EPR Studies of the Addition of Aluminum and Gallium Atoms to Allene: A Rule for Regioselectivity[1]

B. Mile,* J. A. Howard,* and J. S. Tse

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A OR9

Electron paramagnetic resonance spectroscopic studies of the reaction of ground-state aluminum and gallium atoms with allene in an adamantane matrix at 77 K in a rotating cyrostat show exclusive metal atom addition to the central carbon to produce metal-substituted allyls CH_2CMCH_2 with the parameters $a_{Al} < 14$ MHz, $a_H(4) = 38.5 \pm 3$ MHz, and $g_\parallel = g_\perp = 2.0023$ and $a_\parallel(Ga) \approx 51.4 \pm 3$ MHz, $a_\perp(Ga) = 14 \pm 3$ MHz, $a(4\ H) = 40 \pm 3$ MHz, and $g_\parallel = g_\perp = 2.0029 \pm 0.0005$. The similarity to the central atom addition observed for the coinage metal atoms and the marked contrast with other atoms and free radicals which add to the terminal carbon are ascribed to the presence of empty p orbitals on the metal atoms which either facilitate a 1,2 intramolecular atom shift or provide a low-energy pathway for approach to the central carbon along the C_2' axis of the allene molecule. Minor products are the allene radical anion, $C_3H_4^-$, with $a_H(4) = 5.6$ MHz and $g = 2.0023$ and HAlOH (formed from trace H_2O) with $a_\parallel(Al) = 983$ MHz, $a_\perp(Al) = 968$ MHz, $a_\parallel(H) = a_\perp(H) = 240$ MHz, $g_\parallel = 2.0023$, and $g_\perp = 2.0034$.

Introduction

Nonconjugated 1,2-dienes (allenes) provide interesting molecules for studying regioselectivity and stereospecificity in addition reactions to carbon–carbon double bonds.[2-4] Initial attack can occur (Scheme I) at either the terminal carbon (reaction 1a) or the central carbon (reaction 1b) and can be stereospecifically syn (suprafacial) or anti (antarafacial) in substituted allenes.

Addition to allene can produce the less stable of the two products (reaction 1a) in contrast to most additions that lead to the more stable product. This arises because the stability conferred by electron delocalization in the central addition product 1b may not be utilized in the transition state because of the energy needed to twist the two orthogonal π-systems each by 45° so that the full benefits of delocalization can be realized. Hence terminal addition (anti-Markovnikov) can compete and sometimes predominate. Many reactants attack allene with virtually complete regioselectivity. Thus terminal addition occurs exclusively for protons,[3,4] H atoms,[5,6] CH_3, CCl_3, and CF_3 radicals,[3] but Br atoms, thiyl radicals (both RS and PhS), and $Me_3Sn\cdot$ add at both positions, with terminal addition favored at low temperatures.[3,7-10] Electrophiles other than protons (e.g., Br^+, RS^+, $HgBr^+$) undergo exclusive Markovnikov addition to the central carbon atom.[4]

From the rather complex oligomerization and cyclo-oligomerization products of reaction of organometallics with allenes, it appears that the organic group adds to the central carbon while the metal fragment forms a π-allylic complex with the three allene carbons.[11,12] The hydride

Scheme I
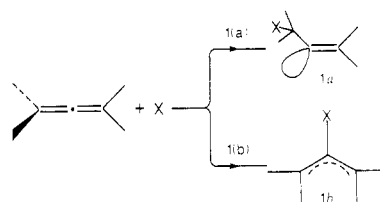
complexes $HCo(CO)_4$ and $HMn(CO)_5$ react similarly.[13] A novel intramolecular rearrangement occurs in the adduct from allenes and carbon monoxide complexes of iron and platinum,[14,15] e.g., $Fe(CO)_4$ and $Fe(C_3H_5)CO_3^+$. NMR studies show that below 213 K the metal atom bonds to only one of the allene π-systems but at higher temperatures the metal atom shifts reversibly from one orthogonal C=C bond to the other, probably through an intermediate in which the metal is strongly coordinated to the central carbon atom and more weakly bound to the terminal carbons which each rotate by 45° to make the two π-systems coplanar;[16] the activation energies of 67–97 kJ mol^{-1} are consistent with such a twisting of the double bonds.[15] We have found that Cu, Ag, and Au atoms add exclusively to the central carbon of allene.[17]

There is no general rationale for such differences in regioselectivity. Although concepts such as localization energy[18,19] and molecular orbital calculations such as MINDO/3[3,20,21] predict the preponderance of terminal

(1) Issued as NRCC No. 28805.
(2) Bowden, F. L.; Giles, R. *Coord. Chem. Rev.* 1976, 20, 81–106.
(3) Landor, S. R. Ed. *The Chemistry of Allenes*; Academic: New York, 1982; Vol. 2.
(4) Smadja, W. *Chem. Rev.* 1983, 83, 263–320.
(5) Bennett, J. E.; Mile, B. *J. Chem. Soc., Faraday Trans 1* 1973, 69, 1398–1414.
(6) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* 1963, 39, 2147–2195.
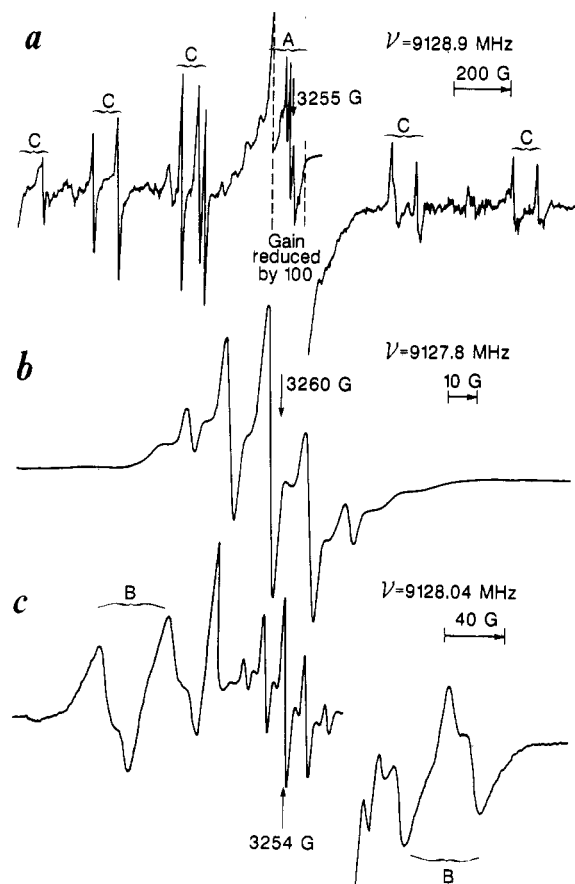(7) Taylor, D. R. *Chem. Rev.* 1967, 67, 317–359.
(8) Griesbaum, K.; Oswald, A. A.; Hall, D. N. *J. Org. Chem.* 1964, 29, 2404–2408.
(9) Heiba, E. *J. Org. Chem.* 1966, 31, 776–780.
(10) Pasto, D. J.; Warren, S. E.; Weyenberg, T. *J. Org. Chem.* 1986, 51, 2106–2110.
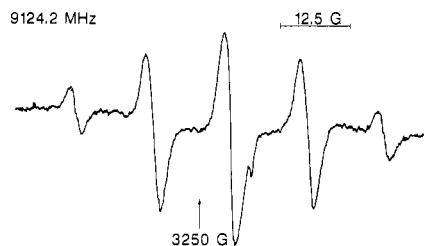(11) Heck, R. F. *Organotransition Metal Chemistry*; Academic: New York and London, 1974.

(12) Keim, W.; Behr, A.; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G. W., Stone, F. G. A., Abel, E. W.; Eds.; Pergamon: Oxford, 1982; Vol. 8, pp 372–454.
(13) Garst, J. F.; Bockman, T. M.; Batlaw, R. *J. Am. Chem. Soc.* 1986, 108, 1689–1691.
(14) Ben-Shoshan, R.; Pettit, R. *J. Am. Chem. Soc.* 1967, 89, 2231–2232.
(15) Foxman, B.; Marten, D.; Rosan, A.; Raghu, S.; Rosenblum, M.; *J. Am. Chem. Soc.* 1977, 99, 2160–2165.
(16) Albright, T. A., Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985; p 363.
(17) Chenier, J. H. B.; Howard, J. A.; Mile, B. *J. Am. Chem. Soc.* 1985, 107, 4190–4191.
(18) Jacobs, T. L.; Illingworth, G. E., Jr. *J. Org. Chem.* 1963, 28, 2692–2698.
(19) Crandall, J. K.; Sojka, S. A. *J. Am. Chem. Soc.* 1972, 94, 5084–5086.
(20) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* 1978, 100, 5290–5295.
(21) Byrd, L. R.; Caserio, M. C. *J. Org. Chem.* 1972, 37, 3881–3891.

Figure 1. EPR spectra at 77 K of the products of reaction of Al atoms with allene in adamantane: (a) full spectrum, (b) central region at reduced gain and scan, and (c) spectrum at 166 K.

Figure 2. EPR spectrum at 218 K of the products from Al and allene.

also add to 1,3-butadiene to give an allyl as the main paramagnetic product.[29]

Experimental Section

The rotating cryostat, EPR spectrometer, and methods used to calibrate spectra, calculate spectra parameters, and simulate spectra have been described previously.[30] Aluminum and gallium atoms, in their ground states, were generated from the metals held in resistively heated molybdenum or tungsten furnaces at 1000–1100 °C. They were deposited on to isolated allene molecules trapped at 77 K on the continually renewed surface of an adamantane matrix. Reaction probably occured at 77 K[30a] and the deposits containing products trapped in interleaving spirals of adamantane were transferred at this temperature and under high vacuum for examination by EPR at temperatures from 4 to 273 K. Allene and perdeuterioallene were obtained from Phillips and from Merck, Sharp and Dohme, Canada Ltd., respectively.

Results

Al + Allene. The EPR spectrum at 77 K of the products from the reaction of Al atoms with allene is shown in Figure 1a and consists of two superimposed spectra, A and C. The much more intense central feature (A) shown expanded in Figure 1b is an almost isotropic quintet, typical of randomly oriented hydrocarbon radicals in polycrystalline solids with some degrees of motional narrowing in some sites.[31,32] The EPR parameters of A are $a_H(4)$ = 39 MHz and g = 2.0023 with no detectable Al hyperfine interaction, i.e., $5a_{Al}$ < 18 MHz. The isotropic quintet spectrum shown in Figure 2 results on annealing to 218 K with $a_H(4)$ = 38.5 MHz, $5a_{Al}$ < 14 MHz, and g = 2.0023. Species C is a much weaker (∼2%) anisotropic sextet of doublets which we interpret in terms of hyperfine interaction with one Al nucleus (I = $^5/_2$) and one proton (I = $^1/_2$) with $a_\parallel(Al)$ = 983 MHz, $a_\perp(Al)$ = 968 MHz, $a_\parallel(H)$ = $a_\perp(H)$ = 240 MHz, $g_\parallel$ = 2.0023, and $g_\perp$ = 2.0034. As shown in Figure 1c, on annealing the sample to 166 K, four new features (B) appear at the outer edges of the central absorption. These features appear and disappear reversibly on cycling the temperature between 77 and 166 K with no significant loss in intensity. They have a separation of 134 MHz and center about g = 2.0023; there are also clear indications of triplet or higher multiplets with a separation of ∼39 MHz on each line. Further annealing to 240 K results in decay of all species but a residual central line, resolved into a weak isotropic quintet with a 5.6 MHz separation and g = 2.0023, which almost certainly arises from the allene radical ion $(CH_2CCH_2)^-$ previously

addition, no explanations have been advanced for the exclusive central addition observed for many reactants, apart from our considerations of the weakening of the C=C double bonds by depopulation of the π-orbitals and population of the π*-orbitals through interaction with metal p and d orbitals.[17] The increased selectivity to terminal addition of RS· and Br· as the temperature is lowered has been explained by reversible terminal addition accompanied by irreversible readdition to the central carbon at the higher temperatures.[9]

We have now studied the reaction of Al and Ga atoms with allene at 77 K for comparison with the coinage metals, in an attempt to delineate the factors that control regioselectivity. Al and Ga differ from the coinage metal atoms in that (i) they form much stronger bonds to carbon (∼280 kJ mol⁻¹[22]), (ii) either they have no filled d orbitals (Al) or such orbitals are far removed energetically from the p orbital nominally bearing the free electron (Ga[23]); and (iii) they have ²P rather than ²S ground-state configurations. However, in common with Cu, Ag, and Au, they have empty p orbitals. It is worth noting that neither the group 11 nor group 13 atoms add to monoalkenes to give β-substituted alkyls but form π-complexes[24,25] although they add to alkynes to give vinyl adducts.[26–28] Al atoms

(22) Fox, D. J.; Ray, D.; Rubesin, P. C.; Shaefer III, H. F. *J. Chem. Phys.* **1980**, *73*, 3246–3254.

(23) Moore, C. E. *Natl. Bur. Stand. (US) Circ.* **1952**, No. 467; **1958**, 3.

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

(25) Kasai, P. H. *J. Am. Chem. Soc.* **1982**, *104*, 1165–1172.

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

(27) Chenier, J. H. B.; Howard, J. A.; Mile, B.; Sutcliffe, R. *J. Am. Chem. Soc.* **1983**, *105*, 788–791.
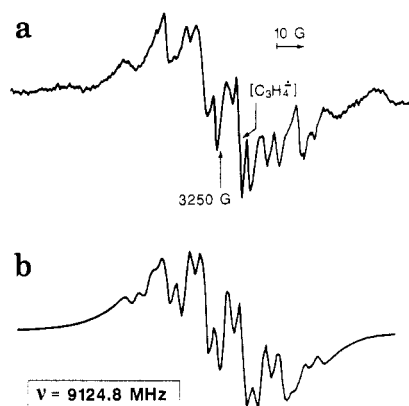
(28) Howard, J. A.; Mile, B.; Sutcliffe, R.; Tse, J. S. *Organometallics* **1984**, *3*, 859.

(29) Chenier, J. H. B.; Howard, J. A.; Tse, J. S.; Mile, B. *J. Am. Chem. Soc.* **1985**, *107*, 7290.

(30) (a) Bennett, J. E.; Mile, B.; Thomas A.; Ward, B. *Adv. Phys. Org. Chem.* **1970**, *8*, 1–77. (b) Buck, A. J.; Mile, B.; Howard, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 3381–3387.

(31) Cochran, E. L.; Adrian, F. J.; Bowers, V. A. *J. Chem. Phys.* **1961**, *34*, 1161–1175.

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

Figure 3. EPR spectra at 158 K of the products of the reaction of Ga atoms with allene in adamantane: (a) experimental spectrum and (b) simulated spectrum using the parameters given in the text.

Figure 4. EPR spectra at 160 K of the products of the reaction of Ga atoms with perdeuterioallene: (a) experimental spectrum and (b) simulated spectrum using the parameters given in the text.

reported by us[17] and which is presumably formed by electron transfer from an aluminum atom to allene with simultaneous production of Al^+.

When perdeuterioallene is used, the central species A is an intense single line at g = 2.0022 with a line width (ΔH_{pp}) of ~56 MHz and no aluminum hyperfine interaction resolving even on annealing. The sextet of doublets (C) is still observed but with diminished intensity (however, we have noticed that the intensity of C is variable from experiment to experiment). We must conclude that the proton in species C is not derived from the allene. Species B is not observed even on annealing to 177 K which may indicate its formation from a trace impurity in the C_3H_4 (e.g., propyne) which is absent in the C_3D_4 or the occurrence of a secondary deuterium isotope effect.

Ga + Allene. Figure 3a shows the rather complex powder EPR spectrum at 158 K from reaction of allene with natural gallium atoms (^{69}Ga = 60.4% and ^{71}Ga = 39.6% both with I = $^3/_2$). A similar, less well-resolved, spectrum is observed at 77 K. The carrier of the spectrum is the Ga analogue of species A from Al and allene but in this case Ga as well as proton hyperfine interactions are resolved although the two gallium isotopes are not differentiated. The spectrum can be simulated by using the parameters $a_\perp$(Ga) ≈ 14.0 ± 3 MHz, $a_\parallel$(Ga) = 51 ± 3 MHz, $a_\parallel$(4 H) = $a_\perp$(4 H) = 40 ± 3 MHz, and $g_\parallel$ = $g_\perp$ = 2.0029 ± 0.0005 with ΔH_{pp}(⊥) = 8 MHz and ΔH_{pp}(∥) = 40 MHz (Figure 3b). Perfect matching of the complete experimental and simulated spectra is difficult because some degree of motional narrowing is present as in the case of the aluminoallyl radical. Unfortunately the "tumbling" motion of the galloallyl radical, even at higher temperatures, is insufficient to give an isotropic spectrum.

With C_3D_4 the broad powder spectrum shown in Figure 4a is observed, and it can be simulated (Figure 4b) with the parameters $a_\perp$(Ga) = 15 ± 3 MHz, $a_\parallel$(Ga) ≈ 51 ± 3 MHz, and g = 2.0025 ± 0.0005 in good agreement with the parameters from Ga and C_3H_4. The central sharp line is due to overlap by the allene radical anion. No lines corresponding to the alumino species B and C are observed in the case of gallium and allene.

Discussion

Species A—Al and Ga Allyls. The major product (species A) of the reaction between Al and Ga atoms with allene is without doubt the metal-substituted allyl formed by addition at the central carbon atom. This follows from (i) the values of the hyperfine interactions with four protons (~40 MHz) which is typical of allyls,[6,33] (ii) the loss
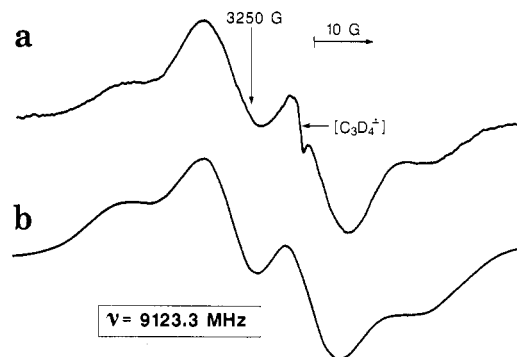
of proton interactions on using C_3D_4, and (iii) the g value near to 2.0023. The values of $a_\perp$(Ga) = 14 MHz and $a_\parallel$(Ga) = 51 MHz for $CH_2C(Ga)CH_2$ when inserted into the relationships

$$a_\parallel = A_{iso} + 2A_{dip}$$

$$a_\perp = A_{iso} - A_{dip}$$

lead to A_{iso}(Ga) = 26 MHz and A_{dip}(Ga) = 12 MHz if $a_\parallel$(Ga) and $a_\perp$(Ga) are of the same sign and A_{iso}(Ga) = 8 MHz and A_{dip}(Ga) = 22 MHz if $a_\parallel$(Ga) and $a_\perp$(Ga) have opposite signs.

Dividing A_{iso} and A_{dip} by the isotropic and anisotropic hyperfine interactions, A = 13 518 MHz and αP = 225.6 MHz (where α is the angular factor of 0.4 for an atomic p orbital) for natural Ga^{34} gives the following unpaired s- and p-spin populations at the Ga nucleus

$$\rho_{4s} = 0.002 \text{ and } \rho_{4p} = 0.05$$

$$\rho_{4s} = 0.0006 \text{ and } \rho_{4p} = 0.1$$

These give a total unpaired spin population of 0.052 or 0.1 compared with 0.006, 0.01, 0.006, and 0.008 for Cu, Ag, Au, and H at the same position.[17] The higher unpaired spin population in the p orbital of Ga is not unreasonable since its 4p orbitals can interact with the Ψ_2 and Ψ_3 orbitals of the allene framework.

If the unpaired spin population in $CH_2C(Al)CH_2$ were similar to that of $CH_2C(Ga)CH_2$, $a_\parallel$(Al) and $a_\perp$(Al) should be ~4–11 MHz and ~6 MHz. Simulated spectra of CH_2CAlCH_2 using these parameters and a_H(4) = 40 MHz indicate that aluminum hyperfine interactions should be observable in the aluminoallyl. Their absence from the experimental spectrum given by Al atoms and allene, where the line width is 14–18 MHz, suggests a smaller unpaired spin population at Al which is perhaps consistent with the less diffuse nature of the Al 3p orbital.

No terminal addition to give a metal-substituted vinyl (reaction 1a) occurs for Ga, and such terminal addition for Al, if it occurs, accounts for less than 1% of the reaction products (see below).

Mechanistic Implications. The exclusive central addition of Al and Ga atoms, with ^{2}P ground states, and Cu, Ag, and Au atoms, with ^{2}S ground states, is in sharp contrast to either the exclusive terminal addition found for radicals such as H, CH_3, CCl_3, and CF_3 or the nonregioselective addition of radicals such as Br, Me_3Sn, RS, and PhS which nominally have ^{2}P ground states (even these add terminally at low temperatures). Central regioselec-

(33) Kochi, J. K.; Krusic, P. J. *J. Am. Chem. Soc.* **1968**, *90*, 7157–7159.
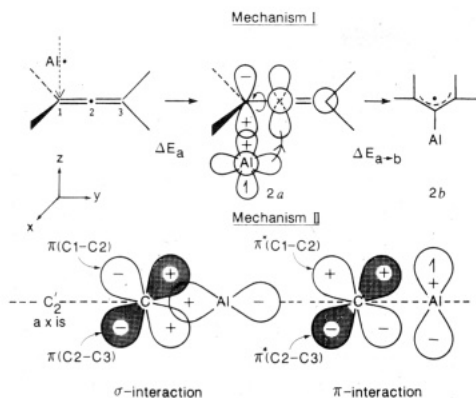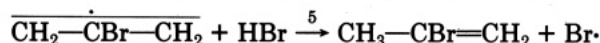(34) Morton, J. R.; Preston, K. F. *J. Magn. Reson.* **1978**, *30*, 577–582.
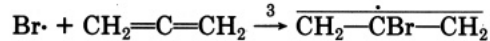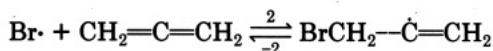
Figure 5. Two possible mechanisms for central addition to allene.

Figure 6. Qualitative MO diagram for mechanism II, approach along the C_2' axis.

tivity is more akin to that observed for electrophiles such as Br^+ and RS^+.

The nonselectivity of Br and thiyl radicals and their increased selectivity toward terminal addition at lower temperatures and higher concentrations of HBr has been interpreted[9] in terms of the following mechanism:

$$Br\cdot + CH_2{=}C{=}CH_2 \underset{-2}{\overset{2}{\rightleftharpoons}} BrCH_2{-}\dot{C}{=}CH_2$$

$$Br\cdot + CH_2{=}C{=}CH_2 \xrightarrow{3} \overline{CH_2{-}\overset{\cdot}{C}Br{-}CH_2}$$

$$BrCH_2{-}\dot{C}{=}CH_2 + HBr \xrightarrow{4} BrCH_2{-}CH{=}CH_2 + Br\cdot$$

$$\overline{CH_2{-}\overset{\cdot}{C}Br{-}CH_2} + HBr \xrightarrow{5} CH_3{-}CBr{=}CH_2 + Br\cdot$$

Terminal addition products are favored at lower temperatures if $\Delta G^a_{-2} > \Delta G^a_4$. A similar explanation is unlikely for Al and Ga atoms since the bond energies $D(C{-}Al)$ and $D(C{-}Ga)$ are too high (-280 kJ mol^{-1})[22] for such bond breakage to occur at 77 K and in fact the selectivity is in the opposite direction to that for Br· and RS· at such low temperatures.

As indicated in the introduction, theoretical calculations based on radical localization energies[18,19] and the MINDO/3 approximation[20] favor terminal addition. Two factors favor central addition: (1) steric effects[3,21] which should apply to all species of similar size and hence cannot explain the different regioselectivities observed and (2) the stability of the resulting allyl if all the delocalization energy is realized early along the reaction coordinate. The favoring of terminal addition in the MINDO/3 treatment arises because of the energy needed to twist the two allene C=C bonds by 45° to achieve a coplanar allyl; this twisting requires 190 kJ mol^{-1} in allene.[35,36] For central addition of Cu, Ag, Au, Al, and Ga atoms a mechanism must exist whereby this energy requirement is reduced. The common feature in these atoms is that they all have at least two empty p orbitals whose energy is either similar to that of the SOMO (Al, Ga) or not far removed from it (Cu, Ag, Au).[23] The electrophiles Cl^+, Br^+, and RS^+ also have an empty p orbital, and we are led to suggest the following general rule for regioselectivity in unsubstituted allene addition reactions: *Central addition to allene is favored for species with empty p orbitals, and terminal addition occurs for those with filled or no readily accessible p orbitals.* To test this, we are undertaking ab initio molecular orbital calculations of allene addition reactions which we will report in a subsequent publication. Here we discuss qualitively two possible mechanisms whereby
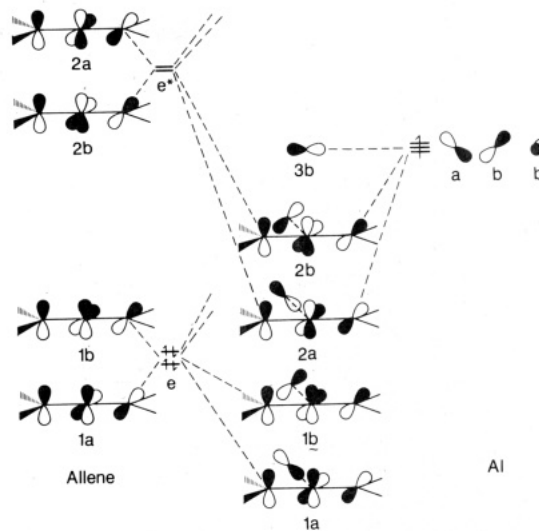

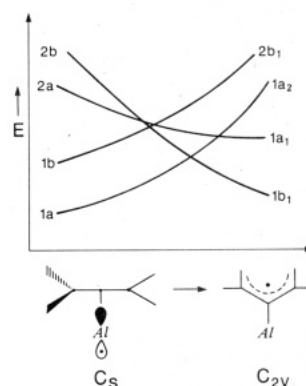**Figure 7.** Walsh diagram for mechanism II.

the energy barrier to C=C twisting is reduced.

Mechanism I: Terminal Addition Followed by a [1,2] Intramolecular Al Shift. Taking aluminum atom addition as an example, as shown by Dewar,[20] the lowest energy path is the one with the atom approaching along a line through the terminal carbon and perpendicular to the nodal plane of the π-MO. Theoretical calculations have shown that addition of an Al atom to form a σ-bond rather than a π-complex occurs for both ethylene[37] and acetylene[38]. σ-Type overlap of the singly occupied $3p_z$ orbital with the carbon $2p_z$ orbital of the π-bond leads to a transient vinyl-like intermediate of C_s symmetry (**2a**) which rapidly undergoes a [1,2] suprafacial intramolecular Al shift to give the allyl **2b** of C_{2v} symmetry (Figure 5). The shift is accompanied by rotation of the CH$_2$Al group about the C–C single bond so as to bring all the carbon $2p_x$ orbitals into the coplanarity required in allyl. This shift from C1 to C2 is facilitated by the empty $3p_y$ and $3p_x$ orbitals on the Al atom, the $3p_y$ orbital overlapping with the $2p_z$ orbital on C2 nominally containing the unpaired electron, and the $3p_x$ orbital overlapping with the filled π_x orbital of C1–C3 in a manner isoconjugate with that in allyl. Such empty p orbitals are not available in the case of the terminal adducts from H and Br atoms and carbon and sulfur radicals which consequently give terminal addition products. Similar factors could facilitate the [1,2] transfer in

(35) Roth, W. R.; Ruj, G.; Ford, P. W. *Chem. Rev.* **1974**, *107*, 48–56.

(36) Bingham, R. C.; Dewar, M. J. S.; Lo, D. H. *J. Am. Chem. Soc.* **1975**, *97*, 1294–1301.

(37) Howard, J. A.; Mile, B.; Morris, H.; Tse, J. S. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3701–3705.

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

the electrophiles that contain one empty and two filled p orbitals. However, in the equivalent vinyl cation intermediate, overlap occurs between the full p_y orbital on the electrophile and the empty $2p_z$ orbital on C2 (which would be nominally positively charged) and between the filled p_x orbital and the antibonding π^*-orbital of C2–C3.

Mechanism II: Central Attack along the C_2' Axis. The metal atom approaches the central carbon atom along the C_2' axis (designated the z axis) at a 45° angle to the two π-systems (Figure 6). Figure 7 shows the qualitative MO correlation diagram of the orbital interactions. The free electron can be in either the 2a or the 2b orbital (i.e., the ground state is either ^2A or ^2B in C_2 symmetry). Both involve some electron donation to the antiboding π^*-orbitals and hence imply a weakening of the C=C double bonds. Likewise the fully occupied 1a and 1b orbitals involve some electron donation from the bonding π-orbitals to the empty Al $3p_z$ and $3p_x$ orbitals and hence also indicate a weakening of these bonds. Twisting is thus easier, and the delocalization energy of the allyl is more readily achieved. The Walsh diagram for the transformation is shown in Figure 7. The 1a and 1b orbital energies increase along the reaction coordinate because twisting reduces the π-bonding while the orbital energies of 2a and 2b decrease because of the concomitant decrease in the antibonding π^*-character. For the coinage metals, an interaction of π^*-orbitals and the fully occupied metal d_{zy} orbitals may aid reaction and compensate for the weaker metal-to-carbon bond although such interactions do not make a significant contribution to bonding in complexes with alkenes[19,20] and CO.[39-42]

Similar interactions to those proposed in mechanism II have been invoked for the intermediate involved in the intramolecular Fe(CO)$_4$/allene exchange.[16]

The electrophiles can also react by a similar mechanism, although the fact that only one of the lower orbitals (probably 1a) can interact with the empty p_z orbital while both the antibonding orbitals 2a and 2b are doubly occupied could result in a higher energy barrier.

It is perhaps worth noting that this is the first report of an addition of Al or Ga atoms to an ethylenic bond, although addition to acetylenic bonds has been observed previously.[26]

Structures of Other Products from Al and Allene. Species C. The EPR parameters are close to those reported for HAlOH in a neon matrix[43] ($a_{\parallel}$(Al) = 1009 MHz, $a_{\perp}$(Al) = 877 MHz, $a_{\parallel}$(H) = $a_{\perp}$(H) = 282 MHz, $g_{\parallel}$ = 2.0021, and $g_{\perp}$ = 2.000). [Previously assigned to AlH⁺. Private communication from Professor L. B. Knight.] Our spectrum is rather more isotropic, $a_{\parallel}$ being lower and $a_{\perp}$ being higher. We have found similar differences for other paramagnetic species,[18] and they arise from partial averaging of anisotropic features due to libration in the adamantane cage at 77 K. We think the species is very likely HAlOH formed by insertion of Al into trace water in the adamantane matrix. Such insertion reactions have been observed for photoexcited Cu,[44] Fe,[45] and Al atoms.[46]

Species B. We cannot make an unambiguous assignment of this species because its central lines may be obscured. It is not propargyl, $\dot{C}H_2C\equiv CH$, formed from possible traces of propyne in the allene, since the propargyl EPR parameters are $a_H(2)$ = 52 MHz and $a_H(1)$ = 36 MHz.[47] The large spacing between the low and high field sets of doublets of $\sim$729 MHz would seem to require interaction with an aluminum nucleus since a single proton or two protons would require rather large proton interactions of 590 or 295 MHz, respectively. Treating these lines as a sextet of doublets gives a(Al) = 118 MHz and a(H) = 131 MHz while a sextet of triplets gives a(Al) = 92 MHz and $a_H(2)$ = 75 MHz with a g value close to 2.0023 in each case. There are multiplets (probably triplets) of about 39 MHz separation on each line. The most likely candidate is the alumino-substituted vinyl formed by terminal addition to the allene. The EPR parameters are then either (i) a(Al) = 118 MHz, a(H)(trans) = 131 MHz, and a(H)(cis) = a(CH$_2$) = 42 MHz or (ii) a(Al) = 92 MHz, a(H)(trans) = a(H)(cis) = 75 MHz, and a(CH$_2$) = 42 MHz. In the analogous methyl vinyl, $CH_3CH=\dot{C}H_2$, the proton hyperfine interaction are a(CH$_2$) = 54 MHz, a(H)(trans) = 160 MHz, and a(H)(cis) = 91 MHz.[6] Thus an alumino-substituted vinyl is feasible, but we cannot exclude the possibility that the species arises from a trace of an unknown unsaturated impurity in the allene.

The reversible appearance and disappearance of the signal as the temperature is cycled between 77 and 166 K is puzzling and difficult to explain in view of the uncertainty about its identity. It could indicate an orthorhombic species with very broad lines at 77 K that become almost isotropic at 166 K because of motional averaging of the dipolar components to zero at the higher temperature.

If the species is aluminomethylvinyl, this would indicate some terminal addition but only to a very small extent (<1%) so that our conclusions regarding the high selectivity for central addition remain.

Conclusions

(1) Ground-state Al and Ga atoms react rapidly with allene at 77 K adding almost exclusively to the central carbon atom to give a resonance-stabilized metal-substituted allyl.

(2) The selective central addition of both group 11 and 13 metal atoms and electrophiles and the selective terminal addition of hydrogen atoms, protons, carbon, and sulfur centered radicals suggest that the selectivity is controlled mainly by the presence or absence of empty low-lying p orbitals on the attacking species.

(3) Minor products of the reaction of Al with allene (<2%) are HAlOH formed from trace water and possibly aluminomethylvinyl, indicating a small extent (<1%) of terminal addition.

(39) Kasai, P. H.; Jones, P. M. *J. Am. Chem. Soc.* 1985, *107*, 813–818.

(40) Howard, J. A.; Mile, B.; Morton, J. R.; Preston, K. F.; Sutcliffe, R. *J. Phys. Chem.* 1986, *90*, 1033–1036.

(41) Kasai, P. H.; Jones, P. M. *J. Phys. Chem.* 1985, *89*, 1147.

(42) Hampson, C. A.; Howard, J. A.; Mile, B. *J. Chem. Soc. Chem. Commun.* 1985, 966–967.

(43) Knight, L. B., Jr.; Martin, R. L.; Davidson, E. R. *J. Chem. Phys.* 1979, *71*, 3991–3995.

(44) Parnis, J. M.; Mitchell, S. A.; Garcia-Prieto, J.; Ozin, G. A. *J. Am. Chem. Soc.* 1985, *107*, 8169–8178 and referernces therein.

(45) (a) Billups, W. E; Konarski, M. M.; Hauge, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* 1980, *102*, 7393–7394. (b) McCaffrey, J. G.; Ozin, G. A. *Inorg. Chem.* 1983, *22*, 1397–1399.

(46) Douglas, M. A.; Hauge, R. H.; Margrave, J. L. *J. Chem. Soc., Faraday Trans. 1* 1983, *79*, 1533–1553.

(47) Nagai, S.; Ohnishi, S.; Nitta, I. *Chem. Phys. Lett.* 1972, *13*, 379–381.