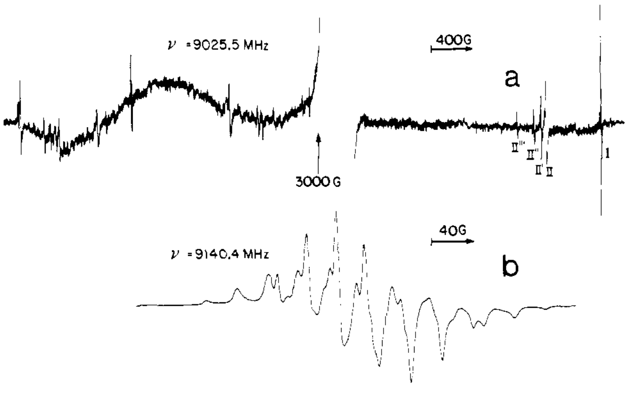


Figure 1. ESR spectra obtained from adamantane containing ^{63}Cu and acetylene at 77 K: (a) scan range 0–6000 G, (b) scan range 3050–3450 G and lower gain than in (a).

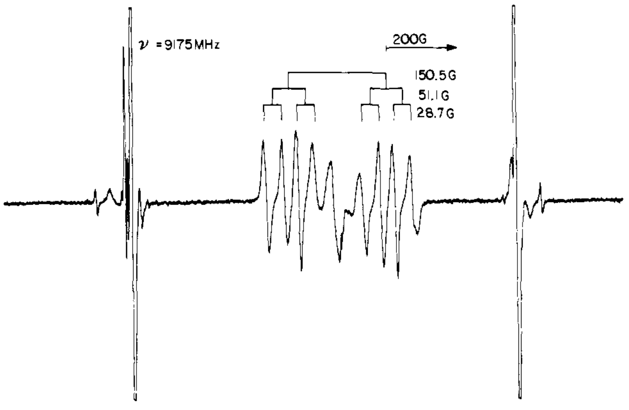
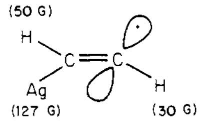


Figure 2. ESR spectrum obtained from adamantane containing Ag and acetylene at 77 K.

Both complexes are assumed to be planar with Cu(C_2H_2) having C_{2v} symmetry and a $^2A_1$ ground state[5] and Cu(C_2H_2)$_2$ D_{2h} symmetry and a $^2B_{3u}$ ground state.

Acetylene–Ag. The ESR spectrum obtained from ^{107}Ag atoms, acetylene, and adamantane is shown in Figure 2 and consists principally of a doublet from isolated ^{107}Ag atoms ($a_{107} = 600.1$ G; $g = 2.0018$) and a doublet of doublets of doublets. The latter spectrum is assigned to the silver-substituted vinyl radical, AgCH=ĊH, with $a_{107} = 150.5$ G, $a_H(1) = 51.1$ G, $a_H(1) = 28.7$ G, and $g = 1.9988$. There was no evidence for spectra which could be assigned to the silver–acetylene complexes, Ag(C_2H_2) and Ag(C_2H_2)$_2$.

Kasai, McLeod, and Watanabe[2] obtained AgCH=ĊH by condensing the products of the vapor-phase reaction of Ag atoms with acetylene at 4 K and reported the following parameters: $a_{Ag} = 127$ G; $a_H(1) = 50$ G, $a_H(1) = 30$ G, and $g = 2.0028$. Thus while there is good agreement between the two sets of data for the hydrogen coupling constants there is some discrepancy in the value of the Ag hyperfine coupling constants and the g factor. These workers concluded[2] that AgCH=ĊH has the vinyl structure with the unpaired electron localized in a predominantly p_y orbital of the terminal carbon:



Reaction of Ag atoms with $^{13}C_2H_2$ and $^{13}C_2D_2$ gave Ag^{13}CH=^{13}ĊH and Ag^{13}CD=^{13}ĊD with $a_{13}(\alpha) \sim 55$ G which is similar to the values reported by Griller, Cooper, and Ingold[7] for some highly substituted vinyls with bent structures.

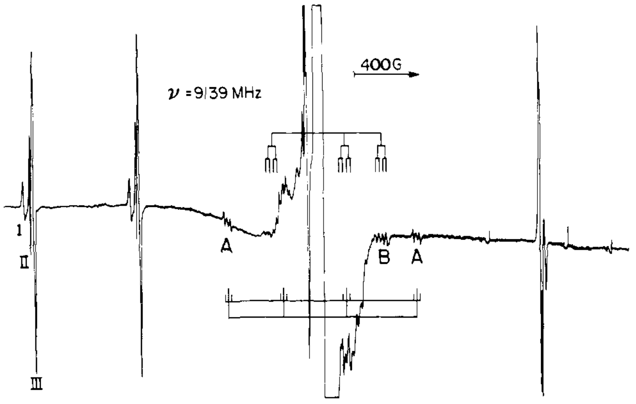


Figure 3. ESR spectrum obtained from adamantane containing Au and acetylene at 77 K.

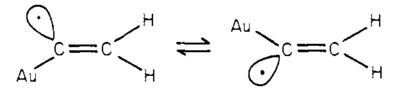
When a sample of AgCH=ĊH was warmed in adamantane the radical decayed slowly at 113 K and quite rapidly at 123 K.

Acetylene–Au. Reaction of Au atoms with acetylene in adamantane gave the ESR spectrum shown in Figure 3. The spectrum is dominanted by three quartets with different intensities and large Au coupling constants which can be attributed to Au atoms trapped in three magnetically inequivalent sites ($a_{Au}{}^{I} = 1046$ G, $g = 2.0016$; $a_{Au}{}^{II} = 1028$ G, $g = 2.0022$; $a_{Au}{}^{III} = 1018.4$ G, $g = 2.0016$) and a strong central feature. In addition to these features there are a number of almost isotropic lines, the high-field sets of which are labeled A and B in Figure 3.

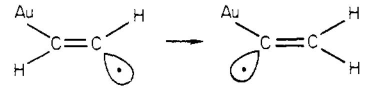
The set of lines labeled A has a Au coupling constant of 386.5 G and two almost equivalent hydrogens of 19.7 G ($g = 1.9938$) suggesting that the metal atom interacts equally with both ends of one C_2H_2; i.e., A is the π complex Au(C_2H_2). For this assignment to be correct, considerably more unpaired spin density would have to be transferred from the metal atom to the ligand than occurs with Cu(C_2H_2). These triplets were replaced by broad singlets, positioned at the center of the triplets, when C_2D_2 was used instead of C_2H_2 and became *doublets*, with $a_{13} \sim 55$ G, when $^{13}C_2D_2$ was used. These results indicate that the super hyperfine interactions exhibited by the Au–C_2H_2 adduct are from two hydrogens and that the paramagnetic species is not Au(C_2H_2), which would have two equivalent ^{13}C nuclei and give a triplet feature.

Variable-temperature studies indicated that the central line of the triplet at 77 K was broader and less intense than the outer lines whereas at 100 K it increased dramatically in intensity relative to the outer lines and gave an almost 1:2:1 triplet. This suggests that A behaves like vinyl[8-10] and that inversion occurs between two equivalent structures with an inversion rate comparable at 77 K to the frequency of a β hydrogen hyperfine coupling constant.

The most reasonable structure of A which is compatible with two equivalent hydrogens at 100 K, its fluxional behavior and the observation of one ^{13}C coupling constant of 55 G is the vinylidene structure:



This does of course require that the initially formed vinyl undergoes a rapid 1,2-hydrogen shift at 77 K:



Such a reaction is not unreasonable in view of the fact that the acetylene–vinylidene reaction has been calculated to be ~11 kcal

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[7] Griller, D.; Cooper, J. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 4269–4275.

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Table I. ESR Parameters for Some Group 1B Substituted Vinyls and α-Styryls at 77 K

radical	matrix	$a_H(\alpha)$/G	$a_H(\beta)$/G	$a_{13}(\alpha)$/G	$a_M(\beta)$/G	g factor
CuCH=CH	adamantane			not detected		
AgCH=CH	adamantane	28.7	50.1	~55	150.5	1.9988
$AuC=CH_2$	adamantane		19.7[a]	~55	386.5	1.9938
AuCH=CH	adamantane	20	41.5	*b*	224.1	1.9938
$CuCH=CC_6H_5$	cyclohexane		45.1		133.7	2.0019
$AgCH=CC_6H_5$	cyclohexane		46.3		109.6	2.0014
trans-$AuCH=CC_6H_5$	cyclohexane		45.6		189.1	1.997
cis-$AuCH=CC_6H_5$	cyclohexane				107	
$CH_2=CH$		15.8	68.5[c] 34.2	107.5		2.0022
$CH_2=CC_6H_5$	adamantane		41.5			2.0023

[a] Two hydrogens. [b] Not resolved. [c] Trans H atom.

mol^{-1} exothermic in the presence of an Al atom[11] and that although the barrier between vinylidene and acetylene is ~8 kcal mol^{-1} [12] there is the possibility that it is reduced by the presence of a metal atom.[11] It should, however, be noted that these calculations were performed on vinylidene with a linear structure at the carbon bearing the unpaired electron whereas the magnitudes of $a_{Au}(\alpha)$ and $a_{13}(\alpha)$ indicate a bent structure for $AuC=CH_2$.

Only the high-field quartet of a second isotropic species, labeled B, was well resolved, the other lines being masked by the intense central feature. If, however, we assume that the g factor for this species is equal to the g factor for A, then the following parameters can be calculated: $a_{Au} = 224$ G, $a_H(1) = 20 \pm 2$ G, and $a_H(1) = 40 \pm 4$ G. This species was extremely unstable and decayed slowly in liquid nitrogen. The most reasonable structure for a radical with these hyperfine coupling constants would be $AuCH=\dot{C}H$. Unfortunately, the spectrum obtained from Au and $^{13}C_2D_2$ was too weak for unambiguous evaluation of a_{13} for this species. It would, however, appear that two vinyls are formed in this system, one with an α Au atom and the other with a β Au atom.

The intense central feature could not be assigned to $Au(C_2H_2)_2$ and was probably produced by Au microcrystallites. We can, therefore, conclude that $Au(C_2H_2)$ and $Au(C_2H_2)_2$ are not formed under our experimental conditions.

Phenylacetylene–Cu, –Ag, and –Au. The ESR spectra obtained when Cu, Ag, and Au atoms, phenylacetylene and cyclohexane are cocondensed in the cryostat are shown in Figure 4. The only spectrum obtained from Cu atoms is the quartet of doublets (Figure 4a) expected from $C_6H_5\dot{C}=CHCu$ with $a_{Cu} = 133.7$ G, $a_H = 45.1$ G, $g = 2.0019$. In the case of silver a trace of a doublet of doublets from isolated atoms is observed along with a very much more intense doublet of doublets in the central region with $a_{Ag} = 109.6$ G, $a_H = 46.3$ G, $g = 2.0014$ which can be assigned to $C_6H_5\dot{C}=CHAg$.

The spectrum obtained from Au atoms ($I = {}^3/_2$) (Figure 4c) is not as simple as the spectrum from Cu atoms ($I = {}^3/_2$) and suggests the presence of two radicals. There is clearly one species with a spectrum consisting of a quartet of doublets with the ESR parameters $a_{Au} = 189$ G, $a_H = 45.6$ G, $g = 1.9970$. This is possibly the trans stereoisomer of $C_6H_5C=CHAu$ and the second species with $a_{Au} \sim 107$ G is the cis stereoisomer. In support of this conclusion the relative ratio of the two Au hfi is that expected for atoms trans and cis to the free electron orbital in vinyls. Attempts to simulate the spectrum were, however, not entirely successful because of the M_I effect on the intensity of the lines. The presence of two radicals was confirmed in experiments using $C_6H_5C{\equiv}CD$.

There is no evidence for the formation of group 1B atom mono- or bis(alkyne) complexes with $C_6H_5C{\equiv}CH$.

Discussion

Under our experimental conditions Ag and Au atoms add to acetylene to give σ-bonded vinyls while Cu forms the mono- and bis(acetylene) π complexes $Cu(C_2H_2)$ and $Cu(C_2H_2)_2$. All three metal atoms add to phenylacetylene and π complexes with this alkyne are not formed. We can, therefore, tentatively conclude that Ag and Au atoms are more reactive than Cu atoms toward addition to the C–C triple bond which probably reflects the relative stabilities of the β-substituted vinyls rather than differences in the strengths of the carbon–metal bonds. The stability of the vinyls increases in the order $AuCH=\dot{C}H < AgCH=\dot{C}H$ and $AuCH=\dot{C}H$ is less stable than $CH_2=\dot{C}Au$. Interestingly $Cu(C_2H_2)_2$ is more stable than $AgCH=\dot{C}H$ and $AuCH=\dot{C}H$ while mono- and bis(acetylene) π complexes of Ag and Au are not observed.

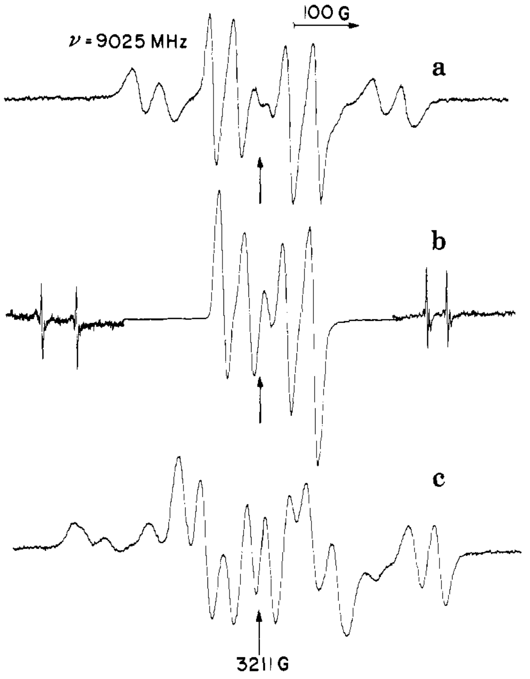

Figure 4. ESR spectra obtained from cyclohexane containing phenylacetylene and (a) Cu, (b) Ag, and (c) Au.

The ESR parameters for the vinyls produced by addition of group 1B metal atoms to acetylene and phenylacetylene are summarized in Table I and are compared with the parameters for vinyl[7-9] and α-styryl.[13]

The β-hydrogen coupling constant in $AgCH=\dot{C}H$ is intermediate between the cis and trans β-H hfi in $CH_2=\dot{C}H$ and is similar to that found in $AlCH=\dot{C}H$.[14,15] This could arise if the organometallic vinyl radical is linear or if it is interconverting rapidly between the cis and trans isomers. It could also indicate simply that replacement of H by metal atoms leads to a reduction in the spin density on a *trans*-β-H. Values of $a_H(\beta) = 48$–54 G

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(11) Trenary, M.; Casida, M. E.; Brooks, B. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 1638–1639.

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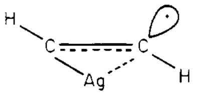
have been reported for $C_6H_5CH{=}\dot{C}C(CH_3)_3$, $C_6H_5CH{=}\dot{C}Si(CH_3)_3$, and $CCl_3CH{=}\dot{C}Si(CH_3)_3$,[7] radicals which, for steric reasons, are believed to be bent with the H atom trans to the orbital containing the unpaired electron. This would seem to suggest that $AgCH{=}\dot{C}H$ is bent with the Ag nucleus cis to the orbital containing the unpaired electron, i.e., the less stable isomer of this radical is formed.[10,14] A bent structure for $AgCH{=}\dot{C}H$ is consistent with its $a_{13}(\alpha)$ value of 55 G which is about twice the value for planar alkyls[8] although smaller than the value for vinyl.[8] The value of θ, the angle between the orbital containing the unpaired electron and the C=C axis must, therefore, be less than 90° but greater than the 50–60° adopted by vinyl and 1-methylvinyl.[7]

The suggestion that $AgCH{=}\dot{C}H$ is formed in the less stable cis form is based on the magnitude of $a_H(\beta)$ which is significantly larger than *cis*-$a_H(\beta)$ in $CH_2{=}\dot{C}H$.[7-9] By analogy Kasai[14] has recently suggested that $AlCH{=}\dot{C}H$ is formed in the cis form from Al atoms and C_2H_2. It has, however, been proposed that cis and trans $AlCH{=}\dot{C}H$ have identical $a_H(\beta)$ and that a_{Al} for the cis isomer is *larger* than for the trans isomer. It should perhaps be noted that although Kasai's assignment is based on EHT-MO calculations, a change in a_{Al} for $AlCH{=}\dot{C}H$ with little or no change in $a_H(\alpha)$ and $a_H(\beta)$ upon photolysis could be due to a small change in the geometry of the radical brought about by softening of the matrix. Matrix effects on ESR parameters for matrix-isolated radicals are not unknown. For instance, a_{Ag} for $AgCH{=}\dot{C}H$ in adamantane (this work) and in argon[2] differ by ~25 G. It is, however, possible that the two forms of $AgCH{=}\dot{C}H$ are interconverting rapidly in adamantane so that average *a* values are observed.

The value of α-hydrogen coupling constant for $AgCH{=}\dot{C}H$ is about twice the value of $a_H(\alpha)$ for $CH_2{=}\dot{C}H$ and larger than values for planar alkyls.[8] This could be due to a weak bonding interaction between the Ag and the α-carbon atom to give the bridged structure.



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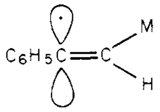
The analogous substituted cyclopropenyls also have large $a_H(\alpha)$ values; e.g., $a_H(\alpha)$ for 2,3-dimethylcyclopropen-1-yl is 37 G.[16]

The 5s spin density on Ag in $AgCH{=}\dot{C}H$ is large (~25%) compared with the spin densities found in the 1s orbital of the cis and trans β hydrogens of vinyl (6.7 and 13%) and the 3s orbital of aluminum in $AlCH{=}\dot{C}H$ (8.6%)[14,15] which is consistent with the "bridged" structure **1**. Alternatively it could indicate that the "excited" structure $\dot{A}gCH{\equiv}CH$ makes an important contribution to the ground-state wave function for $AgCH{=}\dot{C}H$.

The radical that has been assigned the structure $AuCH{=}\dot{C}H$ has $a_H(\alpha)$ and $a_H(\beta)$ values smaller than the corresponding values for *cis*-$AgCH{=}\dot{C}H$; in fact, they are close to the H hfi expected for a linear vinyl. Unfortunately the spectrum from $Au^{13}CD{=}^{13}\dot{C}D$ was too poorly resolved to give meaningful values of $a_{13}(\alpha)$ and the bent structure could not be confirmed. The 6s spin density on Au in $AuCH{=}\dot{C}H$ is very similar to the 5s spin density on Ag in *cis*-$AgCH{=}\dot{C}H$ suggesting that $AuCH{=}\dot{C}H$ is formed in the cis configuration.

The radical that has been assigned the vinylidene structure $CH_2{=}\dot{C}Au$ has about 35% 6s spin density on the α Au atom. The β-hydrogen hyperfine interaction is much less than the average value for vinyl and is consistent with the large 6s spin density on the α Au atom.

The β-hydrogen coupling constants of the adducts to phenylacetylene are all very similar, falling in the range 45.1–46.3 G and are similar to the value of the β-hydrogen coupling constant for α-styryl (41.5 G).[10] This indicates that the metal atoms add to the unsubstituted end of the alkyne to give β-substituted α-styryls. One might, therefore, expect these radicals to have a planar structure like α-styryl with the unpaired electron located in the p_y orbital on the α-carbon:



Comparison of the β-metal atom hfi with the values of a_M found for free atoms in inert hydrocarbon matrices[3] indicates that the β-Cu in $C_6H_5\dot{C}{=}CHCu$ has 6–7% 4s spin density, the β-Ag in $C_6H_5\dot{C}{=}CHAg$ has 16–17% 5s spin density, β-Au in $C_6H_5\dot{C}{=}CHAu$ has 18% 6s spin density, values which are less than the metal atom s spin densities for the β-substituted vinyls. This is consistent with a less bent structure for the substituted α-styryls and some delocalization of the unpaired electron onto the phenyl ring. The difference in the s spin density on Cu and the other two metal atoms is, however, not entirely consistent with a linear structure for these radicals and suggests that $C_6H_5\dot{C}{=}CHCu$ may be formed with the Cu atom cis to the orbital containing the unpaired electron while the other two α-styryls are formed with the metal atom trans. This is, however, not compatible with the values of the β-H hyperfine coupling constants which are independent of the metal atom. Alternatively $C_6H_5\dot{C}{=}CHCu$ may be linear while the other two α-styryls are bent.

It is rather difficult to assign a structure to the second species produced by Au and $C_6H_5C{\equiv}CH$. However, the 6s spin density on the Au atom is ~10%, suggesting that it could be *cis*-$C_6H_5\dot{C}{=}CHAu$ rather than the substituted vinylidene $Au\dot{C}{=}CHC_6H_5$ which by analogy with $CH_2{=}\dot{C}Au$ would be expected to have appreciable s spin density on Au.

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Registry No. Cu, 7440-50-8; Ag, 7440-22-4; Au, 7440-57-5; C_2H_2, 74-86-2; $C_6H_5C_2H$, 536-74-3; $Cu(C_2H_2)$, 65881-80-3; $Cu(C_2H_2)_2$, 65881-79-0; $AgCH{=}\dot{C}h$, 73373-74-7; $AuCH{=}\dot{C}H$, 84074-14-6; $Au\dot{C}{=}CH_2$, 84074-15-7; $CuCH{=}\dot{C}C_6H_5$, 84074-16-8; $AgCH{=}\dot{C}C_6H_5$, 84074-17-9; *trans*-$AuCH{=}\dot{C}C_6H_5$, 84074-18-0; *cis*-$AuCH{=}\dot{C}C_6H_5$, 84074-19-1.

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