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EPR Spectroscopic Study of the Reaction of Aluminium and Gallium Atoms with Acetylenes in a Rotating Cryostat†

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An electron paramagnetic resonance spectroscopic study of the reaction of ground-state Al atoms with acetylene in cyclohexane and adamantane at 77 K has demonstrated that *trans* η^1-aluminovinyl, AlCHCH is the initial paramagnetic product and that it disappears on warming to 100 K. The spectra of cyclohexyl and 2-adamantyl, produced by hydrogen abstraction from the matrix, appear at this temperature. A second aluminium species is formed in adamantane with magnetic parameters which indicate that it is not the π-complex η^2-Al(CHCH) or aluminovinylidene, AlCCH$_2$, but may be a hydrogen-bridged isomer. Substituted acetylenes give either a *trans* vinyl, a π-complex, or a polyvinyl while propyne gives a substantial yield of propargyl.

Ga atoms and acetylene do not give an η^1-gallovinyl but instead give a species, Ga(CHCH) with two magnetically equivalent H and C nuclei that is either a η^2-, π- or σ-complex. Again in this system a significant yield of cyclohexyl and 2-adamantyl is produced by H-atom abstraction from the matrix.

When the matrix is removed from samples of Al and acetylene an Al-substituted polyacetylene remains but in the case of Ga only the metal is left.

Reaction of the group 13 metal atom [27]Al, which has a $^2P_{1/2}$ ground-state, with alkynes was first studied by Skell and Wolf[1] and they concluded that addition took place to produce an aluminoalkene which upon deuteriolysis yielded mainly a dideuteriated alkene. Propyne, for instance, gave mostly propene but propyne also underwent monodeuteriation in either the methyl or ethynyl positions indicating the intermediacy of AlCH$_2$C≡CH and CH$_3$C≡CAl.

The paramagnetic products from reaction of Al atoms with acetylene in rare-gas matrices have been studied by matrix-isolation EPR spectroscopy by Kasai and coworkers.[2,3] They concluded that the initial product was *cis*-β-aluminovinyl, **1**, formed by addition of an Al atom to the unsaturated bond and that it was formed in the vapour phase rather than on the surface of the matrix.

1
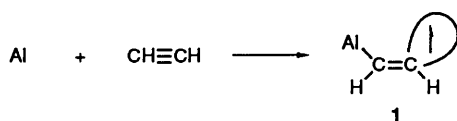
When the deposit containing **1** was photolysed with visible light the spectrum changed to one that was assigned to *trans* β-aluminovinyl, **2**.

2
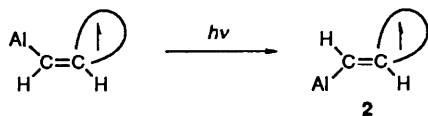
Acetylene would, therefore, appear to behave quite differently from ethylene which reacts with Al in rare gases to give a mononuclear monoligand η^2–π complex[2,3] and in hydrocarbons to give a mixture of the π-complex and aluminocyclopentane.[4,5]

The unexpected difference in the mode of bonding between C$_2$H$_2$ and C$_2$H$_4$ in Al complexes has generated a great deal of theoretical interest. Early MO calculations[6-9] suggested that the η^1–σ adducts are the most stable structures for both C$_2$H$_2$ and C$_2$H$_4$ complexes and that the η^2–π conformers are transition states. More refined calculations employing larger basis sets and including the effects of electron correlation with full gradient optimization have, however, indicated that σ-complexes are unstable relative to the π-complexes. A recent calculation[10] on the Al–C$_2$H$_2$ system has, in fact, found that the σ-bonded *cis* adduct is unstable and the symmetrically bonded π-bonded structure is a local minimum. The binding energy of the π complex (-13.66 kcal mol^{-1}) is similar to that of σ-bonded *trans* AlCH=CH. Furthermore it has been concluded[11] that the only reasonable candidate for the species detected in rare-gas matrices is *trans* AlCHCH.

Because of the small energy differences that have been calculated for the different isomers of AlC$_2$H$_2$, it has been suggested that the matrix may influence the isomer that is formed, so that η^2-Al(C$_2$H$_2$) may actually be more stable than the other isomers in matrices other than rare gases.[10] We therefore embarked on an investigation of the reaction of ground-state Al atoms with acetylene in the inert hydrocarbon matrices, cyclohexane and adamantane, at 77 K and to extend the study to some substituted acetylenes and also to an investigation of the reaction of ground-state Ga atoms with acetylene. The reaction of Ga atoms with alkynes under cryochemical conditions has not been reported whereas it has been established that they react with C$_2$H$_4$ in rare-gas[12] and hydrocarbon[13] matrices to give mostly the η^2-Ga(C$_2$H$_4$) π-complex. The results of this investigation are reported here.

Experimental

Reactions of Al and Ga atoms with acetylene were performed on a rotating cryostat at 77 K[14] by the same procedure as was used to study reactions of Al and Ga with ethylene.[5,13] Cyclohexane and adamantane (Aldrich), C$_6$D$_{12}$ (MSD, Canada), aluminium wire (Alfa), natural Ga (Aldrich), C$_2$H$_2$ (Matheson) and C$_2$D$_2$ and [13]CH[13]CH (MSD, Canada), C$_6$H$_5$-C≡CC$_6$H$_5$ (Chemical Samples, Co.), C$_6$H$_5$C≡CH (Aldrich),
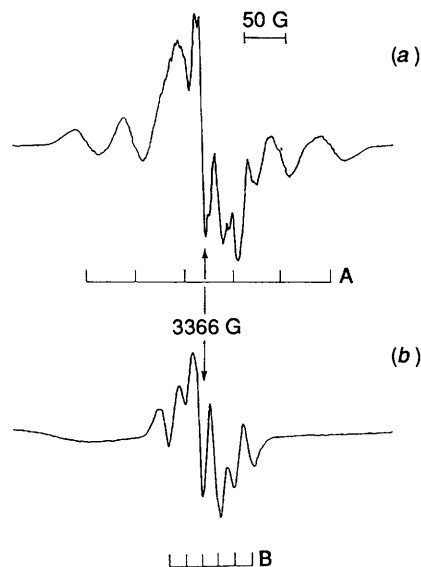
Fig. 1 (*a*) EPR spectrum at 9446.9 MHz given by Al atoms and C_2D_2 in cyclohexane at 77 K; (*b*) spectrum at 9354.9 MHz produced on annealing of the sample to 100 K
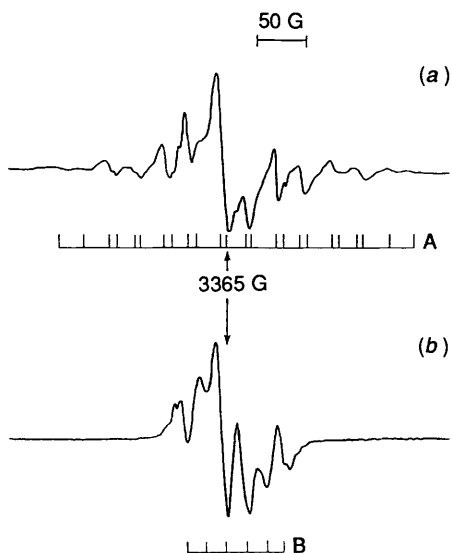

Fig. 2 (*a*) EPR spectrum at 9451 MHz given by Al atoms and C_2H_2 in cyclohexane at 77 K; (*b*) spectrum at 9355.3 MHz produced on annealing of the sample to 100 K

$C_6H_5C\equiv CD$ (MSD, Canada), $(CH_3)_3CC\equiv CH$, and $CH_3C\equiv CH$ were used as received. EPR spectra were obtained on a Bruker ESP300 or Varian E-9 spectrometer at power levels from 20 μW to 50 mW. An Oxford Instruments EPR 9 liquid-helium cryostat, a liquid N_2 Dewar, and a variable-temperature insert were used for temperatures in the range 4–77 K, 77 K and 100–250 K, respectively. A Varian gaussmeter and Systron–Donner frequency counter were used to calibrate spectra.

In most cases magnetic parameters measured from solution-like and powder spectra were confirmed by spectral simulation using programs provided by Dr. K. F. Preston (isotropic spectra) and Professors R. L. Belford[15] and Lon B. Knight, Jr. (powder spectra).

Results

Aluminium.—Cyclohexane. Reaction of Al atoms ($I = 5/2$) with C_2D_2 in C_6H_{12} at 77 K gave a brown deposit that had the EPR spectrum shown in Fig. 1(*a*). It consisted of a sextet of almost isotropic lines, A, with a coupling constant of 59 G
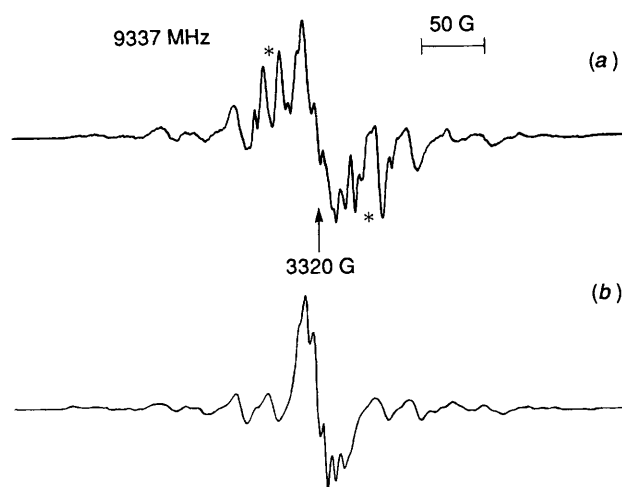

Fig. 3 (*a*) EPR spectrum given by Al atoms and C_2H_2 in perdeuteriocyclohexane at 77 K; (*b*) a composite spectrum of *trans*-AlCHCH and C_6D_{11} simulated from the parameters given in the text. Additional features in the experimental spectrum are highlighted

centred at $g = 2.0018$ indicating a carrier with one Al nucleus. Each of these principal transitions was made up of at least seven poorly resolved lines with a separation of about 3.5 G indicating formation of a mononuclear $Al(0)$–C_2D_2 complex with a_{Al} that was smaller than that of **1** in Ne ($\langle a_{Al}\rangle = 85$ G) but was similar to **2** ($\langle a_{Al}\rangle = 60$ G).[2,3] In addition to the sextet there were other features in the central region of the spectrum.

When the sample was warmed to 100 K the original sextet completely disappeared and was replaced by an almost isotropic sextet, **B**, with a spacing of *ca.* 20 G at $g = 2.0025$ [Fig. 1(*b*)]. A comparison of Figs. 1(*b*) and 1(*a*) showed that the additional features in Fig. 1(*a*) were from spectrum **B**.

Reaction of Al with C_2H_2 in C_6H_{12} at 77 K gave an even more complex spectrum [Fig. 2(*a*)]. There were, however, poorly resolved doublets of doublets at low and high field with spacings of *ca.* 26 and *ca.* 56 G (labelled A), suggesting two non-equivalent H nuclei, with an overall spacing that was consistent with one Al hfi of *ca.* 59 G. It seems reasonable to conclude that the carriers of spectra A were *trans*-β-aluminovinyl, AlCDCD and AlCHCH, **2**. It was however apparent from attempts to simulate the spectrum of AlCHCH that the Al hfi was orthorhombic.

When this sample was warmed to 100 K the low-temperature spectrum was replaced by the sextet with a spacing of *ca.* 20 G [Fig. 2(*b*)]. The high-temperature spectrum from C_2H_2 was slightly better resolved than the one from C_2D_2 but the overall width of the spectrum and the width of the six principal transitions were the same suggesting a carbon-rather than aluminium-centred radical. In fact a satisfactory simulation of **B** was obtained with the magnetic parameters of cyclohexyl[16] [$a_H(1) = 22$ G, $a_H(2) = 41$ G and $a_H(1) = 5$ G and $\Delta H_{pp} = 10$ G]. Only spectrum **B** was observed from reaction of Al with $^{13}CH^{13}CH$ in C_6H_{12} at 77 K suggesting that ^{13}C-labelled A was too broad to detect in C_6H_{12} at this temperature.

Because of complications due to the involvement of matrix-derived radicals, reactions of Al atoms with C_2H_2 and $^{13}CH^{13}CH$ at 77 K were repeated in perdeuteriocyclohexane. C_2H_2 gave a spectrum [Fig. 3(*a*)] similar to Fig. 2(*a*) except that the central region was better resolved. When this sample was warmed above 100 K a six-lined spectrum developed that could be simulated with the magnetic parameters of perdeuteriocyclo-hexyl, C_6D_{11}, [$a_D(1) = 3.2$ G and $a_D(2) = 6.6$ G] confirming that a radical derived from the matrix was produced in this system.

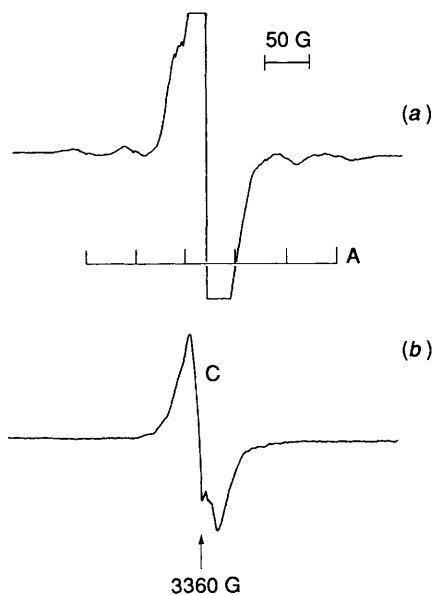A simulation of a mixture of AlCHCH and C_6D_{11} obtained

Fig. 4 (*a*) EPR spectrum at 9446.2 MHz given by Al atoms and C_2D_2 in adamantane at 77 K; (*b*) spectrum at 9352.4 MHz produced on annealing of the sample to 100 K
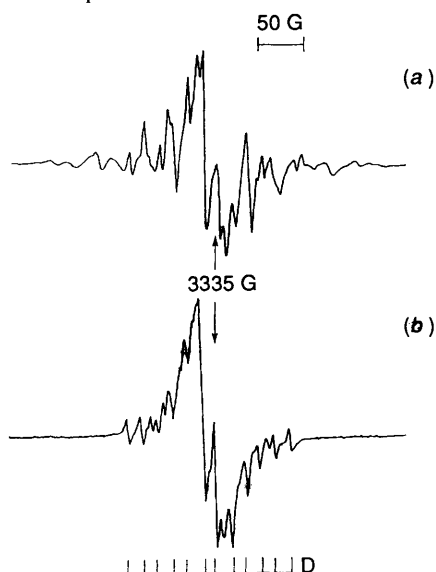

Fig. 5 (*a*) EPR spectrum at 9446.9 MHz given by Al atoms and C_2H_2 in adamantane at 77 K; (*b*) spectrum at 9354.5 MHz produced on annealing of the sample to 100 K

by using the parameters of **2** reported by Kasai[2,3] ($|a_1(\text{Al})|$ = 68 G, $|a_2(\text{Al})|$ = 59 G, $|a_3(\text{Al})|$ = 45 G, $a_H(\text{H})$ = 26 G, $a_H(\text{H})$ = 56 G, and g = 2.0023) and those of C_6D_{12} given above is shown in Fig. 3(*b*). The fit with the experimental spectrum is good but the errors in the hfi are at least ±5 G. There were additional transitions in the centre of the experimental spectrum with spacings that suggested they were from an oligomeric vinyl formed by addition of AlCHCH to C_2H_2.

Al and $^{13}CH^{13}CH$ in C_6D_{12} gave a poorly resolved spectrum of **A** but we were able to estimate a ^{13}C coupling constant of *ca.* 100 G to one ^{13}C nucleus.

Adamantane. Reaction of Al with C_2D_2 in $C_{10}H_{16}$ gave a pinkish brown deposit that had an overall spectrum made up of a sextet of poorly resolved multiplets **A** and a much more intense feature at g = 2.0023 [Fig. 4(*a*)]. Above 100 K only the central feature, **C**, remained [Fig. 4(*b*)] and this spectrum was virtually unchanged, apart from loss of some minor features, upon warming the sample to 250 K. It was almost certainly a poorly resolved spectrum of 2-adamantyl.[16]
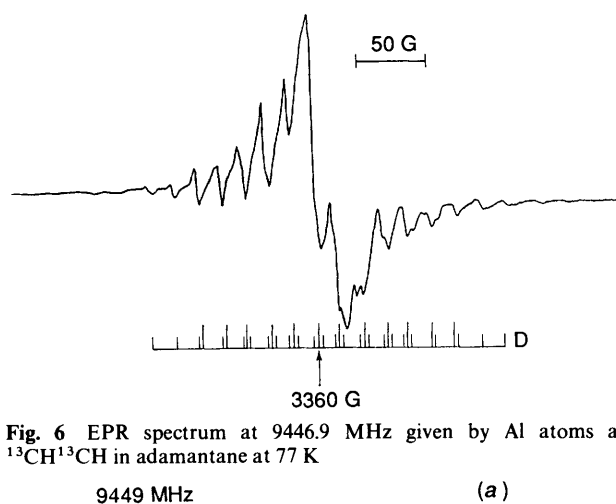

Fig. 6 EPR spectrum at 9446.9 MHz given by Al atoms and $^{13}CH^{13}CH$ in adamantane at 77 K
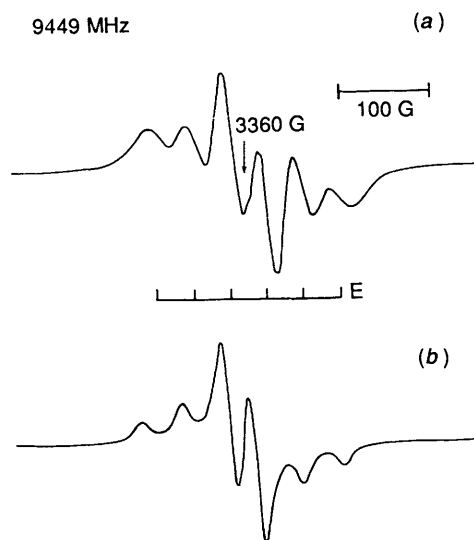

Fig. 7 (*a*) EPR spectrum at 9450 MHz given by Al atoms and $C_6H_5C{\equiv}CD$ in cyclohexane at 77 K; (*b*) simulated spectrum of $Al(C_6H_5C{\equiv}CD)$ with parameters given in the text

Reaction of Al with C_2H_2 in $C_{10}H_{16}$ at 77 K gave the spectrum shown in Fig. 5(*a*) and it was similar but better resolved than the spectrum obtained in C_6H_{12}. When this sample was warmed to 130 K the spectrum shown in Fig. 5(*b*) was obtained and appeared to consist of an isotropic sextet of doublets, **D**, with a_{Al} = 33.3 G and $a_H(1)$ = 16.7 G superimposed on central features that were probably associated with 2-adamantyl.

Reaction of Al with $^{13}CH^{13}CH$ in $C_{10}H_{16}$ at 77 K gave the spectrum shown in Fig. 6. This spectrum consisted of a sextet of doublets of triplets with a doublet splitting of 17 G and a triplet splitting of 36 G, superimposed on the spectrum of 2-adamantyl, and was the ^{13}C analogue of **D**.

Other acetylenes. Al and [1-^2H]phenylacetylene ($C_6H_5C{\equiv}$ CD) in *c*-C_6H_{12} gave the spectrum labelled **E** in Fig. 7(*a*). It has an overall shape similar to the powder spectra of $Al(C_2H_4)$[5] and $Al(NH_3)_2$[17] in solid C_6H_{12}, complexes that have the unpaired spin population on Al located in a 3p orbital. A satisfactory simulation of this spectrum [Fig. 7(*b*)] was obtained with $|a_{\parallel}|$ = 43 G, $|a_{\perp}|$ = 6 G, $g_{\parallel}$ = $g_{\perp}$ = 2.0009. At low microwave power (20 μW) there was an additional sharper spectrum **F** that appeared to be a quartet with a spacing of about 6 G that increased in intensity relative to the spectrum from **E** as the sample was annealed to 150 K.

Reaction of Al with $C_6H_5C{\equiv}CH$ in C_6H_{12} gave the spectrum shown in Fig. 8(*a*) that could be simulated with same Al hfi as **E** plus $a_H(1)$ = 36 G and an additional line at g = 2.0025 [Fig. 8(*b*)]. When this sample was annealed a poorly resolved
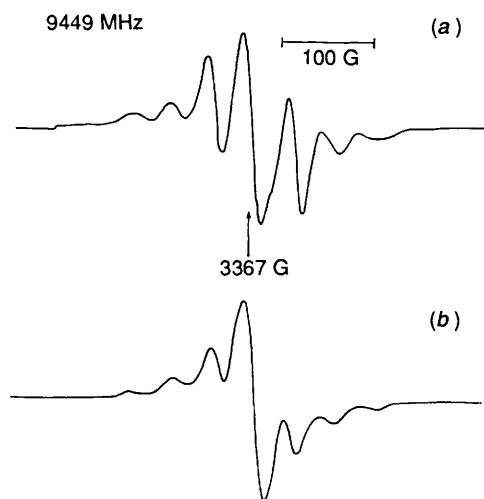
Fig. 8 (a) EPR spectrum at 9450 MHz given by Al atoms and $C_6H_5C\equiv CH$ in cyclohexane at 77 K; (b) simulated spectrum of $Al(C_6H_5C\equiv CH)$ with the parameters given in the text
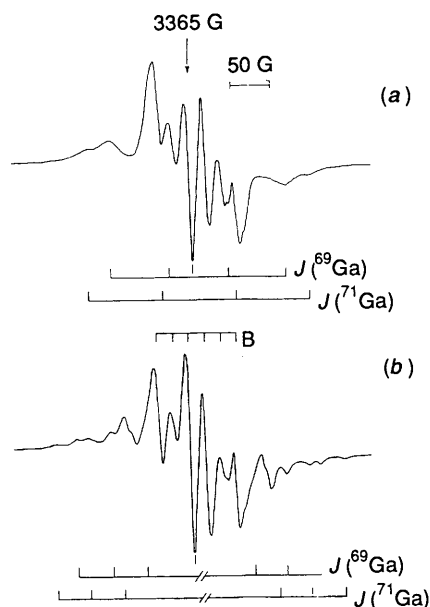

Fig. 9 EPR spectrum given by natural Ga atoms and C_2D_2 (a) and C_2H_2 (b) in cyclohexane at 77 K

spectrum of **F** was obtained that was indicative of a small H hfi in addition to the 6 G coupling.

Al and $C_6H_5C\equiv CC_6H_5$ in C_6H_{12} gave a sextet of transitions with $a_{Al} = 58$ G and $g = 2.0036$ from a mono nuclear Al species **G** and Al and $(CH_3)_3CC\equiv CH$ gave a sextet of doublets **H** with $a_{Al} = 60$ G, $a_H = 40$ G and $g = 2.0023$.

Although the major paramagnetic species from reaction of Al with propyne was CH_2CH with $a_H(2) = 18.9$ G, $a_H(1) = 14$ G and $g = 2.0023$ there was a weak sextet of doublets **I** with $a_{Al} = 50$ G and $a_H(1) = 30$ G from $Al(CH_3C\equiv CH)$.

Gallium.—Reaction of natural Ga atoms (70% ^{69}Ga and 30% ^{71}Ga, $I = 3/2$ for both isotopes) with C_2D_2 and C_2H_2 in C_6H_{12} gave deposits that had the powder EPR spectra shown in Figs. 9(a) and 9(b). The low- and high-field components ($m_I = \pm 3/2$) had the appearance of parallel transitions from which we constructed the quartet stick spectrum **J** in Fig. 9(a). An analysis of these spectra gave $|a_1(69)| = 73.2$ G, $|a_1(71)| = 92.2$ G and $g_1 = 2.0082$. In addition the $m_I = 3/2$ line of the ^{69}Ga quartet showed an hfi of ca. 6.5 G from at least two D nuclei.

When C_2H_2 was used instead of C_2D_2 the $m_I = \pm 3/2$

components of the spectrum were triplets indicating two equivalent H nuclei with $a_H(2) = 43$ G and when $^{13}CH^{13}CH$ was used the spectrum suggested two equivalent C nuclei with $a_{13}(2) = 30$ G while the central features were similar to those found with C_2D_2. When samples containing Ga and C_2D_2 or C_2H_2 were warmed to 100 K a triplet of doublets developed with $a(1) = 22$ G, $a(2) = 41$ G and $g = 2.002$, parameters that are readily assigned to the α and one of the β protons of cyclohexyl.[16] The spectrum then remained unchanged until it disappeared at 190 K. In cyclohexane the α and major β splittings of cyclohexyl are poorly resolved and the small splitting is not resolved.[18]

Because spectra of the gallium–acetylene adduct, even at 77 K, were dominated by the spectrum of cyclohexyl the reaction was repeated in perdeuteriated cyclohexane. In this case better spectra of **J** were obtained [Figs. 10(a), (b) and (c)] and could be analysed in terms of one Ga coupling constant and coupling to two equivalent H and C nuclei confirming the number of interacting H and C nuclei and the coupling constants obtained in the light matrix.

Reaction of Ga atoms with C_2D_2 or C_2H_2 in adamantane at 77 K gave spectra that consisted mainly of a doublet with $a(1) = 21$ G from 2-adamantyl;[16] there was no evidence for Ga–acetylene complexes.

Reaction of Ga atoms with $C_6H_5C\equiv CD$ gave a poorly resolved quartet (Fig. 11) with a spacing of ~37 G which disappeared upon warm-up and was replaced by a spectrum identical with **F**. Because of the poor quality of the spectrum from Ga and $C_6C_5C\equiv CD$ reactions with other substituted alkynes were not attempted.

Discussion

Aluminium.—Two mono nuclear Al(o) complexes, **A** and **D** have been detected by EPR spectroscopy from reaction of ground-state Al atoms with acetylene at 77 K in inert hydrocarbon matrices in a rotating cryostat. The magnetic parameters of these species and the other species produced by reaction of Al and Ga atoms with alkynes in hydrocarbon matrices are summarized in Table 1.

Species **A**. This species has two inequivalent H hfi that are close to those of the σ-complexes *cis-* and *trans-*η^1-AlCHCH while the Al hfi are similar to the values of the *trans* conformer. It should however be noted that *cis-*AlC_2H_2 has been assigned a larger Al hfi than *trans* AlC_2H_2[2] whereas in CH_2CH the *trans* β-H hfi is larger than the *cis* β-H hfi.[16] MO calculations do, however, support the original assignment in that the *trans* conformer is calculated to be more stable than the *cis* conformer.[10] If **A** is *trans-*η^1-AlCHCH then it is only stable below 100 K and *cis-*η^1-AlCHCH is not produced in the hydrocarbon matrices.

Species **B**. When cyclohexane is used as the matrix this species is present in samples prepared at 77 K and has hfi consistent with cyclohexyl. It is interesting that this radical is formed when Al atoms react with acetylene in cyclohexane but not when they react with ethylene in this matrix. This may be associated with the high reactivity of aluminovinyl compared with that of the η^2–π complex $Al(C_2H_4)$.

Species **C**. When the matrix is changed from cyclohexane to adamantane η^1-AlCHCH is formed at 77 K along with 2-adamantyl, **C**, although there is less compelling evidence for its formation than there is for cyclohexyl in cyclohexane.

Species **D**. A third spectrum **D** develops in $C_{10}H_{16}$, upon annealing, that is isotropic with coupling of the unpaired electron to one Al, one H, and two C nuclei. The Al and H hfi are smaller than the values of η^1-AlCHCH. The ^{13}C hfi, from *two* equivalent carbons is significantly smaller than the value of $a_{13}(\alpha) = 107.5$ G for CH_2CH[19] and is smaller than the values of about 55 G for the organometallic vinyls AgCHCH[1] and
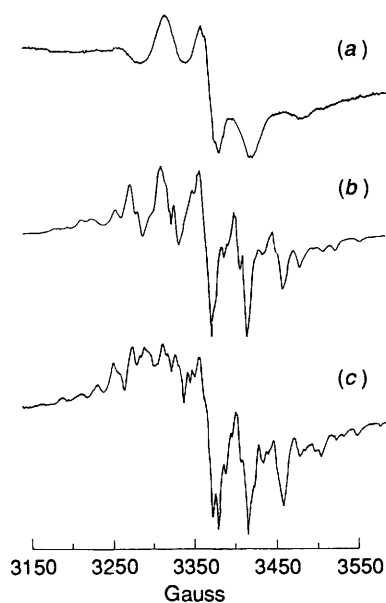
Fig. 10 EPR spectrum given by natural Ga atoms and C_2D_2 (a), C_2H_2 (b) and $^{13}CH^{13}CH$ (c) in perdeuteriocyclohexane at 77 K
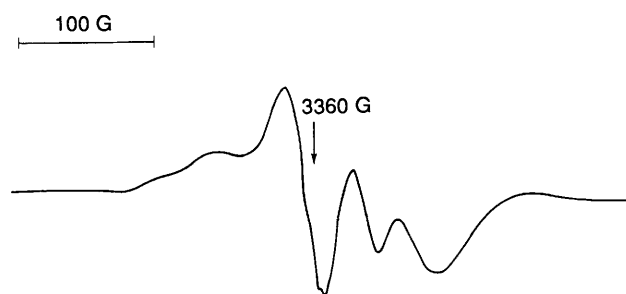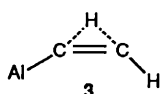

Fig. 11 EPR spectrum given by natural Ga atoms and $C_6H_5C\equiv CD$ in cyclohexane at 77 K

AuCHCH.[20] This is the most difficult spectrum to assign in the Al–C_2H_2 system but the EPR data suggest it is not the insertion product HAlCCH[11] or an H-bridged species which would be an intermediate in the vinyl–vinylidene transformation. The C

nuclei of these species would not be expected to be magnetically equivalent and there should be coupling to a second proton.

Species E. Reaction of Al with $C_6H_5C\equiv CH$ gives a complex E with a small and highly anisotropic Al hyperfine tensor suggesting an $\eta^2-\pi$ complex. If $|a_\parallel|$ and $|a_\perp|$ are positive the isotropic coupling constant, $a_{iso'} = 18$ G and the dipolar coupling constant, $P_{exptl'} = 31$ G can be calculated. Dividing these values by the one-electron parameters for the Al 3s and 3p orbitals[21] gives the unpaired spin populations of $\rho_{3s} = 0.01$ and $\rho_{3p} = 0.42$. On the other hand, if $|a_\parallel|$ is positive and $|a_\perp|$ is negative, as is usually found for Al(o) species,[22,23] $a_{iso'} = 10$ G and $P_{exptl} = 41$ G and $\rho_{3s} = 0.007$ and $\rho_{3p} = 0.55$. This latter analysis is consistent with a large contribution to the SOMO from an unpaired electron located in an Al 3p orbital; the value of ρ_{3p} is in fact identical with $\rho_{3p} = 0.55$ for $\eta^2-Al(C_2H_4)$.[5] The H coupling constant of 36 G is, however, much larger than the value of 2.7 G for $\eta^2-Al(C_2H_4)$[5] and is more suggestive of an η^1-adduct.

Species F. This species F does not have an Al hfi but the

Table 1 EPR parameters of the paramagnetic products from reaction of Al and Ga atoms with acetylenes[a]

| Species	a_1(Al)	a_2(Al)	a_3(Al)	a_H[b]	a_C[b]	g
A	68	59	45	26 (1)	100	2.0023
B				56 (1) 22 (1) 41 (2) 5 (1)		2.0025
C				21 (1)		2.0023
D	33.3			16.7 (1)	36 (1)	2.0030
E	43	6	6	36		2.0009
F				6		2.0025
G	58					2.0036
H	60			40 (1)		2.0023
I	50			30 (1)		2.0023
J	73.2[c]			43 (2)	30 (2)	2.0082

[a] Hyperine interactions in gauss. [b] The number in parentheses refers to the number of equivalent nuclei. [c] ^{69}Ga.

proton hfi from both $C_6H_5C\equiv CH$ and $C_6H_5C\equiv CD$ are similar to the *ortho* and *para* ring protons of α-styryl[24] and is most likely the oligomeric vinyl 4.
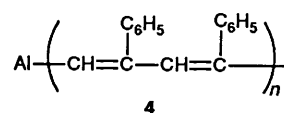

Species G, H *and* I. These species have Al hfi that are consistent with η^1-adducts and are most probably *trans*-vinyls.

Interestingly there is no evidence for insertion of Al into C–H bonds of alkynes or oligomerization to give aluminocyclopentenes 5.
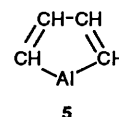
Gallium.—Species J. Only one Ga-containing radical has been detected from reaction of Ga atoms with acetylene and it has one Ga coupling constant and coupling to two equivalent H and C nuclei. The carrier of the spectrum is, therefore, not a gallovinyl, η^1-GaCHCH or gallovinylidene, GaCCH$_2$ but appears to be the symmetrically bonded complex 6, 7, which
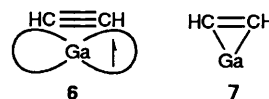
may have π (6) or σ (7) bonding between the metal centre and the ligand. The shape of the spectrum does, however, suggest σ rather than π bonding.

An unusual feature of this work is the presence of radicals formed by abstraction of an H atom from the matrix suggesting formation of a reactive radical species which is possibly a gallovinyl.

Conclusions

(i) Al and acetylene react at 77 K in cyclohexane to give η^1-aluminovinyl that appears to be the *trans* rather than *cis* complex. This species is either unstable or extremely reactive above 77 K because cyclohexyl is the only paramagnetic species detected above 100 K. There is no EPR spectroscopic evidence

for a $\eta^2-\pi$ complex $Al(C_2H_2)$, analogous to $Al(C_2H_4)$, or aluminovinylidene, $AlCCH_2$, formed by complete transfer of an H atom from the α to the β carbon of an initially formed β-aluminovinyl. In adamantane, η^1-AlCHCH is formed at low temperatures while a second Al(0) species appears on warm-up that is not $AlCCH_2$, HAlCCH or an H-bridged AlCHCH complex. Again a radical derived from the matrix is formed.

(*ii*) Most substituted alkynes give an alumino-substituted vinyl although $C_6H_5C\equiv CH$ appears to give a π-complex and $CH_3C\equiv CH$ gives mainly propargyl.

(*iii*) Ga and acetylene in cyclohexane do not give a gallovinyl complex but appear to give the complex η^2-Ga(CHCH) with σ rather than π bonding. Cyclohexyl is formed in significant yields and only 2-adamantyl is formed in adamantane.

(*iv*) Both Al and Ga give a polymeric vinyl with $C_6H_5C\equiv CH$ but when the matrix is removed only Al and acetylene give a metal-doped polyacetylene.

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