

An ESR Study of the Addition of Metal Atoms to Allene: Metal-Substituted Allyl Radicals¹

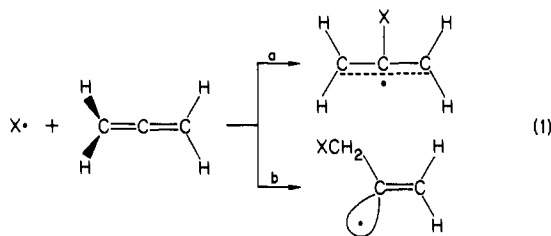
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Abstract: The group 11²⁷ metal atoms Cu, Ag, and Au (M) react with allene in a rotating cryostat at 77 K to give the organometallic allyls CH₂C(M)CH₂ but not the substituted vinyls MCH₂C=CH₂. These substituted allyls have *g* factors close to the free-spin value and small metal hyperfine interactions which arise by spin polarization.

It is interesting to note that matrix isolation electron spin resonance (ESR) spectroscopic studies have demonstrated that while group 11 metal atoms (Cu, Ag, and Au) readily add to alkynes at cryogenic temperatures (4–77 K) to give organometallic vinyls^{2–5} there is no direct evidence that they add to alkenes to give β -substituted organometallic alkyls. Instead they appear to give, almost exclusively, the mono- and diligand π complexes, e.g., with ethylene they give M[C₂H₄] and M[C₂H₄]₂.^{2,6–8}

During the course of our search for an authentic metal atom addition to an alkene we decided to investigate the reaction of Cu, Ag, and Au atoms with allene in a rotating cryostat^{9–11} at 77 K. This alkene is an interesting candidate for study because addition could occur either at the central carbon to give an allyl (reaction 1a) or at the terminal atom to give a vinyl (reaction 1b).



Reaction might be expected to occur principally at the least substituted carbon,¹² but this reaction would give the vinyl. On the other hand, although central atom addition gives a resonance stabilized allyl this pathway requires contra-twisting of the two terminal CH₂ groups through 45° so that the two π orbitals, which are orthogonal in allene, can become coplanar to allow the full delocalization energy of the allyl to be achieved. It is, therefore, not easy to predict where addition would occur.

Direct ESR studies of the initial free radical products have shown that the hydrogen atom, which bears a formal resemblance to the group 11 atoms in having the free electron in an *s* orbital, adds almost exclusively to the terminal carbon of allene in adamantane at 77 K¹³ and in ethane at 101 K.¹⁴ Central carbon atom addition does, however, occur for a range of radicals reacting with two substituted di-*tert*-butylvinylidenecyclopropanes¹⁵ but they are rather atypical allenes, and allyls with the semioccupied *p*_z orbital on the α carbon orthogonal to the π bond of the double bond are formed.¹⁶

Conventional studies of the final molecular products have shown that most free radicals also add at the terminal position of allene.¹⁷ The exceptions to this are Br• and RS• which add at both carbons.^{18,19} The effect of concentration and temperature on selectivity in these cases has been interpreted in terms of a reversible attack at the terminal carbon accompanied by an irreversible attack at the central carbon,¹⁹ but the results can be equally well explained by a competition between an intramolecular 1,2 shift of the Br and RS groups and a chain transfer reaction to produce the final molecular product; a bridged radical intermediate may

also be involved.²⁰ Clearly central addition is exceptional and the reasons for its occurrence remain obscure.

In the rotating cryostat isolated Cu, Ag, and Au atoms trapped on the surface of an inert matrix at 77 K were bombarded with allene and the primary product species themselves trapped in the interleaving spirals of matrix and reactants. Reactions probably occurred near 77 K,⁴ and the deposits were transferred at this temperature for examination by ESR. The spectra of the primary paramagnetic products from reaction of allene with group 11 metal atoms in cyclohexane are shown in Figure 1.

In the spectra from Cu and Au the main absorptions at *g* = 2 clearly show proton hyperfine interactions (hfi) of about 14 G which are typical of an allylic species,¹⁴ and we assign these absorptions to the metal-substituted allyls CH₂C(Cu)CH₂ and CH₂C(Au)CH₂. The values of the proton hfi make it unlikely that the spectra are of bridged radicals.²⁰ Similarly the spectrum from Ag, although not showing the 14-G interaction so clearly, is also readily assignable to a silver-substituted allyl. Computer simulations based on the Lefebvre and Maruani program²¹ gave good fits with the principal features by using the following ESR parameters: CH₂C(Cu)CH₂, *a*₆₃ = 13 ± 0.5 G, *a*_{H(2)} = 14 ± 0.5 G, *a*_{H(2)} = 15 ± 0.5 G, *g* = 2.0020; CH₂C(Ag)CH₂, *a*₁₀₇ = 7 ± 1 G, *a*_{H(2)} = 14 G, *a*_{H(2)} = 15 G, *g* = 2.0045; CH₂C(Au)CH₂, *a*_{Au} = 6.5 ± 0.5 G, *a*_{H(2)} = 14 G, *a*_{H(2)} = 15 G, *g* = 2.0020. The stick representation of the simulated spectra is shown beneath each spectrum. For Ag all the lines are accounted for by a single species with the parameters given. However, in the Cu and Au spectra there are less intense residual lines which can be fitted reasonably with simulated spectral lines based on

(1) Issued as NRCC No. 24351.

(2) Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179–190.

(3) Kasai, P. H. *J. Am. Chem. Soc.* **1983**, *105*, 6704–6710.

(4) Chenier, J. H. B.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Am. Chem. Soc.* **1983**, *105*, 788–791.

(5) Howard, J. A.; Sutcliffe, R.; Tse, J. S.; Mile, B. *Organometallics* **1984**, *3*, 859–866.

(6) Kasai, P. H. *J. Phys. Chem.* **1982**, *86*, 3684–3686.

(7) Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 6704–6710.

(8) Kasai, P. H. *J. Am. Chem. Soc.* **1984**, *106*, 3069–3075.

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

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

(11) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381–3387.

(12) Tedder, J. M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 401–410.

(13) Bennett, J. E.; Mile, B. *J. Chem. Soc., Faraday Trans 1* **1973**, *69*, 1389–1414.

(14) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147–2195.

(15) Griller, D.; Cooper, J. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1975**, *97*, 4269–4275.

(16) Regenstein, H.; Berndt, H. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 145–146.

(17) Taylor, O. R. *Chem. Rev.* **1967**, *67*, 317–359.

(18) Gresbaum, K.; Oswald, A. A.; Hall, D. N. *J. Org. Chem.* **1964**, *29*, 2404–2408.

(19) Heiba, E. T. *J. Org. Chem.* **1966**, *31*, 776–780.

(20) Skell, P. S.; Traynham, J. G. *Acc. Chem. Res.* **1984**, *17*, 160–166.

(21) Lefebvre, R.; Maruani, J. *J. Chem. Phys.* **1965**, *42*, 1480–1496.

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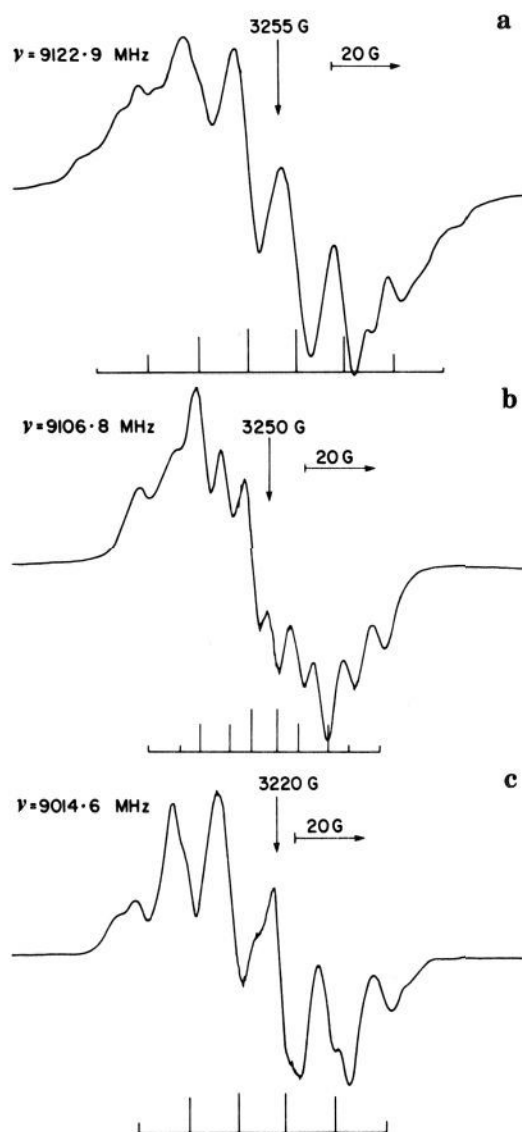


Figure 1. ESR spectra from reaction of allene with (a) ^{63}Cu , (b) ^{107}Ag , and (c) Au atoms in cyclohexane at 77 K in a rotating cryostat.

the g and a_{H} parameters already given but having values of a_{63} and a_{Au} of 8 ± 0.5 and 4 ± 0.5 G, respectively. It appears that another trapping site is occupied in these cases and that the metal hfi, which arise by spin polarization, is particularly susceptible to the environment of the radical. It is worth stressing that the spectra for all three metals show no trace of a substituted vinyl with its characteristic large interactions of 58 and 33 G for the two β -protons.²² On annealing all the spectra decayed but a residual central line resolved into a quintet with 2-G spacing and $g = 2.002$. We assign this line to the allene negative ion ($\text{C}-\text{H}_2\text{CCH}_2^-$) because of the smallness of the proton hfi which is even lower than those observed in the benzene and butadiene negative ions.^{23,24} Further details of this new species will be published later.

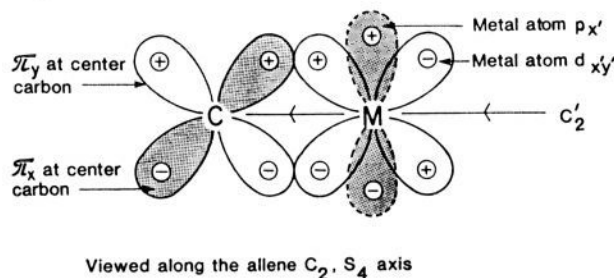
(22) Fessenden, R. W. *J. Phys. Chem.* **1967**, *71*, 74–83.

(23) Tuttle, T. R.; Weissman, S. I. *J. Am. Chem. Soc.* **1958**, *80*, 5342–5344.

(24) Levy, D. H.; Myers, R. J. *J. Chem. Phys.* **1962**, *41*, 1062–1065.

The a_{H} values in the metal allyls are close to those in most allyls. The a_{63} , a_{107} , and a_{Au} values give spin populations²⁵ of 0.006, 0.01, and 0.006 at the metal atom compared with 0.008 for hydrogen at the central carbon atom. All the interactions probably arise by spin polarization and are, therefore, negative.

Three aspects of our results are of interest: (i) the first direct observation of metal atom addition to a carbon–carbon double bond; (ii) the first observation of a metal-substituted allyl; and (iii) that the group 11 metal atoms add selectively at the central carbon in complete contrast to terminal addition by the hydrogen atom. This last aspect probably indicates that the energy needed for twisting the two orthogonal π bonds has somehow been lowered in the case of the metal atoms. The lowering can be most readily understood if the metal atom approaches the central carbon atom along the C_2' axis of the allene at an angle of 45° to the two π systems. Two interactions are then possible; first the two lobes of a d orbital of opposite sign can readily overlap with both π^* systems at the central carbon which can lead to a population of the π^* orbitals by electrons from the filled d orbitals; secondly, the unfilled metal p orbitals can overlap with the two π systems again to form δ bonds but in this case electrons will leave the bonding π orbitals for the metal.



The depopulation of the bonding π orbitals and population of the antibonding π^* orbitals both lead to a weakening of the π bonds and hence a reduction in the energy barrier to the twisting of the terminal CH_2 groups.

It is possible that central addition results from a 1,2 atom shift or even a reversible dissociation of the terminal C–M bond followed by readdition at the central carbon. We disfavor this explanation because of the low temperatures being used which in the case of Br· and RS· result in addition to the terminal and not the central atom. However, we cannot discount this possibility completely since the strengths of the C–M bonds are unknown. These aspects together with studies of the reaction of other metal atoms and of the ^{13}C hfi in the metal-substituted radicals will be reported in a future paper.

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Registry No. Cu, 7440-50-8; Ag, 7440-22-4; Au, 7440-57-5; allene, 463-49-0.

(25) Estimated from the one-electron parameters (A) calculated by Morton and Preston.²⁶

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

(27) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designated is preserved for the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)