(Co)cyclodimerization of Alkynes by Aluminum Halides. Synthesis of Pyridines from Aluminum Halide σ Complexes of Cyclobutadienes and Nitriles

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The Lewis acid promoted cyclodimerization of monoalkyl-substituted alkynes and cocyclodimerization of monoalkyl(aryl)- and dialkyl-substituted alkynes are described. It has been found that the corresponding aluminum halide σ complexes of the cyclobutadienes react with activated nitriles, e.g., ethyl cyanoformate, to yield substituted pyridines. The substitution pattern of the pyridines formed constitutes the basis of the proposed mechanism for these reactions.

The synthesis of aluminum halide σ complexes of cyclobutadienes has thus far been limited mainly to the use of dialkyl-substituted alkynes,[1] which in some cases contained a heteroatom.[2] Recently, the cyclodimerization of propyne was described as well as the cocyclodimerization of propyne and 2-butyne.[3] In the present paper the results of a further exploration of the (co)cyclodimerizations of mono- and dialkyl-substituted alkynes will be given. Cocyclodimerizations of alkynes have been performed previously by using an organotransition-metal complex: e.g., preformed π-alkyne complexes of Co react with external alkynes to afford metallocyclopentadienes containing two different alkynes.[4] In addition to cooligomerization of α,ω-diynes with bis(trimethylsilyl)acetylene and di-*tert*-butylacetylene, use of CpCo(CO)₂ as a catalyst has been shown to afford mixed cyclobutadiene cobalt sandwich complexes.[5]

Pyridines are known to be accessible via a variety of synthetic[6] methods. As a novel synthesis the cobalt-catalyzed cotrimerization of alkynes and nitriles has attracted much attention in recent years.[7] For example, it was found that monoalkyl-substituted alkynes and nitriles afford a mixture of pyridines.[7] The catalytic cotrimerization of acetylene, propyne, and acetonitrile led to a mixture of mono-, di-, and trimethyl-substituted pyridines, showing a poor selectivity for the intermediate cobaltocyclopentadiene complex.[7b] A few years ago, the reaction of aluminum halide σ complexes of substituted cyclobutadienes with ethyl cyanoformate was reported in
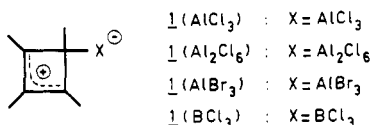
a preliminary paper to yield pyridines.[1d,8] The present

Scheme I

Scheme II
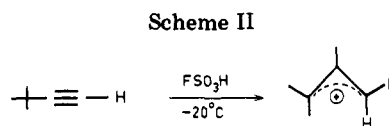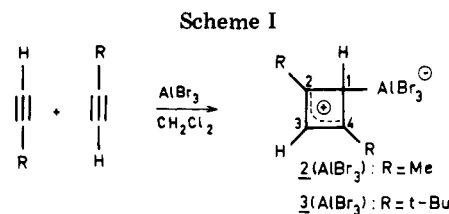
paper deals with new results concerning this reaction in which the structure of the obtained pyridines has afforded an insight in the mechanism.

Results and Discussion

Aluminum Halide σ Complexes of Cyclobutadienes. (I) Cyclodimerization of Monoalkyl-Substituted Alkynes. Reaction of propyne with AlBr₃ at -85 °C in CH₂Cl₂ affords complex 2 (AlBr₃)[3,9] (Scheme I). The use of aluminum trichloride instead of aluminum tribromide in CH₂Cl₂ at both -85 and 0 °C does not afford complex 2(AlCl₃); ¹H NMR spectroscopic measurements reveal only the presence of some propyne and probably polymeric material as indicated by a broad absorption at 1-2 ppm. However, when aluminum tribromide and CH₂Cl₂ are used at -85 °C,[10] complex 2(AlBr₃) is formed in 70 ± 5% yield (according to integration of the ¹H NMR spectrum). The beneficial effect of a low temperature on the yield is exemplified by the fact that if the cyclodimerization is performed at -40 °C, the yield drops to 35 ±5%.[3] It is of interest to mention that reaction of propyne with HCl and HBr leads to mixtures of products including chlorinated and brominated cyclobutanes, respectively.[11] With *tert*-butylacetylene and aluminum tribromide in a 2:1 molar ratio at -85 °C in CH₂Cl₂, cyclodimerization is observed, affording complex 3(AlBr₃) (Scheme I). In comparison, no cyclodimerization of *tert*-butylacetylene is observed when this compound is treated with FSO₃H; instead, at -78 °C a complex mixture of unidentifiable products is

(1) (a) Koster, J. B.; Timmermans, G. J.; Van Bekkum, H. *Synthesis* **1971**, 139. (b) Hogeveen, H.; Jorritsma, H.; Wade, P. A.; Van Rantwijk, F.; Koster, B. J.; Prooi, J. J.; Sinnema, A.; Van Bekkum, H. *Tetrahedron Lett.* **1974**, 3915. (c) Driessen, P. B. J.; Hogeveen, H. *J. Am. Chem. Soc.* **1978**, *100*, 1193. (d) Driessen, P. B. J.; Hogeveen, H. *J. Organomet. Chem.* **1978**, *156*, 265. (e) Driessen, P. B. J. Thesis, University of Groningen, 1979. (f) Hogeveen, H.; Kok, D. M. "The Chemistry of Acetylenes"; Patai, S., Ed.; Wiley: New York, in press (Supplement C).

(2) Eleveld, M. B.; Vogel, W., unpublished results. See also ref 1f.

(3) Hogeveen, H.; Kok, D. M. *Tetrahedron Lett.* **1980**, 659.

(4) Wakatsuki, Y.; Kuramitso, T.; Yamazaki, H. *Tetrahedron Lett.* **1974**, 4549. Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc., Chem. Commun.* **1973**, 280.

(5) Hillard, R. L., III; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1977**, *99*, 4058.

(6) Smith, D. M. In "Heterocyclic Compounds"; Coffey, S., Ed.; 1976; Vol. IV, Section F, Chapter 24.

(7) (a) Wakatsuki, Y.; Yamazaki, H. *Synthesis* **1976**, 26. (b) Bönnemann, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 505.

(8) Driessen, P. B. J.; Grace, D. S. B.; Hogeveen, H.; Jorritsma, H. *Tetrahedron Lett.* **1976**, 2263.

(9) The aluminum halide in parentheses indicates the Lewis acid which is attached to the cyclobutadiene moiety.

(10) Aluminum tribromide is known to undergo halogen exchange with CH₂Cl₂ above about -40 °C. See: Mirda, D.; Rapp, D.; Kramer, G. M. *J. Org. Chem.* **1979**, *44*, 2619.

(11) Griesbaum, K.; Naegele, W.; Wanless, G. G. *J. Am. Chem. Soc.* **1965**, *87*, 3151. Griesbaum, K.; Singh, A.; El Abed, M. *Tetrahedron Lett.* **1978**, 1159.

Table I. ^{1}H NMR Chemical Shift Values^a of Complexes 2(AlBr$_3$)-7(AlBr$_3$)

complex	hydrogen(s) in position			
	1	2	3	4
2(AlBr$_3$)	2.94 (d, J = 4.1 Hz)	2.74 (s, CH$_3$)	7.70 (d, J = 4.1 Hz)	2.74 (s, CH$_3$)
3(AlBr$_3$)	3.34 (d, J = 4.5 Hz)	1.54 (s, t-Bu)	7.74 (d, J = 4.5 Hz)	1.54 (s, t-Bu)
4(AlBr$_3$)	2.42^b	2.42 (s, CH$_3$)	2.21 (s, CH$_3$)	2.42 (s, CH$_3$)
5(AlBr$_3$)	2.92 (br s)	2.64 (s, CH$_3$)	2.34 (br s, CH$_3$)	6.9-8.5 (m, phenyl)
6(AlBr$_3$)^d	c	2.38 (br s, CH$_3$)	2.16 (br s, CH$_3$)	0.8-1.9 (br, CH$_2$) 2.3-3.1 (br, CH$_2$)
7(AlBr$_3$)	c	2.37 (s, CH$_3$)	2.21 (br s, CH$_3$)	2.01 (t, J = 2.0 Hz, H), 2.4-3.2 (br, CH$_2$)

^{a} Chemical shift values have been measured relative to CH$_2$Cl$_2$ and converted to δ_{Me_4Si} values by using $\delta_{CH_2Cl_2}$ = 5.29 ppm. The spectra were recorded in CH$_2$Cl$_2$ solution at -70 to -80 °C. ^{b} This absorption is obscured by the absorption of the methyl groups in the 2,4-positions. ^{c} The chemical shift values of these hydrogen atoms could not be determined, due to the presence of broad methylene absorptions in the region expected for these hydrogen atoms. ^{d} See ref 20.

found, whereas at -20 °C the 1,1,2-trimethylallyl cation is formed[12] (Scheme II).

Unfortunately,[13] (trimethylsilyl)acetylene does not give a cyclodimerization with aluminum tribromide: at -85 °C in CH$_2$Cl$_2$ no reaction occurs, and at -50 °C decomposition of trimethylsilylacetylene takes place, according to ^{1}H NMR spectroscopic measurements. Attempts to cyclodimerize phenylacetylene under identical conditions lead only to decomposition. Cyclodimerization of phenylacetylene with FSO$_3$H has been reported to fail also;[14] reaction at -78 °C leads to the formation of polymeric material only. In the following section it will be shown, however, that phenylacetylene can be used in the cocyclodimerization with 2-butyne.

(II) Cocyclodimerization of Monoalkyl(aryl)- and Dialkyl-Substituted Alkynes. When a 1:1 mixture of 2-butyne and propyne in CH$_2$Cl$_2$ is added to aluminum tribromide in CH$_2$Cl$_2$ at -85 °C, the formation of complex 4(AlBr$_3$) is observed (Scheme III). Also, consecutive addition of CH$_2$Cl$_2$ solutions of 2-butyne and propyne to the suspension of aluminum tribromide in CH$_2$Cl$_2$ affords complex 4(AlBr$_3$). ^{1}H NMR and ^{13}C NMR spectroscopic measurements of the reaction mixture reveal the absence (at least less than 5%) of both complexes 2(AlBr$_3$) and 1(AlBr$_3$). In contrast to the cyclodimerization of propyne, no large temperature effect on the yield is noted: complex 4(AlBr$_3$) is formed in 76 ± 5% yield at -85 °C and in 68 ± 5% yield at -40 °C.

The consecutive addition of CH$_2$Cl$_2$ solutions of 2-butyne and of phenylacetylene in a 1:1.2 molar ratio to a suspension of aluminum tribromide in CH$_2$Cl$_2$ at -85 °C leads to the formation of complex 5(AlBr$_3$). A 20% excess of phenylacetylene is necessary in order to consume all the 2-butyne (according to ^{1}H NMR spectroscopic measurements), which is probably due to some decomposition of phenylacetylene by aluminum tribromide. On the other hand, total decomposition of phenylacetylene is apparently inhibited by the initial formation of the AlBr$_3$-2-butyne π complex.[3]

Similar to the case of cocyclodimerization of 2-butyne and propyne, 2-butyne and 1,9-decadiyne, when used in a 2:1 molar ratio, cocyclodimerize to complex 6 (AlBr$_3$).

Scheme III

4 (AlBr$_3$): R = Me
5 (AlBr$_3$): R = Ph
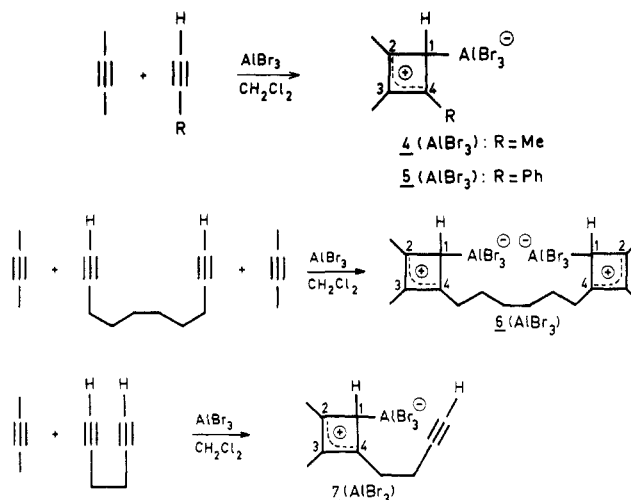
6 (AlBr$_3$)

7 (AlBr$_3$)

When 2-butyne and 1,5-hexadiyne are used in a 1:1 molar ratio, complex 7(AlBr$_3$) is obtained. A cocyclodimerization of 2-butyne and 1,5-hexadiyne, if used in a 2:1 molar ratio, affords complex 7(AlBr$_3$) also; i.e., no addition of 2-butyne to complex 7(AlBr$_3$) occurs.

(III) NMR Spectroscopic Measurements of Complexes 2(AlBr$_3$)-7(AlBr$_3$). For assignment of the structures of these complexes, ^{1}H NMR and ^{13}C NMR spectroscopic measurements have been performed. The number of peaks in the ^{1}H NMR spectra of complexes 2(AlBr$_3$)-4(AlBr$_3$) (Table I) are in accord with a structure having a plane of symmetry. Furthermore, the presence of only one methyl and *tert*-butyl resonance in the ^{1}H NMR spectrum of complexes 2(AlBr$_3$) and 3(AlBr$_3$), respectively, implicates that the aluminum tribromide group is bonded at a carbon atom bearing a hydrogen atom. The chemical shift values of 7.70 and 7.74 ppm for the hydrogen atom in the 3-position is comparable with a value of 8.03 ppm found in cation 8.[15] The absence of this absorption

8 9 2 (AlBr$_3$)
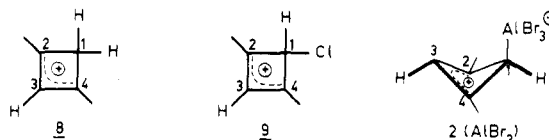
in the ^{1}H NMR spectra of complexes 4(AlBr$_3$)-7(AlBr$_3$) means that the aluminum tribromide group is attached to

(12) Olah, G. A.; Mayr, H. *J. Am. Chem. Soc.* **1976**, *98*, 7333.

(13) The trimethylsilyl group can be easily converted into other organic functionalities (See: Vollhardt, K. P. C. *Acc. Chem. Res.* **1977**, *10*, 1. Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1979**, *101*, 215. Funk, R. L.; Vollhardt, K. P. C. *Ibid.* **1980**, *102*, 5253) and as a consequence (trimethylsilyl)acetylene would have been a very useful substrate in the cyclodimerization and subsequent reactions of the corresponding σ complex.

(14) Olah, G. A.; Spear, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 1845.

(15) Olah, G. A.; Staral, J. S.; Spear, R. J.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 5489.

Table II. ^{13}C NMR Chemical Shift Values^a of Complexes 2(AlBr$_3$)–7(AlBr$_3$)

| compd | cyclobutenyl C | | other C^d |
	allylic	C(Al)^b	
2(AlBr$_3$)	184.0, 152.4 (d, J = 210 Hz)	62.1	20.0 (CH$_3$)
3(AlBr$_3$)	182.0, 150.3 (d, J = 205 Hz)	57.9	37.0 (C(CH$_3$)$_3$), 27.2 (C(CH$_3$)$_3$)
4(AlBr$_3$)	165.4, 162.8	61.9	15.8, 10.3 (CH$_3$)
5(AlBr$_3$)	196.6, 178.7, 150.3	51.5	19.9, 11.7 (CH$_3$), 141.0, 136.9, 130.0, 125.5 (phenyl)
6(AlBr$_3$)	166.1, 166.0, 163.6, 163.4, 161.3^c	60.8	15.8, 10.9 (CH$_3$), 28.6, 25.3^c (br, CH$_2$)
7(AlBr$_3$)	167.4, 159.8, 158.1	60.3	16.3, 11.1 (CH$_3$), 27.7, 14.2 (CH$_2$), 80.2 (d, J = 50 Hz) (HC≡C), 70.6 (d, J = 250 Hz) (HC≡C)

^{a} Chemical shift values have been measured relative to CDCl$_3$ and converted to δ_{Me_4Si} values by using δ_{CDCl_3} = 76.9 ppm. The spectra are taken of CDCl$_3$/CH$_2$Cl$_2$ (1.5:2.5 v/v) solutions at −70 to −80 °C. ^{b} The signals due to the carbon atoms bearing the aluminum tribromide group are broad. The $^1J_{^{13}C,^1H}$ coupling constants of these carbon atoms have values in the range of 130–135 Hz. ^{c} See the text. ^{d} The $^1J_{^{13}C,^1H}$ coupling constants for methyl and methylene carbon atoms have values in the range of 130–135 Hz, and those of the phenyl group are in the range of 160–170 Hz.

the carbon atom bearing the hydrogen atom. In the ^{1}H NMR spectra of complexes 2(AlBr$_3$) and 3(AlBr$_3$) a $^4J_{^1H_{1,3}}$ long-range coupling is found of 4.1 and 4.5 Hz, respectively. A similar coupling of 4.0 Hz has been reported[15] for ion 9 but not for ion 8. If one assumes that complexes 2(AlBr$_3$) and 3(AlBr$_3$) and ion 9 have structures similar to that of complex 1(AlCl$_3$) (which has been determined by X-ray diffraction[16]), the $^4J_{^1H_{1,3}}$ long-range coupling is explained by the presence of a W conformation [as shown for complex 2(AlBr$_3$)] between H$_1$ and H$_3$.[17]

The ^{13}C NMR spectroscopic measurements of complexes 2(AlBr$_3$)–7(AlBr$_3$) (Table II) are in agreement with the assigned structures; the C-3 carbon atom of complexes 2(AlBr$_3$) (at 152.4 ppm) and 3(AlBr$_3$) (at 150.3 ppm) shows a $^1J_{^{13}C,^1H}$ coupling of 210 and 205 Hz, respectively. The absorption of the carbon atom in complexes 2(AlBr$_3$)–7-(AlBr$_3$) bearing the aluminum tribromide group is broadened; the broadening is probably due to the close proximity of the aluminum atom.[18] In all cases this resonance displays a $^1J_{^{13}C,^1H}$ coupling of 130–135 Hz, which sustains the structure of the σ complexes. The values of ^{13}C NMR chemical shifts of complex 4(AlBr$_3$) can be interpreted in terms of a considerable contribution of the homocyclopropenium ion structure;[15] the same is thought to be true for complexes 6(AlBr$_3$) and 7(AlBr$_3$) (Table II).

Let us now focus attention on complex 6(AlBr$_3$). At −78 °C the ^{13}C NMR spectrum of this complex (Figure 1) shows two absorptions for the methylene carbon atoms which are more broadened (20 Hz) than those of the other carbon atoms (5 Hz; except for the aluminum-bonded carbon atom, see above). Furthermore, five signals due to allylic ring carbon atoms are observed in the region of 160–167 ppm. When the temperature of the sample is raised the methylene absorptions gradually sharpen, until at −1 °C[19] they have become almost as narrow as the other absorptions in the spectrum[20] (Figure 1). The absorption

due to the aluminum-bonded carbon atom gradually broadens on raising of the temperature. Small chemical shift differences are observed between −1 and +78 °C: in the regions of 160–167 and 10–30 ppm these amount up to 2.5 and 0.2 ppm, respectively.

The (reversible) line broadening of the methylene absorptions has been observed also in other systems. When a mixture (ratio 1:3:2) of pyridines 10a–c is cooled, the
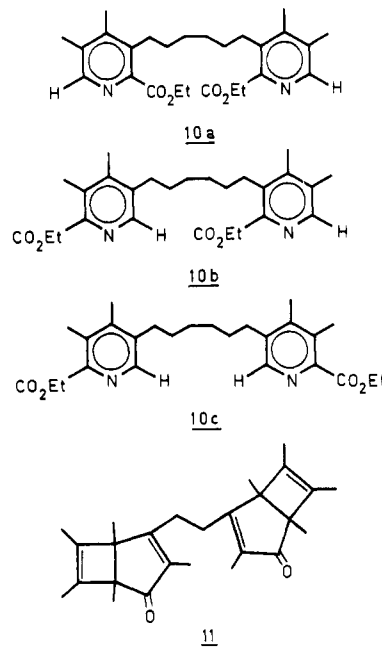
methylene absorptions show relatively more broadening than the other absorptions in the spectrum, and diketone 11 shows a similar phenomenon.[21] The temperature-dependent line broadening might be explained by rotational barriers in the methylene chain. The observation of absorptions of five different allylic carbon atoms at −78 °C might be due to the presence of an asymmetric center (the carbon bearing the aluminum tribromide group) in both cyclobutenyl rings of complex 6(AlBr$_3$). This could mean that the difference between the diastereomeric meso and dl compounds is observed by ^{13}C NMR spectroscopy. If this were true, one would expect that the mixture of positionally isomeric pyridines 10a–c would display in the

(16) Krüger, C.; Roberts, P. J.; Tsay, Y. H.; Koster, J. B. *J. Organomet. Chem.* **1974**, 78, 69.

(17) Günther, H. "NMR Spektroskopie"; Georg Thieme Verlag: Stuttgart, 1973; Chapter IV.

(18) Westmoreland, T. D., Jr.; Bhacca, N. S.; Wander, J. D.; Day, M. C. *J. Am. Chem. Soc.* **1973**, 95, 2019.

(19) Above this temperature halogen exchange between CDCl$_3$ and the aluminum tribromide group of complex 6(AlBr$_3$) is observed. See also ref 10.

(20) When the temperature is raised from −78 to 0 °C, all broad absorptions in the ^{1}H NMR spectrum of complex 6(AlBr$_3$) sharpen. These measurements, however, are less informative than the corresponding ^{13}C NMR spectroscopic measurements about the process(es) responsible for it.

(21) Van Kruchten, E. M. G. A. Thesis, University of Groningen, 1981.
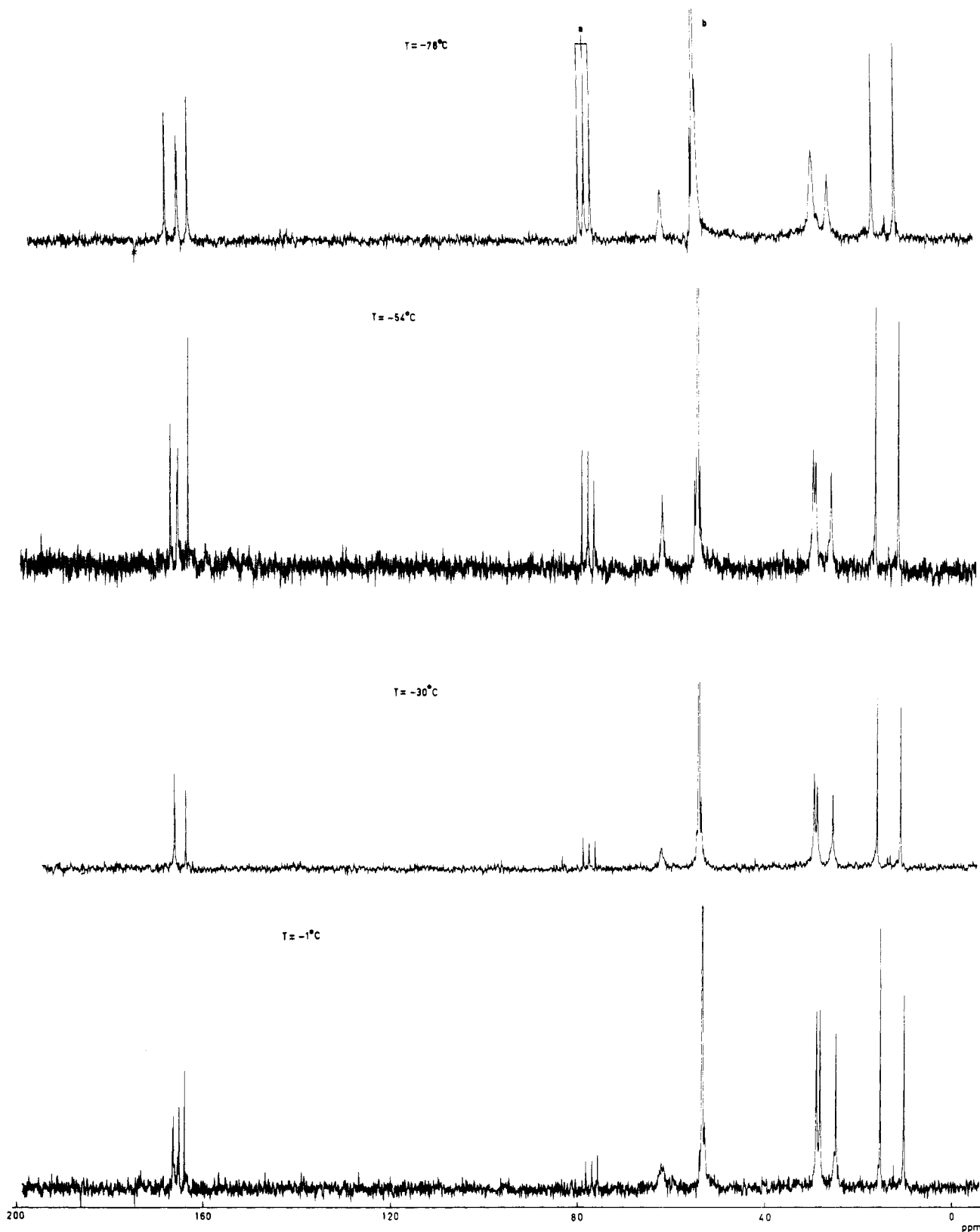
Figure 1. ^{13}C NMR spectra of complex 6(AlBr$_3$) at variable temperatures (the spectral changes are reversible on changing the temperature); (a) CDCl$_3$, (b) CH$_2$Cl$_2$.

^{13}C NMR spectrum more than ten signals due to pyridine ring carbon atoms. This is not the case, however; at -15 °C only nine signals[22] are observed, which means that within one bipyridine the aromatic rings do not influence each other, an effect probably due to the distance between

the pyridine rings. It is conceivable that in the case of complex 6(AlBr$_3$) the observed chemical shift differences between the diastereomeric meso and *dl* compounds are due to a cyclic structure of type 6a(AlBr$_3$), in which the cyclobutenyl rings are proximate enough to influence each other. Bearing in mind that distance is important for observation of differences between diastereomeric meso and *dl* compounds, one expects, on the basis of structure

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(22) Probably two ^{13}C absorptions of the pyridine rings coincide.

(meso) **6a**(AlBr₃)
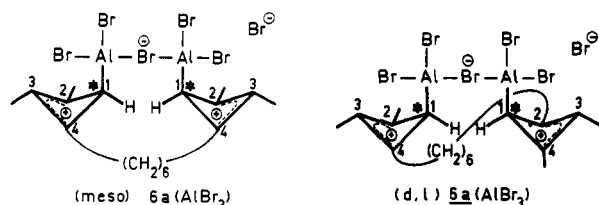
(d,l) **6a**(AlBr₃)

6a(AlBr₃), that at −78 °C the four most deshielded absorptions are due to C-2 and C-4. This is in agreement with the assignment (on the basis of intensities) of the most deshielded signal (165.4 ppm) of complex 4(AlBr₃) to the 2(4)-carbon atoms.

The effect of temperature on the chemical shifts on the allylic ring carbon atoms (maximum being 2.5 ppm) contrasts with that of the methyl absorptions (<0.2 ppm). A similar effect is observed for diketone 11 on varying the temperature from −7 to −73° C: the ring carbon atoms show chemical shift differences of a maximum of 0.8 ppm, whereas the methyl carbon atoms have differences of less than 0.2 ppm.[21] Finally, the signal of the aluminum-bonded carbon atom is found to broaden on raising of the temperature but is still present in the spectrum taken at −1 °C. This contrasts with the tetraalkyl-substituted aluminum halide σ complexes of cyclobutadienes: e.g., at −91 °C a broad signal of the aluminum-bonded carbon atom of complex 1(AlBr₃) is observed at 64.9 ppm, whereas the same carbon atom is not detected at 0 °C.[1c,e] This might be due to the presence of a hydrogen atom in the former case, which enhances the relaxation of the carbon atom[23] and facilitates its observation.

Reactions of Aluminum Halide σ Complexes of Cyclobutadienes with Nitriles. (I) Reactions of Complexes 2(Al₂Br₆)–7(Al₂Br₆) with Ethyl Cyanoformate. When complex 2(AlBr₃) is allowed to react with ethyl cyanoformate between −85 and +20 °C, a 6:1 mixture of pyridines 12a,b (Table III) is isolated in 12% yield. This yield is rather poor, if compared with those of the reactions of tetraalkyl-substituted aluminum halide σ complexes of cyclobutadienes with ethyl cyanoformate.[1e,8] However, when complex 2(Al₂Br₆), prepared by using a 100% excess of aluminum tribromide with regard to complex 2(AlBr₃), is treated with ethyl cyanoformate, the yield drastically increases to 54% (Table III). In a similar way, complex 4(AlBr₃) affords pyridine 13 in 26% yield, whereas reaction of 4(Al₂Br₆) with ethyl cyanoformate produces a 58% yield of 13. Under identical conditions complexes 3(Al₂Br₆) and 5(Al₂Br₆)–7(Al₂Br₆) react with ethyl cyanoformate to form pyridines 10a–c and 14–16a,b in yields varying from 38% to 59%. The isomers 12a,b were separated by a combination of crystallization and TLC, and isomers 10a–c, 15a,b, and 16a,b were separated by HPLC.

(II) Structure Assignment of Pyridines 10a–c and 12a,b–16a,b. The structure of pyridines 10a–c and 12a,b–16a,b has been elucidated by ¹H NMR and ¹³C NMR spectroscopic measurements. In the ¹H NMR spectra of pyridines 12a and 14 the most deshielded aromatic proton is observed at 8.34 and 8.43 ppm, respectively, while in the ¹H NMR spectra of pyridines 10a–c, 15a,b, and 16a,b the aromatic proton falls in the region of 8.1–9.1 ppm (see Experimental Section), which is a common chemical shift value for hydrogen atoms attached to the α-carbon atom in alkyl-substituted pyridines.[24] In the ¹³C NMR spectra of compounds 10a–c and 12a,b–

(23) Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; Chapter 2.

(24) Batterham, T. J. "NMR Spectra of Simple Heterocycles"; Wiley: New York, 1973; Chapter 2.
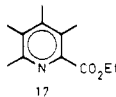
Table III. Reactions of Complexes 2(Al₂Br₆)–7(Al₂Br₆) with Ethyl Cyanoformate

complex	product(s)	% yield[a]
2(Al₂Br₆)	**12a** **12b**	54 (a/b, 6/1)
3(Al₂Br₆)	**14**	38
4(Al₂Br₆)	**13**	58
5(Al₂Br₆)	**15a** **15b**	40 (a/b, 1/6)
6(Al₂Br₆)	**10a** **10b** **10c**	59 (a/b/c, 1/3/2)
7(Al₂Br₆)	**16a** **16b**	45 (a/b, 1/1)

[a] Yields are based on the amount of alkyne used.

16a,b the carbon atom α to the nitrogen atom, and not bonded to the ethoxycarbonyl group, is observed between 146.0 and 150.8 ppm, which is a characteristic region for this kind of carbon atom;[25] it displays in the ¹³C NMR proton-coupled spectrum a ¹J₁₃C,¹H coupling with values in the range of 165–180 Hz (Table IV). The assignment of the structure of isomers 10a–c, 15a,b, and 16a,b has been made on the basis of the hyperfine splitting pattern due to the ³J₁₃C,¹H coupling (Table IV); the presence of a phenyl, methyl, or methylene substituent on the carbon atom adjacent to the α-carbon atom bearing the hydrogen atom is manifested by a singlet, quartet, or triplet hyperfine splitting on each of the C(H) doublets, respectively.

(III) Reactions of Complex 1(Al₂Cl₆) with Nitriles. As shown above for a few cases, the yield of pyridine depends strongly on whether the reaction was performed with the AlBr₃ or Al₂Br₆ σ complex of the cyclobutadienes. Similarly, complex 1(AlCl₃) and 1(Al₂Cl₆) give a different yield of pyridine 17 on reaction with ethyl cyanoformate: 1(AlCl₃), 60%;[1e,8] 1(Al₂Cl₆), 83%. In order to determine what causes a difference in yield, we performed ¹H NMR spectroscopic measurements. At −50 °C, complex 1(AlCl₃)
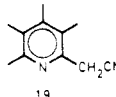
(25) Reference 24, Chapter 7.

Table IV. ^{13}C NMR Chemical Shifts and $^1J_{^{13}C,^1H}$ and $^3J_{^{13}C,^1H}$ Coupling Constants of the α-Carbon Atom (Bearing a Hydrogen Atom) of Pyridines 10a-c, 12a, 13, 14, 15a,b, and 16a,b

	chemical shift, δ	$^1J_{^{13}C,^1H}$, Hz	$^3J_{^{13}C,^1H}$, Hz (multiplicity)
10a	147.6	175	5 (q)
10b	147.4	175	5 (q)
	146.6	175	5 (t)
10c	146.9	175	5 (t)
12a	148.8	170	a
13	146.0	175	5 (q)
14	150.8	165	a
15a	147.5	180	5 (q)
15b	146.6	180	0 (s)
16a	147.3	175	5 (t)
16b	147.9	175	5 (q)

^{a} In these cases the $^3J_{^{13}C,^1H}$ could not be determined due to the presence of an additional $^3J_{^{13}C,^1H}$ coupling.

Table V. Reactions of Complex 1(Al$_2$Cl$_6$) with Nitriles

nitrile	product	% yield^a
N≡CCO$_2$Et	 17	83
N≡CCN	 18	66
N≡CCH$_2$CN	 19	22
N≡CPh	 20	18
N≡CCH$_3$	 21	0

^{a} Yields are based on the amount of alkyne used.

shows only 15% conversion to pyridine 17 in 1.5 h, and complex 1(Al$_2$Cl$_6$) gives 65% conversion under the same conditions, showing that complex 1(Al$_2$Cl$_6$) reacts faster with ethyl cyanoformate than complex 1(AlCl$_3$). A possible explanation could be that in the case of complex 1(Al$_2$Cl$_6$) there is a rapid transfer of AlCl$_3$ from 1(Al$_2$Cl$_6$) to ethyl cyanoformate, affording 1(AlCl$_3$) and NCCO$_2$Et·AlCl$_3$, followed by reaction by pyridine 17. However, ^{1}H NMR spectroscopic measurements at −50 °C indicate that complex NCCO$_2$Et·AlCl$_3$ gives less than 5% conversion with complex 1(AlCl$_3$) to pyridine 17 in 1.5 h. It is therefore concluded that the observed difference between complex 1(AlCl$_3$) and 1(Al$_2$Cl$_6$) is caused by a difference between the reactivities of the complexes themselves. The difference in yields between reaction of complex 1(AlCl$_3$) and 1(Al$_2$Cl$_6$) with ethyl cyanoformate—in warming the solution from −50 °C to room temperature as performed in the preparative experiments—can now be explained by the occurrence of a side reaction(s) in the former case, in which reaction with the nitrile is slower. The NMR dynamic behavior[1e] and the reaction with water[1e] of complexes 1-(AlCl$_3$) and 1(Al$_2$Cl$_6$) differ also.
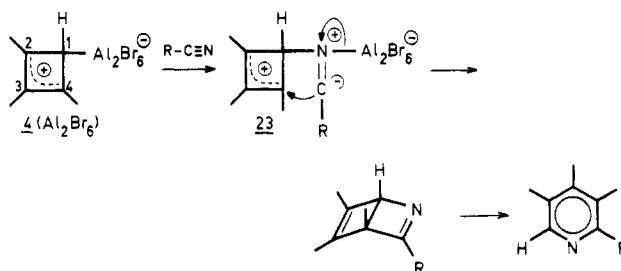
Scheme IV
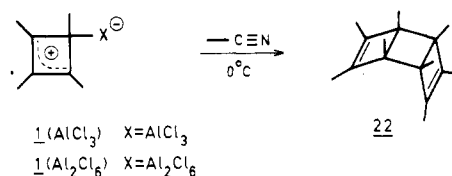
Scheme V

Scheme VI

As shown in Table V, cyanogen, malonitrile, and benzonitrile react with complex 1(Al$_2$Cl$_6$) to give 18–20 in yields of 66%, 22%, and 18%, respectively. In addition, both 1(AlCl$_3$)[1e,8] and 1(Al$_2$Cl$_6$) do not give pentamethylpyridine (21) on reaction with acetonitrile; instead, the dimer of tetramethylcyclobutadiene, 22, is isolated in both cases (Scheme IV). It appears therefore, that the yield on pyridine drops with a decreasing electronegativity of the substituent of the nitrile. It is of interest to note, however, that complex 1(BCl$_3$) has been found to react with acetonitrile, affording 21 in 22% yield[26] (Scheme V).

The results of the reactions of complexes 2(Al$_2$Br$_6$)–7-(Al$_2$Br$_6$) with ethyl cyanoformate show that the major (or even exclusive) pyridine isomer obtained in each case has the hydrogen atom bonded at the α-carbon atom. This means a preferential attack of the nitrile nitrogen atom on the carbon atom of the complexes bearing the aluminum bromide group. Therefore, the mechanism of the reaction probably involves an insertion of the nitrile nitrogen atom in the carbon–aluminum bond[27] followed by ring closure, as exemplified for complex 4(Al$_2$Br$_6$) in Scheme VI. This mechanism differs from the one proposed previously which involved the intermediate formation of a cyclobutadiene.[1d,7,28] Formation of structure 23 will be favored by electron-withdrawing substituents on the carbon atom of the nitrile group, because of stabilization of the negative charge on this carbon atom. It should be pointed out that this mechansm does not allow for the formation of a minor quantity of pyridine 12b when complex 2(Al$_2$Br$_6$) is used, which indicates that the nitrile

(26) Fongers, K. S., unpublished results.

(27) It is of interest to speculate whether some of the reported reactions of methylaluminum dichloride and diethylaluminum chloride with nitrile proceed via an initial insertion of the nitrile into the carbon aluminum bond. See: Jennings, R.; Lloyd, J. E.; Wade, K. *J. Chem. Soc.* 1965, 5083. Kuran, W.; Pasynkiewics, S.; Salek, A. *J. Organomet. Chem.* 1974, 73, 199.

(28) In ref 1d it has already been mentioned that in the mechanism involving a cyclobutadiene there should be a preference for formation of a bond between the nitrogen atom and the ring carbon atom bonded originally to the aluminum atom.

Scheme VII
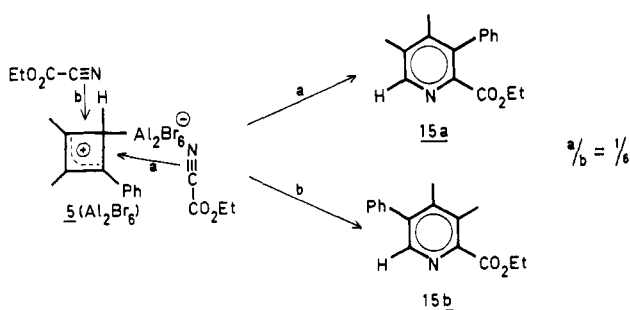
nitrogen atom has reacted on the allylic cation moiety in this case.[29]

The effect of substituents on the aluminum halide σ complexes of cyclobutadiene is demonstrated by pyridines **10a,b**, **15a,b**, and **16a,b**. From the formation (6:1) of pyridines **15a,b** it is concluded that in the ring closure of the intermediate immonium ion a methyl-substituted allylic carbon atom is favored (Scheme VII, path a) over a phenyl-substituted one (Scheme VII, path b), which might be due to steric effects. The difference between a methylene chain and a methyl group is small; the 1:1 ratio of isomers **16a,b** indicates that there is no preference for addition of the nitrile to complex **7(Al_2Br_6)**. From the 1:3:2 ratio of isomers **10a–c** it is deduced that a slight preference (4:3 ratio) for addition at the methyl-substituted site over addition at the methylene-substituted site is present in the case of complex **6(Al_2Br_6)**.

Experimental Section

General Remarks. Melting points (uncorrected) were determined on a Reichert apparatus by the Kofler method. Elemental analyses were performed in the Analytical Section of our department. Mass spectra were obtained on an AEI MS-902 mass spectrometer. IR spectra were obtained on a Perkin-Elmer 177 spectrometer. HPLC separations were carried out on a Waters ALC/GPC 201 HPLC apparatus equipped with a differential refractometer and a Schoeffel spectroflow monitor, SF-770. ^{1}H NMR spectra were recorded on a JEOL C 60-HL spectrometer equipped with a variable-temperature probe or on a Varian A-60 spectrometer. Unless stated otherwise, the ^{1}H NMR spectra were recorded on solutions in $CDCl_3$, and chemical shifts are given in parts per million downfield from tetramethylsilane (δ 0.00). ^{13}C NMR spectra were recorded by using a Varian XL-100 spectrometer with a variable-temperature probe and operating at 25.16 MHz, with the aid of Fourier transform, and were proton-noise decoupled. Proton-coupled ^{13}C NMR spectra were recorded in the gyrogate mode. Chemical shifts were measured relative to $CDCl_3$ and converted to δ_{Me_4Si} values by using $\delta_{CDCl_3} = 76.9$ ppm. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. The solvents were distilled before use and stored over 3–4-Å molecular sieves. All reagents were commercially available and used as such with the exception of $AlCl_3$, which was sublimed before use. The reactions of the aluminum halide σ complexes of cyclobutadienes were carried out under a dry nitrogen atmosphere.

Preparation of ^{1}H NMR and ^{13}C NMR Samples of Complexes 2(AlBr₃)–7(AlBr₃). The preparation of solutions of complexes 2($AlBr_3$) and 3($AlBr_3$) was performed by the following procedure. To a weighed quantity of aluminum tribromide (0.2–0.5 mmol) in an NMR tube was added a solution of the alkyne (0.4–0.5 mmol) in methylene chloride, kept at –90 to –100 °C. The solution was slowly warmed by removing the tube from the cold bath and stirred with a rod which afforded a homogeneous solution of the complexes. In the case of complexes 4(AlBr₃)–7(AlBr₃) a solution of 2-butyne in methylene chloride was added to the

(29) Similarly, only the formation of the major pyridine in the reaction of the aluminum trichloride σ complex of 1,2-dimethyl-3,4-tetramethylene cyclobutadiene with ethyl cyanoformate is explained by this mechanism.[1d,8]

aluminum tribromide, followed by stirring with a rod until all aluminum tribromide had dissolved. Thereafter, a solution of the terminal alkyne in methylene chloride was added to the former solution, kept at –90 to –100 °C, and stirring was continued in order to obtain a homogeneous solution of the complexes. For the ^{13}C NMR spectroscopic measurements $CDCl_3$ (final ratio of $CDCl_3/CH_2Cl_2$ of 1.5/2.5 v/v) was added to the solutions for lock purposes. The ^{1}H NMR and ^{13}C NMR spectroscopic data of complexes 2(AlBr₃)–7(AlBr₃) are given in Tables I and II, respectively.

Attempted Cyclodimerization of Phenylacetylene and of (Trimethylsilyl)acetylene. The experiments were carried out in a manner analogous to the synthesis of complexes 2($AlBr_3$) and 3($AlBr_3$) (see above). Upon addition of phenylacetylene to aluminum tribromide, the solution instantly turned black, and the ^{1}H NMR spectrum revealed no cyclodimerization at –85 °C. When the solution of (trimethylsilyl)acetylene and aluminum tribromide was warmed to –50 °C, irreversible decomposition of (trimethylsilyl)acetylene took place, which was manifested by the appearance of many signals in the ^{1}H NMR spectrum between 0.0 and 0.5 ppm.

Attempted Cyclodimerization of Propyne by Aluminum Trichloride. A CH_2Cl_2 solution (25 mL) of 0.8 g of propyne was added dropwise to a mechanically stirred suspension of 1.46 g of $AlCl_3$ (11 mmol) in 25 mL of CH_2Cl_2 kept at –85 °C. After the addition was complete, a ^{1}H NMR spectrum of the solution indicated only the presence of some propyne (2.0 ppm) and a broad absorption at 1–2 ppm. When the reaction was performed at 0 °C under otherwise identical conditions, the ^{1}H NMR spectrum of the solution showed the same absorptions.

Preparation of 2(Al_2Br_6) and 3(Al_2Br_6). To a mechanically stirred suspension of 5.4 g of aluminum tribromide (20 mmol) in 25 mL of CH_2Cl_2 cooled to –85 °C (internal temperature) was added a solution of 0.8 g of propyne (20 mmol) or 1.64 g of *tert*-butylacetylene (20 mmol) in 25 mL of CH_2Cl_2 dropwise.

Preparation of 4(Al_2Br_6) and 7(Al_2Br_6). To a mechanically stirred suspension of 5.4 g of aluminum tribromide (20 mmol) in 15 mL of CH_2Cl_2 cooled to –85 °C was added a cooled (–85 °C) solution of 2-butyne (0.54 g, 10 mmol) in 10 mL of CH_2Cl_2 followed by a dropwise addition of 0.4 g of propyne (10 mmol) or 0.78 g of 1,5-hexadiyne (10 mmol) in 25 mL of CH_2Cl_2. Complex 4-(Al_2Br_6) was also obtained by following the procedure for complexes 2(Al_2Br_6) and 3(Al_2Br_6) and using a mixture of 0.4 g of propyne (10 mmol) and 0.54 g of 2-butyne (10 mmol) in 25 mL of CH_2Cl_2.

Preparation of 5(Al_2Br_6). To a mechanically stirred suspension of 2.7 g of aluminum tribromide (10 mmol) in 15 mL of CH_2Cl_2 cooled to –85 °C was added a cooled (–85 °C) solution of 0.54 g of 2-butyne (10 mmol) in 10 mL of CH_2Cl_2 followed by a dropwise addition of 1.22 g of phenylacetylene (12 mmol). After 15 min, 2.7 g of aluminum tribromide (10 mmol) was added to the solution.

Preparation of 6(Al_2Br_6). The procedure to obtain this complex was essentially the same as that with complexes 4(Al_2Br_6) and 7(Al_2Br_6) with the reagents in the following quantities: 5.4 g of aluminum tribromide (20 mmol), 0.54 g of 2-butyne (10 mmol), and 0.67 g of 1,9-decadiyne (5 mmol).

Preparation of Pyridines 10a–c and 12a,b–16a,b. General Procedure. To a solution of complexes 2(Al_2Br_6)–7(Al_2Br_6) (for the preparation and quantities see above) kept at –85 °C was added 2.5 g of ethyl cyanoformate (25 mmol) in 1–3 mL of CH_2Cl_2. After warming to 0 °C, the reaction mixture was poured out into 200 mL of an aqueous 1 N NaOH solution under vigorous mechanical stirring. The water layer was extracted with ether (three times), and the combined organic layers were dried over $MgSO_4$, followed by evaporation of the solvent. Further purification of the pyridines was as follows.

2-(Ethoxycarbonyl)-3,5-dimethylpyridine (12a) and 2-(Ethoxycarbonyl)-4,6-dimethylpyridine (12b) from 2(Al_2Br_6). Distillation of the oily residue (1.9 g) at 94–96 °C (0.03 mmHg) afforded 0.97 g (54% yield) of a mixture of **12a,b** in a 6:1 ratio (according to the ^{1}H NMR spectrum). Recrystallization from *n*-pentane (–50 °C) afforded pure **12a**: mp 57–58 °C; ^{1}H NMR 1.43 (t, *J* = 7.5 Hz, 3 H), 2.30 (s, 6 H), 4.38 (q, *J* = 7.5 Hz, 2 H), 7.79 (s, 1 H), 8.34 (s, 1 H); ^{13}C NMR 13.1, 15.1, 17.7 (3 q, *J* = 130 Hz), 60.1 (t, *J* = 150 Hz), 124.5 (d, *J* = 170 Hz), 134.8 (s), 144.8

(s), 145.2 (s), 148.8 (d, J = 170 Hz), 164.0 (s); IR (Nujol) 1710 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 179. Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.1; H, 7.4; N, 7.7. Evaporation of the pentane yielded as residue a mixture of **12a,b** which was separated by TLC (SiO$_2$/ether), affording **12b** as an oil: ^{1}H NMR 1.45 (t, J = 7.5 Hz, 3 H), 2.40 (s, 3 H), 2.63 (s, 3 H), 4.53 (q, J = 7.5 Hz, 2 H), 7.28 (s, 1 H), 7.93 (s, 1 H); ^{13}C NMR 14.2 (q, J = 125 Hz), 20.7, 24.3 (2 q, J = 130 Hz), 63.4 (t, J = 145 Hz), 123.2 (d, J = 170 Hz), 127.4 (d, J = 165 Hz), 147.5 (s), 148.2 (s), 158.6 (s), 165.5 (s); IR (neat) 1715 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 179; exact mass m/e 179.096, calcd for $C_{10}H_{13}NO_2$ m/e 179.095.

Pyridine 12a,b from 2(AlBr$_3$). Complex 2(AlBr$_3$) was prepared in a manner analogous to the procedure used for complex 2(Al$_2$Br$_6$), only the amount of AlBr$_3$ was reduced to 2.7 g (10 mmol). Distillation of the oily residue (1.3 g), obtained after workup, at 90–92 °C (0.03 mmHg) afforded 0.23 g (12% yield) of a 6:1 mixture of **12a,b** (according to the ^{1}H NMR spectrum).

2-(Ethoxycarbonyl)-3,5-di-*tert*-butylpyridine (14) from 3(Al$_2$Br$_6$). The oily residue was dissolved in 150 mL of hexane, which was extracted with an aqueous 1 N HCl solution (3 × 100 mL). The combined acidic layers were made alkaline with concentrated aqueous NaOH and extracted with CH$_2$Cl$_2$ (2 × 100 mL). After the solution was dried over MgSO$_4$, the CH$_2$Cl$_2$ was evaporated, leaving 0.98 g (38% yield) of 14 as a slightly yellow solid. Analytically pure material was obtained by recrystallization from *n*-pentane (−50 °C): mp 62.5–63.5 °C; ^{1}H NMR 1.48 (t, J = 7.5 Hz, 3 H), 1.60 (s, 9 H), 1.63 (s, 9 H), 4.53 (q, J = 7.5 Hz, 2 H), 8.43 (s, 1 H), 9.06 (s, 1 H); ^{13}C NMR 13.6, 33.0, 33.4 (3 q, J = 125 Hz), 36.2 (s), 37.1 (s), 60.7 (t, J = 150 Hz), 124.2 (d, J = 160 Hz), 144.5 (s), 146.8 (s), 150.8 (d, J = 165 Hz), 157.9 (s), 164.9 (s); IR (Nujol) 1720 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 263. Anal. Calcd for $C_{16}H_{25}NO_2$: C, 72.97; H, 9.57; N, 5.32. Found: C, 73.1; H, 9.5; N, 5.3.

2-(Ethoxycarbonyl)-3,4,5-trimethylpyridine (13) from 4(Al$_2$Br$_6$). The crude oil (1.8 g) was distilled at 84–86 °C (0.03 mmHg), leaving 1.12 g (58% yield) of product. Another distillation at 85–87 °C (0.03 mmHg) gave analytically pure 13 (slightly yellow oil): ^{1}H NMR 1.43 (t, J = 7.5 Hz, 3 H), 2.24 (s, 3 H), 2.30 (s, 3 H), 2.43 (s, 3 H), 4.43 (q, J = 7.5 Hz, 2 H), 8.29 (s, 1 H); ^{13}C NMR 13.2, 14.2 (2×), 16.3 (3 q, J = 125 Hz), 60.3 (t, J = 150 Hz), 130.7 (s), 133.2 (s), 145.1 (s), 145.8 (s), 146.0 (d, J = 175 Hz), 166.1 (s); IR (neat) 1720 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 193. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.7; H, 8.0; N, 7.2.

Pyridine 13 from 4(AlBr$_3$). Complex 4(AlBr$_3$) was prepared in a manner analogous to the procedure used for complex 4-(Al$_2$Br$_6$), only the amount of AlBr$_3$ was reduced to 2.7 g (10 mmol). Distillation of the oily residue (1.8 g), obtained after workup, at 88–90 °C (0.03 mmHg) afforded 0.51 g (26% yield) of 13.

2-(Ethoxycarbonyl)-4,5-dimethyl-3-phenylpyridine (15a) and 2-(Ethoxycarbonyl)-3,4-dimethyl-5-phenylpyridine (15b) from 5(Al$_2$Br$_6$). The mixture of pyridines 15a,b was isolated by using the same procedure as for pyridine 14, leaving 1.02 g (40% yield) of a mixture of 15a,b in a 6:1 ratio (according to the ^{1}H NMR spectrum). The isomers were separated by means of HPLC on a 20-cm "Si60 5μ" column (7.5 mm i.d.) with a 2.5% solution of dioxane in CH$_2$Cl$_2$ as the eluent and by maintaining a flow of 5.0 mL/min and a pressure of ±3000 psi (sequence from column: 15b, 15a). 15b: ^{1}H NMR 1.41 (t, J = 7.5 Hz, 3 H), 2.20 (s, 3 H), 2.48 (s, 3 H), 4.38 (q, J = 7.5 Hz, 2 H), 7.0–7.48 (m, 5 H), 8.28 (s, 1 H); ^{13}C NMR 13.8, 15.1, 16.5 (3 q, J = 130 Hz), 61.1 (t, J = 150 Hz), 127.4, 128.0, 128.9 (3 d, J = 160 Hz), 132.0 (s), 137.4 (s), 139.1 (s), 144.7 (s), 146.6 (d, J = 180 Hz), 147.4 (s), 166.7 (s); IR (neat) 1715 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 255; exact mass m/e 255.128, calcd for $C_{16}H_{17}NO_2$ m/e 255.126. For 15a: ^{1}H NMR 1.41 (t, J = 7.5 Hz, 3 H), 2.00 (s, 3 H), 2.16 (s, 3 H), 4.35 (q, J = 7.5 Hz, 2 H), 6.80–7.50 (m, 5 H), 8.29 (s, 1 H). ^{13}C NMR 14.1, 16.6, 17.7 (3 q, J = 130 Hz), 61.4 (t, J = 150 Hz), 127.6, 127.8, 128.7 (3 d, J = 160 Hz), 131.7 (s), 133.8 (s), 137.6 (s), 146.7 (s), 147.5 (d, J = 180 Hz), 151.2 (s), 166.9 (s); IR (Nujol) 1715 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 255; exact mass m/e 255.127, calcd for $C_{16}H_{17}NO_2$ m/e 255.126.

1,6-Bis[2-(ethoxycarbonyl)-4,5-dimethyl-3-pyridyl]hexane (10a), 1-[2-(Ethoxycarbonyl)-3,4-dimethyl-5-pyridyl]-6-[2-(ethoxycarbonyl)-4,5-dimethyl-3-pyridyl]hexane (10b), and 1,6-Bis[2-(ethoxycarbonyl)-3,4-dimethyl-5-pyridyl]hexane (10c) from 6(Al$_2$Br$_6$).** The oily residue (2.0 g) was dissolved in ether, and purification was carried out as for pyridine 14, giving 1.41 g of material (93% pure, according to the ^{1}H NMR spectrum; 59% yield). The mixture of 10a–c, which were present in a 1:3:2 ratio according to a chromatogram (UV detection), was separated by HPLC with two 30-cm and one 20-cm "Si60 5μ" columns diameter (7.5 mm i.d.) with ethyl acetate as the eluent and by maintaining a flow of 5.0 mL/min and a pressure of 5500 psi (sequence from column: 10c, 10b, 10a). 10c: ^{1}H NMR 1.41 (t, J = 7.5 Hz, 3 H), 1.10–1.83 (br m, 8 H), 2.21 (s, 6 H), 2.38 (s, 6 H), 2.08–2.88 (br m, 4 H), 4.34 (q, J = 7.5 Hz, 4 H), 8.13 (s, 2 H); ^{13}C NMR 14.0, 14.8, 15.1 (3 q, J = 125 Hz), 28.9, 29.7, 30.9 (3 t, J = 125 Hz), 61.2 (t, J = 150 Hz), 132.0 (s), 137.9 (s), 145.1 (s), 146.6 (s), 146.9 (d, J = 175 Hz), 167.0 (s); IR (Nujol) 1705 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 440; exact mass m/e 440.270, calcd for $C_{26}H_{36}N_2O_4$ m/e 440.267. 10b: ^{1}H NMR 1.41 (t, J = 7.5 Hz, 6 H), 1.10–1.83 (br m, 8 H), 2.23 (s, 3 H), 2.26 (s, 3 H), 2.39 (s, 6 H), 2.09–2.88 (br m, 4 H), 4.33 (q, J = 7.5 Hz, 4 H), 8.13 (s, 2 H); ^{13}C NMR 13.8 (2×), 14.3, 14.6, 15.0, 16.4 (all q, J = 125 Hz), 27.8, 28.7, 28.8, 29.4, 29.6, 30.8 (6 t, J = 125 Hz), 61.0 (t, J = 150 Hz), 130.7 (s), 131.8 (s), 133.2 (s), 137.7 (s), 145.0 (s), 146.5 (s), 146.7 (d, J = 175 Hz), 147.1 (s), 147.4 (d, J = 175 Hz), 149.5 (s), 166.9 (s); IR (Nujol) 1705 cm^{-1} (ester); mass spectrum, molecular ion peak at m/e 440; exact mass m/e 440.270, calcd for $C_{26}H_{36}N_2O_4$ m/e 440.267. 10a: ^{1}H NMR 1.41 (t, J = 7.5 Hz, 6 H), 1.18–1.65 (br m, 8 H), 2.28 (s, 6 H), 2.41 (s, 6 H), 2.04–2.88 (br m, 4 H), 4.33 (q, J = 7.5 Hz, 4 H), 8.13 (s, 2 H); ^{13}C NMR 14.1, 14.5, 16.6 (3 q, J = 125 Hz), 28.0, 29.1, 29.6 (3 t, J = 125 Hz), 61.3 (t, J = 150 Hz), 131.0 (s), 133.4 (s), 147.3 (s), 147.6 (d, J = 175 Hz), 149.6 (s), 167.0 (s); IR (Nujol) 1705 cm^{-1} ester); mass spectrum, molecular ion peak at m/e 440; exact mass m/e 440.271, calcd for $C_{26}H_{36}N_2O_4$ m/e 440.267.

4-[2-(Ethoxycarbonyl)-3,4-dimethyl-5-pyridyl]-1-butyne (16a) and 4-[2-(Ethoxycarbonyl)-4,5-dimethyl-3-pyridyl]butyne (16b) from 7(Al$_2$Br$_6$). The oily residue (1.8 g) was dissolved in benzene and purified as in the case of pyridine 14, leaving 1.12 g (45% yield) of an oil (90% pure, according to the ^{1}H NMR spectrum). The isomers, which were present in a 1:1 ratio according to a chromatogram (UV detection), were separated by HPLC on three "Si60 5μ" columns (7.5 mm i.d.) with a 10% solution of dioxane in CH$_2$Cl$_2$ as the eluent and by maintaining a flow of 5.0 mL/min and a pressure of ±5000 psi (sequence from column: 16a, 16b). 16a: ^{1}H NMR 1.43 (t, J = 7.5 Hz, 3 H), 2.00 (t, J = 2.3 Hz, 1 H), 2.30 (s, 3 H), 2.43 (s, 3 H), 2.15–2.65 (m, 2 H), 2.76–3.13 (m, 2 H), 4.44 (q, J = 7.5 Hz, 2 H), 8.35 (s, 1 H); ^{13}C NMR 14.1, 15.0, 15.3 (3 q, J = 125 Hz), 19.1 (t, J = 135 Hz), 29.8 (t, J = 130 Hz), 61.4 (t, J = 145 Hz), 69.7 (d, J = 250 Hz), 82.3 (s), 132.1 (s), 135.8 (s), 145.6 (s), 147.2 (s), 147.3 (d, J = 175 Hz), 167.1 (s); IR (neat) 1715 cm^{-1} (ester), 3270 cm^{-1} (C–H, alkyne); mass spectrum, molecular ion peak at m/e 231; exact mass m/e 231.125, calcd for $C_{14}H_{17}NO_2$ m/e 231.126. 16b: ^{1}H NMR 1.43 (t, J = 7.5 Hz, 3 H), 2.00 (t, J = 2.3 Hz, 1 H), 2.38 (s, 3 H), 2.50 (s, 3 H), 2.13–2.58 (m, 2 H), 2.78–3.18 (m, 2 H), 4.43 (q, J = 7.5 Hz, 2 H), 8.33 (s, 1 H); ^{13}C NMR 14.1, 14.7, 16.8 (3 q, J = 125 Hz), 17.2 (t, J = 130 Hz), 28.0 (t, J = 130 Hz), 61.4 (t, J = 145 Hz), 69.3 (d, J = 250 Hz), 82.4 (s), 131.5 (s), 134.0 (s), 147.4 (s), 147.5 s), 147.9 (d, J = 175 Hz), 167.0 (s); IR (neat) 1715 cm^{-1} (ester), 3270 cm^{-1} (C–H, alkyne); mass spectrum, molecular ion peak at m/e 231; exact mass m/e 231.126, calcd for $C_{14}H_{17}NO_2$ m/e 231.126.

^{1}H NMR Spectroscopic Measurements of 1(AlCl$_3$) and 1(Al$_2$Cl$_6$) with Ethyl Cyanoformate. To a cooled (−60 °C) CH$_2$Cl$_2$ solution of complex 1(AlCl$_3$) or complex 1(Al$_2$Cl$_6$) in an NMR tube was added a solution of ethyl cyanoformate in CH$_2$Cl$_2$. Final concentrations: 1(AlCl$_3$), 1.25 mol L^{-1}; 1(Al$_2$Cl$_6$), 1.25 mol L^{-1}; NCCO$_2$Et, 2.50 mol L^{-1} (in both cases). A ^{1}H NMR sample of complex 1(AlCl$_3$) and NCCO$_2$Et·AlCl$_3$ was prepared by adding complex 1(AlCl$_3$) to a cooled (−60 °C) solution of NCCO$_2$Et·AlCl$_3$. Final concentrations: 1(AlCl$_3$), 1.25 mol L^{-1}; NCCO$_2$Et·AlCl$_3$, 1.25 mol L^{-1}. ^{1}H NMR spectroscopic measurements were performed at −50 °C. The conversion of the complexes and ethyl cyanoformate in pyridine 17 was determined by integrating the low-field methyl absorptions of complex 1(AlCl$_3$) (2.39 and 2.26 ppm) and complex 1(Al$_2$Cl$_6$) (2.43 and 2.28 ppm) and the methyl absorptions

of pyridine 17 (2.50 (2×), 2.75, and 2.93 ppm). The results are given in the text.

Preparation of 2-(Ethoxycarbonyl)-3,4,5,6-tetramethyl-pyridine (17). A solution of 6.25 g of ethyl cyanoformate (62.5 mmol) in 2 mL of CH_2Cl_2 was added at –50 °C to a solution of complex $1(Al_2Cl_6)$, prepared from 6.67 g of $AlCl_3$ (50 mmol) and 2.70 g of 2-butyne (50 mmol), in 50 mL of CH_2Cl_2.[1c] After slowly warming to room temperature, the reaction mixture was poured out into 200 mL of an aqueous 1 N NaOH solution under mechanical stirring. The water layer was extracted with pentane (2 × 100 mL). The combined organic layers were extracted with an aqueous 1 N HCl solution (3 × 100 mL), and the combined acidic layers were washed with 50 mL of pentane. The acidic layers were made alkaline with K_2CO_3 and subsequently extracted with CH_2Cl_2 (3 × 100 mL). The combined CH_2Cl_2 layers were dried over K_2CO_3, and the solvent was evaporated, affording 4.32 g (83% yield) of 17 (pure, according to the ^{1}H NMR spectrum[1e,7]).

Preparation of 2-Cyano-3,4,5,6-tetramethylpyridine (18). At 0 °C cyanogen was bubbled through a solution of complex $1(Al_2Cl_6)$, prepared from 2.7 g of $AlCl_3$ (20 mmol) and 1.08 g of 2-butyne (20 mmol),[1c] in 40 mL of CH_2Cl_2 under a hood. The reaction was followed by ^{1}H NMR spectroscopic measurements, and the addition of cyanogen was stopped when complex $1(Al_2Cl_6)$ had disappeared. Compound 18 was isolated as described above for pyridine 17 followed by sublimation at 100 °C (0.1 mmHg), giving 1.05 g (66% yield) of 18, which was resublimed twice at 100 °C (0.1 mmHg) to give analytically pure material: mp 83.5–85.0 °C; ^{1}H NMR 2.26 (s, 6 H), 2.43 (s, 3 H), 2.48 (s, 3 H); ^{13}C NMR 14.9 (2×), 15.6, 22.3 (3 q, J = 130 Hz), 116.5 (s), 128.8 (s), 133.5 (s), 133.7 (s), 144.5 (s), 155.1 (s); IR (Nujol) 2230 cm^{-1} (nitrile); mass spectrum, molecular ion peak at m/e 160. Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 75.0; H, 7.6; N, 17.4.

Preparation of 2-(Cyanomethyl)-3,4,5,6-tetramethyl-pyridine (19). A solution of 5.0 g of malonitrile (75 mmol) in 10 mL of CH_2Cl_2 was added at –50 °C to a solution of complex $1(Al_2Cl_6)$, prepared from 8.0 g of $AlCl_3$ (60 mmol) and 3.24 g of 2-butyne (60 mmol), in 75 mL of CH_2Cl_2.[1c] Pyridine 19 was isolated as described for pyridine 17 and was purified by Kugelrohr distillation at 115 °C (0.01 mmHg) followed by recrystallization from methylcyclohexane (–50 °C), giving analytically pure 19: 1.15 g (22% yield); mp 109–110 °C; ^{1}H NMR 2.16 (s, 6 H), 2.21 (s, 3 H), 2.41 (s, 3 H), 3.73 (s, 2 H); ^{13}C NMR 14.9, 15.1, 15.6, 22.8 (4 q, J = 125 Hz), 25.4 (t, J = 135 Hz), 117.1 (s), 127.2 (s), 129.7 (s),

144.2 (s), 144.9 (s), 153.5 (s); IR ($CHCl_3$) 2240 cm^{-1} (nitrile); mass spectrum, molecular ion peak at m/e 174. Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.83; H, 8.10; N, 16.38. Found: C, 75.6; H, 8.2; N, 16.2.

Preparation of 2-Phenyl-3,4,5,6-tetramethylpyridine (20). A solution of 7.7 g of benzonitrile (75 mmol) in 10 mL of CH_2Cl_2 was added at –50 °C to a solution of complex $1(Al_2Cl_6)$, prepared from 8.0 g of $AlCl_3$ (60 mmol) and 3.24 g of 2-butyne (60 mmol), in 75 mL of CH_2Cl_2.[1c] Pyridine 20 was isolated as described for pyridine 17 and purified by Kugelrohr distillation at 130 °C (0.01 mmHg), giving 1.12 g (18% yield) of 20 as an oil: ^{1}H NMR 2.13 (s, 3 H), 2.20 (s, 6 H), 2.48 (s, 3 H), 7.28 (br s, 5 H); ^{13}C NMR 14.7, 15.3, 16.2, 22.7 (4 q, J = 125 Hz), 126.0 (s), 126.6 (d, J = 160 Hz), 127.4 (d, J = 160 Hz), 127.6 (s), 128.6 (d, J = 160 Hz), 141.2 (s), 144.0 (s), 152.4 (s), 154.6 (s); mass spectrum, molecular ion peak at m/e 211; exact mass m/e 211.139, calcd for $C_{15}H_{17}N$ m/e 211.136.

Reaction of $1(Al_2Cl_6)$ with Acetonitrile. A solution of 0.82 g of acetonitrile (10 mmol) in 2 mL of CH_2Cl_2 was added at –50 °C to a solution of complex $1(Al_2Cl_6)$, prepared from 0.67 g of $AlCl_3$ (5 mmol) and 0.27 g of 2-butyne (5 mmol), in 10 mL of CH_2Cl_2.[1c] After warming to room temperature, the reaction mixture was poured out into 100 mL of an aqueous 1 N NaOH solution. The alkaline layer was extracted with pentane (2 × 100 mL), followed by drying of the combined organic layers over K_2CO_3. After evaporation of the solvent, 0.24 g of a slightly yellow semisolid was obtained. According to the ^{1}H NMR spectrum the crude product contained no 2,3,4,5,6-pentamethylpyridine (21); it consisted mostly of octamethyl-*syn*-tricyclo[4.2.0.0^{2,5}]octadiene (22).

One-Pot Nonphotochemical Synthesis of Dewar Pyridones from Alkynes and Isocyanates

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A one-pot synthesis of substituted 3-oxo-2-azabicyclo[2.2.0]hex-5-enes (Dewar pyridones) from alkynes, aluminum halides, and isocyanates is described. The mechanism of the reaction of isocyanates with the intermediate aluminum halide σ complexes of cyclobutadienes is discussed on the basis of the substitution pattern of the obtained bicyclic products. The thermal and acid-promoted reactions of some of the compounds are reported.

It has been shown previously that aluminum halide σ complexes of cyclobutadienes react with a variety of reagents to yield four-, five-, and six-membered-ring compounds.[1] These complexes are especially useful in the synthesis of Dewar benzene derivatives[1a] and substituted bicyclo[2.2.0]hexenes.[1b] In this paper, a new reaction of

these complexes with isocyanates is described, leading to the formation of substituted 3-oxo-2-azabicyclo[2.2.0]-hex-5-enes ("Dewar pyridones"). This class of compounds is known to be accessible by irradiation of 2-pyridones.[2]

There exists an important difference between the presently reported reaction and comparable reactions involving organotransition-metal complexes. Thus, reactions

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