for a Fulbright grant which made her stay at Cornell possible and the National Science Foundation for its support of this work through research Grant CHE 84-06119. We were stimulated to do this work through the friendly communication of his group's results by Malcolm Chisholm.

Appendix

Calculations were made by using the extended Hückel method,[1] with weighted H_{ij}'s. The parameters for W, C, H, N, and O were taken from previous work.[1] Geometries were modelled after the X-ray determined structure of $W_2(NMe_2)_2(C_2Me_2)Cl_4(py)_2$.[1] The following bond distances were used: C_{ac}–C_{ac} = 1.376 Å, C_{ac}–H = 1.09 Å, W–Cl = 2.40 Å, W–H = 1.70 Å, W–N = 2.18 Å, N–H = 1.02 Å, and W–W = 2.436 Å. An octahedral environment around each tungsten was kept. The acetylene was allowed to rotate at a distance 1.87 Å above the W–W axis.

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Cationic 2-Azaallenylidene Complexes of Chromium and Tungsten. Complexes with a Novel Metallaheterocumulene System[1]

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The reaction of $(CO)_5M[C(OEt)N{=}CR_2]$ with BF_3 yields 2-azaallenylidene complexes $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ (M = Cr ([**3**]BF_4), W ([**4**]BF_4); CR_2 = $C(C_6H_4Br\text{-}4)_2$ (**a**), CPh_2 (**b**), $C(C_6H_4OMe\text{-}4)_2$ (**c**), $C(C_6H_4)_2O$ (**d**), $C(2,4,6\text{-}C_6H_2Me_3)_2$ (**e**), $C(CMe_3)_2$ (**f**)). The abstraction of Cl^- from $(CO)_5Cr{-}C{\equiv}N{-}CCl_3$ by $AlCl_3$ gives $[(CO)_5Cr{=}C{=}N{=}CCl_2]AlCl_4$ ([**3a**]$AlCl_4$). IR, ^{13}C NMR, and electronic spectra reveal the high degree of electron delocalization within the metallaheterocumulene system. The structure of [**3d**]$BF_4{\cdot}CH_2Cl_2$ has been determined by an X-ray diffraction analysis (crystal data: monoclinic, space group $P2_1/c$, a = 15.811 (4) Å, b = 12.657 (4) Å, c = 12.966 (3) Å, β = 111.98 (2)°, and Z = 4). The Cr–C–N–C fragment is almost linear (Cr–C–N = 179.0 (5)°; C–N–C = 171.1 (5)°) and allows the formation of two orthogonal π-systems. Both C–N distances (118.4 (7) and 134.3 (7) pm, respectively) differ significantly. Therefore, the complexes are best described as resonance hybrids of the two limiting structures A and B: the 2-azaallenylidene complex A and the carbocationic isonitrile complex B. [**3d**]BF_4 reacts with $Me_3N^+{-}O^-$ to yield the ketone $O{=}C(C_6H_4)_2O$. On near-UV irradiation of [**3b**]BF_4 and [**3d**]BF_4, the olefins $R_2C{=}CR_2$ (CR_2 = CPh_2, $C(C_6H_4)_2O$) are formed.

Heterocumulene systems can act as nonbridging ligands in transition-metal complexes in one of the following ways: η^2 side on, as in several ketene complexes[2–5] and a 1,3-diphosphaallene complex;[6] η^3 side on, as in a 1-azaallyl complex[7] and a 1,3-diphosphaallyl complex;[8] singly bonded end on, as in ketenyl,[9,10] keteniminyl,[11] and 2-azaallenyl complexes;[12] and multiply bonded end on, in a fashion analogous to allenylidene complexes.[13] This latter type of bonding seems particularly interesting, as a new, longer cumulene system is created thereby, with the metal now being part of the cumulene system.

The extended π-system in these complexes lends itself to studying the effects of electron delocalization on structure and reactivity, which is an important field with regard to catalytic and biological processes (e.g., electron transfer). However, only a few metal heterocumulene systems are known, e.g., 1-azavinylidene complexes,[7,14] a 1-phosphavinylidene complex,[15] and a oxapropatrienylidene complex.[16] Therefore we decided to develop more general synthetic routes to metal heterocumulene systems and chose 2-azaallenylidene complexes, i.e., complexes that

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contain $C{=}N{=}CR_2$ as a ligand, as our first target. These are formally derived from allenylidene complexes by isoelectronic substitution of the central carbon atom by N^+.

Experimental Section

Instruments and Equipment. IR spectra were recorded by using a Perkin-Elmer 580 spectrometer. UV–vis spectra were recorded by using a Cary 17D spectrophotometer equipped with a thermostated cell holder. The instrumentation for measuring the emission and excitation spectra and for measuring the luminescence lifetime has been described elsewhere.[17,18] ^1H NMR spectra and ^{13}C NMR spectra were recorded by using a JEOL PMX-60, a JEOL FX-60, or a JEOL FX-90Q spectrometer. ^{13}C NMR spectra are broad-band-decoupled. EI mass spectra were recorded by using a Varian MAT 311A spectrometer. Irradiations were carried out in a falling film reactor according to Prof. Dr. de Meijere, manufactured by Normag, with a high-pressure mercury lamp (TQ718) of Heraeus Hanau as the light source.

Chemicals. All reactions involving organometallic compounds were carried out in a purified (BASF-CuO-Catalyst, molecular sieve (4-Å), Merck) N_2 atmosphere by using standard Schlenk techniques. Before use all solvents were distilled from appropriate drying agents (CaH_2 for pentane and hexane, Na/K alloy for Et_2O and benzene, P_2O_5 and Na/Pb alloy for CH_2Cl_2), then saturated with N_2, and stored over molecular sieve. The silica used for chromatography (no. 60, 0.062–0.2 mm, Merck) was dried and deoxygenated at high vacuum for 8 h at ambient temperature.

Reported yields refer to analytically pure compounds and are not optimized. BF_3 was a gift of BASF. $AlCl_3$ was obtained from Merck and sublimed before use. $(CO)_5M{-}C{\equiv}N{-}CCl_3$ (M = Cr, W) was synthesized as described in ref 19. The 2-azaallenyl complexes **1a–d**, **1f**, **2a–d**, and **2f** were prepared by using a previously described procedure.[12]

Preparation of $(CO)_5Cr[C(OEt)N{=}CMes_2]$ (1e). Complex **1e** was prepared by the same route as **1a–d**:[12] yellow crystals; yield 46%; mp 146 °C; IR (hexane) $\nu(CO)$ 2058 m, 1978 vw, 1940 vs, 1924 s cm^{-1}; ^1H NMR (CD_3COCD_3) δ 1.38 (t, 3), 2.28 (s, 12), 2.36 (s, 6), 4.31 (q, 2), 7.04 (s, 4); MS, *m/e* 513 (M^+) and peaks for $[M - n(CO)]^+$, *n* = 1–5. Anal. Calcd for $C_{27}H_{27}CrNO_6$ (513.5): C, 63.15; H, 5.30; Cr, 10.13; N, 2.73; O, 18.69. Found: C, 63.28; H, 5.20; Cr, 9.75; N, 2.63; O, 18.59.

Preparation of $(CO)_5W[C(OEt)N{=}CMes_2]$ (2e). Complex **2e** was prepared by the same method as **2a–d**:[12] yellow crystals; yield 37%, mp 158 °C; IR (hexane) $\nu(CO)$ 2064 m, 1976 vw, 1937 vs, 1920 s cm^{-1}; ^1H NMR (CD_3COCD_3) δ 1.40 (t, 3), 2.29 (s, 12), 2.38 (s, 6), 4.17 (q, 2), 7.05 (s, 4); MS, *m/e* 645 (M^+) and peaks for $[M - n(CO)]^+$, *n* = 1–5. Anal. Calcd for $C_{27}H_{27}NO_6W$ (645.4): C, 50.25; H, 4.22; N, 2.17; O, 14.87; W, 28.49. Found: C, 50.28; H, 4.23; N, 2.11; O, 14.74; W, 28.49.

Preparation of $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ Complexes (M = Cr (3); M = W (4); R = Aryl, Alkyl). General Procedure. $(CO)_5M[C(OEt)N{=}CR_2]$ (3 mmol) was dissolved in 25 mL of CH_2Cl_2/pentane (4/1, v/v) and cooled to −100 °C. Through this solution was slowly bubbled BF_3 for 15 min. The solution was then kept at −60 °C for 2 h. After removal of the solvent (−40 °C), an oily residue was obtained. In most cases, crystallizing the residue proved to be difficult. Additionally, if crystals could be obtained, they contained varying amounts of CH_2Cl_2 depending on the crystallization conditions. If no crystals could be obtained, the residue was redissolved in cold CH_2Cl_2 and the solution was used without further purification.

$[(CO)_5Cr{=}C{=}N{=}C(C_6H_4)_2O]BF_4{\cdot}CH_2Cl_2$ ([3d]BF_4). The residue was dissolved in a few milliliters of CH_2Cl_2 at −20 °C, and the solution was slowly cooled to −78 °C. Intensely blue crystals were obtained, which were dried at −30 °C for 15 h in vacuo; yield 1.3 g (76% relative to **2b**). Anal. Calcd for $C_{19}H_8BCrF_4NO_6{\cdot}CH_2Cl_2$ (570.0): C, 42.14; H, 1.77; Cl, 12.44; Cr, 9.12; F, 13.33; N, 2.46. Found: C, 41.96; H, 1.77; Cl, 12.49; Cr, 8.89; F, 13.89; N, 2.46.

$[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4{\cdot}0.75CH_2Cl_2$ ([3e]BF_4). The residue was dissolved in a few milliliters of CH_2Cl_2 at −20 °C and cooled to −78 °C. Twice the amount (v/v) of Et_2O (cooled to −78 °C) was added carefully without mixing the layers. After 15 h at −78 °C the solvent was decanted and the microcrystalline material obtained was dried in vacuo for 15 h at −30 °C; yield 61%. Anal. Calcd for $C_{25}H_{22}BCrF_4NO_5{\cdot}0.75CH_2Cl_2$ (619.0): C, 49.97; H, 3.83; Cl, 8.59; Cr, 8.40; F, 12.28; N, 2.26. Found: C, 49.83; H, 3.98; Cl, 8.39; Cr, 8.22; F, 12.63; N, 2.03.

$[(CO)_5W{=}C{=}N{=}CMes_2]BF_4{\cdot}0.8CH_2Cl_2$ ([4e]BF_4). Essentially the same procedure as for the preparation of the chromium analogue was used, but in this case due to reaction with Et_2O some decomposition occurred; yield 24%. Anal. Calcd for $C_{25}H_{22}BF_4NO_5W{\cdot}0.8CH_2Cl_2$ (755.0): C, 41.04; H, 3.15; Cl, 7.51; F, 10.06; N, 1.86; W, 24.35. Found: C, 40.78; H, 3.13; Cl, 7.22; F, 10.28; N, 1.82; W, 24.30.

$[(CO)_5Cr{=}C{=}N{=}CCl_2]AlCl_4$ ([3g]$AlCl_4$). $AlCl_3$ (130 mg, 0.97 mmol) was dissolved in 5 mL of CH_2Cl_2, cooled to −30 °C, and added to 300 mg (0.89 mmol) of $(CO)_5Cr{-}C{\equiv}N{-}CCl_3$. The solution turned immediately red. After a few minutes another 100 mg of $AlCl_3$ was added. The solution was then concentrated to about 2 mL and cooled to −78 °C to yield 200 mg of red crystals, which on drying (2 days, −30 °C) turned green due to partial decomposition.

Reaction of [3d]$BF_4{\cdot}CH_2Cl_2$ with Me_3NO. [**3d**]$BF_4{\cdot}CH_2Cl_2$ (1.0 g, 1.9 mmol) was dissolved in 30 mL of CH_2Cl_2 at −20 °C. Me_3NO (150 mg, 2.0 mmol) was added, the solution was warmed to room temperature, and another 75 mg (1.0 mmol) of Me_3NO was added in small amounts. After the solvent was evaporated in vacuo, the residue was extracted with benzene. The product was purified by TLC with benzene as the eluent and identified by comparison with an authentic sample of xanthone (TLC, IR); yield 150 mg (40% relative to [**3d**]$BF_4{\cdot}CH_2Cl_2$).

Photolysis Studies. Photolysis of $[(CO)_5Cr{=}C{=}N{=}CPh_2]BF_4$ ([3b]BF_4). A sample of [**3b**]BF_4 prepared from 900 mg (2.1 mmol) of $(CO)_5Cr[C(OEt)N{=}CPh_2]$ (**1b**) and BF_3 was dissolved in 250 mL of CH_2Cl_2 and irradiated for 1 h at −20 °C. After the solvent was removed in vacuo, the residue was extracted with benzene and the benzene solution was filtered through a 5-cm layer of silica. The product was recrystallized from pentane/benzene (2/1, v/v). It was identified as tetraphenylethylene by its melting point (222 °C; cf. 225 °C[20]), its mass spectrum, and its UV–vis spectrum (by comparison with ref 21); yield 120 mg (34%).

Photolysis of $[(CO)_5Cr{=}C{=}N{=}C(C_6H_4)_2O]BF_4{\cdot}CH_2Cl_2$ ([3d]BF_4). A solution of 1.0 g (1.9 mmol) of [**3d**]$BF_4{\cdot}CH_2Cl_2$ was irradiated for 5 h at −20 °C. After evaporation of the solvent in vacuo, the residue was extracted with benzene and the product was purified by TLC with hexane/benzene as the eluent and identified by mass spectroscopy; yield 110 mg (29%).

X-ray Diffraction Analysis of [3d]$BF_4{\cdot}CH_2Cl_2$: $C_{19}H_8BCrF_4NO_6{\cdot}CH_2Cl_2$ (M_r 570.0); monoclinic; $P2_1/c$; a = 15.811 (4) Å, b = 12.657 (4) Å, c = 12.966 (3) Å; β = 111.98 (2)°; V = 2406 Å^3, Z = 4; ρ(calcd) = 1.57 g·cm^{-3}. Crystals suitable for X-ray measurements were obtained by slow diffusion of pentane into a dichloromethane solution of [**3d**]BF_4 at −78 °C. The measurements were made at −50 °C with a crystal of appropriate dimensions, 0.2 × 0.3 × 0.3 mm, mounted in a glass capillary on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). Intensity data ($2° \leq 2\theta \leq 47°$) were collected by the ω scan technique ($\Delta\omega$ = 1°; scan rate 0.9–29.3°/min). Lorentz–polarization effects but no absorption effects were corrected (μ = 7.9 cm^{-1}). After equivalent reflections were averaged, a total of 3495 independent reflections was obtained, of which the 2364 reflections with $I(hkl) > 1.96\sigma(I(hkl))$ were used in the subsequent calculations. The initial coordinates of the Cr atom were determined by Patterson methods, and the remaining non-hydrogen atoms were located by subsequent Fourier syntheses. Relatively high anisotropic thermal parameters for the methylene chloride Cl atoms indicated partial disorder and/or high thermal movement of these atoms. Attempts to resolve the disorder were made by first refining the site occupancy factor of the Cl atoms with B_{iso} fixed at 6.0, which resulted in equal partial

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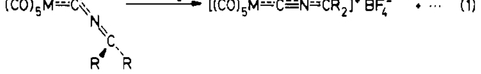
occupancies of 0.74. A successive difference map calculated with the Cl atoms partially occupied resulted in two side peaks for each of these. Final refinement was done with inclusion of these side peaks which were treated isotropically with site occupancy factors of 0.13 each and the main Cl atoms treated anisotropically. The disorder treated as such amounts to a rotation of about ±20° about the CCl_2 bisector. Full-matrix least-squares refinement (H atoms were held constant at idealized calculated positions, 322 refined parameters, 2356 F_o) converged at $R = 0.056$, $R_w = 0.046$, and $w = 1/\sigma^2(F_o)$. All calculations were done on a Nova 1200 computer using the Syntex XTL program package.

Results

Two routes appear conceivable for the synthesis of 2-azaallenylidene complexes: (a) abstraction of a leaving group from the metal-bonded carbon of 2-azaallenyl complexes or (b) abstraction of a leaving group from the isonitrile α-carbon atom of isonitrile complexes.

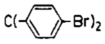
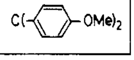
Synthesis of $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ Complexes. Already at −60 to −100 °C 2-azaallenyl complexes $(CO)_5M[C(OEt)N{=}CR_2]$[12] [M = Cr (**1a–f**); M = W (**2a–f**)] react with BF_3 in CH_2Cl_2 with loss of the ethoxy group and formation of cationic 2-azaallenylidene complexes (eq 1).

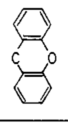
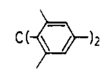


(1)

1,2 3,4

1,3: M = Cr; 2,4: M = W

1-4	a	b	c
CR_2		CPh_2	

1-4	d	e	f
CR_2			CBu^t_2

Analogous products are obtained from the reaction of **1a–f** and **2a–f** with $AlBr_3$ at −10 °C or of **1b** with BCl_3 at −40 °C. The product of the latter reaction, [**3b**]BCl_4, is rather unstable. However, by reaction with $SbCl_5$ it can be transformed into a more stable form, [**3b**]$SbCl_6$. Solutions of the product complexes in CH_2Cl_2 are intensely blue (**3a–e**, **4a–e**), red (**3f**), or yellow (**4f**). In agreement with their ionic nature, **3** and **4** are insoluble in hydrocarbon solvents.

Since the 2-azaallenyl precursor **1g** could not be obtained by the method employed for the preparation of **1a–f**,[12] the dichloro-substituted 2-azaallenylidene complex was synthesized via route b. The isonitrile complex $(CO)_5Cr{-}C{\equiv}N{-}CCl_3$[19] (**5**) immediately reacts with $AlCl_3$ in CH_2Cl_2 even at −30 °C to yield a deep red solution of [**3g**]$AlCl_4$ (eq 2). A similar color change is observed, when the

$$\underset{5}{(CO)_5Cr{-}C{\equiv}N{-}CCl_3} \xrightarrow{AlCl_3} \underset{3g}{[(CO)_5Cr{=}C{\equiv}N{=}CCl_2]^+AlCl_4^-} \qquad (2)$$

analogous tungsten isonitrile complex reacts with $AlCl_3$, but the product turned out to be too unstable even for spectroscopic characterization.

Spectroscopic Properties. Relevant IR data of the 2-azaallenylidene complexes are summarized in Table I. A comparison of the spectra of [**3b**]X (X = BF_4, $AlBr_4$, $SbCl_6$) shows that the position of the absorptions is almost independent of the counterion. In addition to the three bands expected for a $(CO)_5M$ fragment of local C_{4v} symmetry another absorption of medium to very strong intensity is observed in the range between 1940 and 1840 cm^{-1}. When the ability of the substituents R to π-donate electron density is increased, the frequencies of the three absorptions highest in energy generally shift toward *lower* energy, whereas the frequency of the low-energy absorption shifts toward *higher* energy.

Table I. IR Data for the Complexes [3a–g]BF_4 and [4a–f]BF_4[a]

	ν(CO)			
	A_1^2	A_1^1	E	ν(C=N=C)
3a	2106 vs	2038 m	2009 s	1882 m
3b	2103 vs	2031 s	2008 s	1888 m
3c	2103 m	2000 sh	1991 s	1932 vs
3d	2107 m	2005 sh	1994 s	1926 vs
3e	2104 s	2032 s	2005 vs	1890 vs
3f[b]	2140	2062	2024	1850
3g	2153 s	2070 s, sh	2062 vs	2130[c]
4a	2117 vs	2028 m	1999 s	1872 m
4b	2117 s	2024 s	1999 s	1880 m
4c	2113 m	1993 sh	1984 s	1918 s
4d	2117 m	1998 sh	1988 s	1919 s
4e	2115 s	2020 s	1997 vs	1881 vs
4f[b]	2129	2055	2022	1846

[a] cm^{-1}; CH_2Cl_2; −20 °C. [b] No relative intensities can be given for **3f** and **4f** because of their extreme lability. [c] Assignment is uncertain.

The three bands at higher wavenumbers can be ascribed to ν(CO) absorptions. The detailed assignment is based on the assumption that the trans CO group is more strongly influenced by varying the substituents R of the 2-azaallenylidene ligand than are the cis CO ligands. The absorption at the lowest wavenumber can be assigned to the antisymmetrical stretching mode of the C=N=C system. The antisymmetrical vibration of those 2-azaallenium cations $[R^1R^2C{=}N{=}CR^3R^4]^+$ (R = H, aryl, alkyl) in which the C=N=C group is almost linear is also observed in the range between 1800 and 1964 cm^{-1}.[22-24] An absorption in the cyanoisocyanide complex $(CO)_5Cr{-}C{\equiv}N{-}C{\equiv}N$ (**6**) at 1952 cm^{-1} was assigned by isotopic labeling as an isonitrile vibration.[25]

In the ^{13}C NMR spectrum of [**3b**]BF_4 (−30 °C; solvent and standard, CD_2Cl_2) the assignment of the signals of C6 (for the numbering scheme of the atoms see Figure 2) of the 2-azaallenylidene ligand and of trans CO causes problems due to the similar electronic properties of both types of ligands. On the basis of $^1J_{WC}$ coupling constants, the most deshielded carbon signal in the allenylidene complex $(CO)_5W{=}C{=}C{=}C(Ph)NMe_2$ was ascribed to the trans CO carbon.[26] Therefore, we tentatively also assign the most deshielded signal in the spectrum of [**3b**]BF_4 to the trans CO carbon. However, a reversal of the assignments of C6 and trans CO hardly modifies the interpretation. The resonance of C6 in [**3b**]BF_4 (200.4 ppm) is comparable with the chemical shift of the corresponding metal-bonded carbon in $(CO)_5Cr{=}C^1{=}C^2{=}C^3(Ph)NMe_2$

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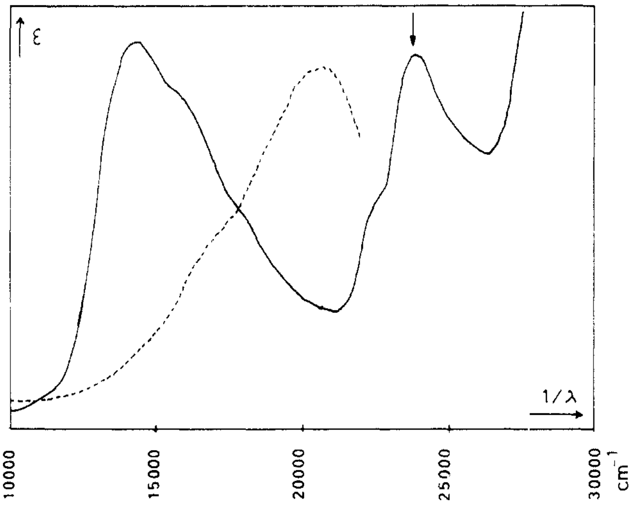

Figure 1. Absorption (—) and emission spectrum (- - -) of $[\mathbf{3b}]BF_4$ (CH_2Cl_2, −60 °C).

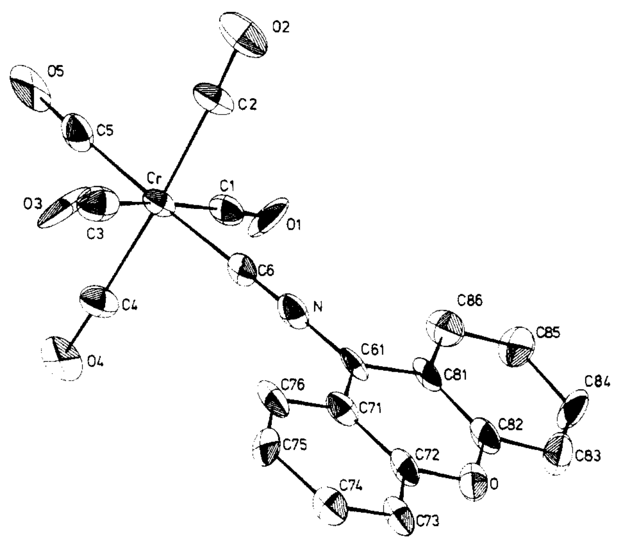

Figure 2. ORTEP plot of the cation in $[\mathbf{3d}]BF_4{\cdot}CH_2Cl_2$. BF_4^- and CH_2Cl_2 are omitted for clarity as are the hydrogen atoms.

(**7**) (C1, 222.6 ppm)[26] and $(CO)_5Cr{-}C{\equiv}N{-}C{\equiv}N$ (**6**) (200.0 ppm).[25] In contrast, the carbyne carbon in cationic aminocarbyne complexes such as $[(CO)_5Cr{\equiv}C{-}NPh_2]SbCl_6$ (273.7 ppm)[27] as well as the "carbene" carbon in **1** and **2** (e.g., **1b**, 243.1 ppm)[12] are significantly more deshielded. The signal of C61 is observed at 166.5 ppm. The resonance of C3 in **7** is found at 155.6 ppm[26] and the CPh_2 resonance of **1b** at 146.5 ppm.[12] These values nicely illustrate the extent of electron delocalization within the MCNC fragment. The other resonances of $[\mathbf{3b}]BF_4$ are in the range usually observed for the signals of comparable carbons (cis CO, 209.5 ppm; trans CO, 211.8 ppm; aromatic C, 137.0, 135.5, 134.3, and 130.1 ppm). The variation of the central metal (**3b** → **4b**) causes a diamagnetic shift of all metal-bonded carbons (C6, 182.3 ppm; cis CO, 189.1 ppm; trans CO, 191.7 ppm). The same effect has been observed with allenylidene complexes.[26] The remaining resonances are hardly influenced (C61, 166.1 ppm; aromatic C, 138.8, 133.9, 131.1, and 129.7 ppm).

Table II. UV-vis Data of the Complexes $[\mathbf{3a{-}g}]BF_4$ and $[\mathbf{4a{-}f}]BF_4$[a]

3a	715	645	458
3b	700	630	417
3c	690	630	518
3d	675	605	377
3e	696	625	506
3f	535	485	
3g	485	450	
4a	655	590	456
4b	640	595	415
4c	640	600	518
4d	620	565	377
4e	644	608	504
4f	485	455	

[a] nm; CH_2Cl_2; −20 °C. The extinction coefficients are approximately 5×10^3 L mol^{-1} cm^{-1}.

In the ^1H NMR spectra of $[\mathbf{3b}]BF_4$ and $[\mathbf{4b}]BF_4$ (in CD_2Cl_2) the proton resonances are at 8.08 and 7.81 ppm, respectively. Their paramagnetic shift relative to **1b** and **2b** indicates the participation of the phenyl rings in the electron delocalization.

In the visible and near-UV region of the electronic spectrum the 2-azaallenylidene complexes **3** and **4** generally display three bands (Table II, Figure 1). On the basis of MO calculations, the two bands lowest in energy, which strongly overlap, can be assigned to metal to ligand charge-transfer transitions. When the π-donor ability of R is increased, these bands shift toward higher energy, as is expected for bands with predominant MLCT character.[28] The third absorption is only observed in those complexes $[\mathbf{3}]BF_4$ and $[\mathbf{4}]BF_4$ with aromatic substituents R. Its position is almost independent of the central metal and changes on variation of the substituents, although there is no clear correlation between the donor capacity of R and the energy of this transition. A similar transition has also been found in 2-azaallenium ions $[R_2C{=}N{=}CR_2]^+$ with aromatic substituents R.[29] Therefore, we tentatively assign the third band to a transition from the π-orbitals of the substituents into the LUMO of the complexes. Unfortunately, the electronic spectra of allenylidene complexes and of $(CO)_5Cr{=}C{=}C{=}C{=}O$ have not been published. However, their colors are similar to those of $[\mathbf{3}]BF_4$ and $[\mathbf{4}]BF_4$ ($(CO)_5M{=}C{=}C{=}C(R^1)R^2$ (M = Cr, W), blue for R^1, R^2 = aryl,[30] purple for R^1 = Ph and R^2 = NMe_2,[26] and red for R^1, R^2 = alkyl,[31] $(CO)_5Cr{=}C{=}C{=}C{=}O$, black-violet[16]). In contrast, the cyanoisocyanide complex **6** is colourless.[25]

We also recorded the emission spectra of the BF_4 salts of **3b**, **3d**, and **4b** in fluid solution (−60 °C, CH_2Cl_2; Figure 1) and observed an emission from the third excited state (excitation wavelengths in parentheses; **3b**, 480 nm (420 nm); **3d**, 425 nm (380 nm); **4b**, 460 nm (415 nm)). Since the excitation spectra of these emissions agree well with the absorption spectra, emission due to impurities can be ruled out. The lifetime of the emitting state in $[\mathbf{3d}]BF_4$ is 11 ns. Since the luminescence quantum yield is low ($\Phi < 10^{-3}$), the lifetime is certainly not determined by the luminescence rate but rather by the rate of radiationless deactivation. Emission from higher excited states is rarely found,[32,33] especially in organometallic compounds.

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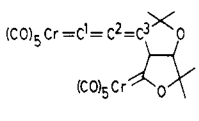
Table III. Bond Lengths (pm) and Bond Angles (deg) of the Cation in [3d]BF_4•CH_2Cl_2

	Bond Lengths		
Cr–C1	191.4 (6)	C71–C72	140.3 (8)
Cr–C2	191.8 (6)	C72–C73	141.8 (8)
Cr–C3	190.1 (7)	C73–C74	134.2 (9)
Cr–C4	191.8 (6)	C74–C75	141.1 (9)
Cr–C5	191.8 (6)	C75–C76	137.1 (8)
Cr–C6	189.5 (6)	C71–C76	140.4 (8)
C1–O1	112.9 (8)	C81–C82	140.2 (8)
C2–O2	113.8 (8)	C82–C83	139.1 (9)
C3–O3	114.1 (8)	C83–C84	136.8 (9)
C4–O4	113.3 (8)	C84–C85	139.1 (10)
C5–O5	113.5 (8)	C85–C86	135.6 (10)
C6–N	118.4 (7)	C81–C86	141.8 (8)
N–C61	134.3 (7)	C72–O	135.6 (7)
C61–C71	141.6 (7)	C82–O	134.6 (7)
C61–C81	139.9 (8)		
	Bond Angles		
C1–Cr–C2	90.5 (3)	C4–Cr–C5	90.1 (3)
C1–Cr–C3	174.7 (3)	C5–Cr–C6	178.2 (3)
C1–Cr–C4	89.2 (3)	Cr–C6–N	179.0 (5)
C1–Cr–C5	91.9 (3)	C6–N–C61	171.1 (5)
C1–Cr–C6	87.3 (3)	N–C61–C71	119.3 (5)
C2–Cr–C5	85.8 (3)	N–C61–C81	120.0 (5)
C3–Cr–C5	93.2 (3)	C71–C61–C81	120.7 (5)

Table IV. Final Positional Parameters of [3d]BF_4•CH_2Cl_2

atom	*x/a*	*y/b*	*z/c*	*B*, Å^2
Cr	0.09841 (5)	0.14260 (6)	0.22155 (6)	
C1	0.1692 (4)	0.0177 (5)	0.2308 (5)	
O1	0.2139 (3)	–0.0539 (4)	0.2396 (4)	
C2	0.1107 (4)	0.1812 (4)	0.0848 (5)	
O2	0.1146 (3)	0.2016 (3)	0.0012 (3)	
C3	0.0374 (4)	0.2715 (5)	0.2238 (5)	
O3	0.0050 (3)	0.3510 (4)	0.2285 (4)	
C4	0.0786 (4)	0.0980 (4)	0.3521 (5)	
O4	0.0645 (3)	0.0696 (3)	0.4270 (4)	
C5	–0.0117 (4)	0.0729 (5)	0.1298 (5)	
O5	–0.0771 (3)	0.0338 (3)	0.0725 (4)	
C6	0.2088 (4)	0.2109 (4)	0.3086 (4)	
N	0.2770 (3)	0.2545 (3)	0.3636 (3)	
C61	0.3594 (3)	0.2890 (4)	0.4316 (4)	
C71	0.3659 (3)	0.3846 (4)	0.4908 (4)	
C72	0.4526 (4)	0.4124 (5)	0.5673 (4)	
C73	0.4663 (4)	0.5064 (5)	0.6311 (4)	
C74	0.3933 (5)	0.5669 (5)	0.6181 (5)	
C75	0.3054 (4)	0.5422 (5)	0.5409 (5)	
C76	0.2923 (4)	0.4522 (5)	0.4780 (5)	
C6	0.5271 (2)	0.3509 (3)	0.5858 (3)	
C81	0.4374 (4)	0.2295 (4)	0.4450 (4)	
C82	0.5206 (4)	0.2628 (5)	0.5252 (4)	
C83	0.6009 (4)	0.2057 (5)	0.5483 (5)	
C84	0.5975 (4)	0.1150 (5)	0.4895 (6)	
C85	0.5160 (5)	0.0813 (5)	0.4082 (5)	
C86	0.4373 (4)	0.1360 (5)	0.3848 (4)	
B	0.3383 (4)	0.3511 (6)	0.1458 (6)	3.5 (1)
F1	0.4317 (2)	0.3413 (3)	0.1706 (3)	
F2	0.3022 (2)	0.2537 (3)	0.1432 (3)	
F3	0.2991 (2)	0.4023 (3)	0.0433 (3)	
F4	0.3256 (2)	0.4152 (2)	0.2273 (2)	
C9	0.8147 (6)	0.1065 (7)	0.3692 (7)	8.1 (2)
Cl1	0.8286 (3)	0.1600 (5)	0.2527 (4)	
Cl2	0.8215 (4)	0.1944 (4)	0.4708 (5)	
Cl1′	0.827 (2)	0.113 (2)	0.255 (2)	6.5 (8)
Cl2′	0.852 (2)	0.210 (2)	0.459 (3)	6.1 (7)
Cl1″	0.840 (2)	0.192 (3)	0.287 (2)	7.2 (9)
Cl2″	0.819(2)	0.179 (2)	0.508 (2)	4.0 (5)
H73	0.527	0.526	0.683	5.0
H74	0.401	0.630	0.664	5.0
H75	0.254	0.589	0.533	5.0
H76	0.232	0.435	0.424	5.0
H83	0.658	0.230	0.605	5.0
H84	0.653	0.073	0.505	5.0
H85	0.515	0.016	0.367	5.0
H86	0.381	0.111	0.327	5.0
H91	0.863	0.053	0.401	8.0
H92	0.755	0.072	0.345	8.0

X-ray Diffraction Analysis of [3d]BF_4·CH_2Cl_2. Crystals suitable for an X-ray study could be grown of [**3d**]BF_4. The atomic numbering scheme is defined in Figure 2. Intramolecular bond distances and angles are reported in Table III and final positional parameters in Table IV. The Cr–C–N–C fragment is almost linear (Cr–C6–N = 179.0 (5)°; C6–N–C61 = 171.1 (5)°). Similarly, a small but significant deviation from a perfectly linear structure is also observed in allenylidene complexes (e.g., C1–C2–C3 = 170.9 (15)° in **7**,[26] 174.3 (7)° in **8a**,[34] and



8a

175.1 (6)° in (η^5-C_5H_5)(CO)$_2$Mn=C^1=C^2=C^3(C_6H_{11})$_2$ (**8b**)[35]) and in the cyanoisocyanide complex **6** (168.5 (4)°[25]). Obviously, the amount of energy required for bending the ligand in these complexes is small. Ab initio calculations performed with $[H_2C{=}N{=}CH_2]^+$ reveal that the energy required for contracting the C–N–C angle from 180° to 160° is only 16 kJ mol^{-1}.[36] The Cr–C6 bond length in [**3d**]BF_4 (189.5 (6) pm) is comparable to that of Cr–C1 in **8a** (191.3 (7) pm)[34] and in **6** (188.3 (3) pm),[25] but shorter than that in **7** (201.5 (15) pm)[26] or the Cr–C "double bond" of heteroatom-stabilized carbene complexes (ca. 197–213 pm).[37] Both carbon–nitrogen distances differ significantly (C6–N = 118.4 (7) pm; N–C61 = 134.3 (7) pm). The corresponding C1–N bond length in **6** is 116.7 (5) pm.[25] Since C6 is sp- and C61 is sp^2-hybridized, one would expect that C6–N is shorter than N–C61. However, the difference of the C–N distances in the cation **3d** is unusually large. Different bond lengths in the cumulene system are also encountered in allenylidene complexes (e.g., **7**, C1–C2 = 123.6 (22), C2–C3 = 137.2 (21) pm;[26] **8a**, C1–C2 = 126 (1), C2–C3 = 135.9 (9) pm;[34] **8b**, C1–C2 = 125.2 (8), C2–C3 = 134.2 (8) pm[35]).

The plane of the CR_2 substituent, defined by the atoms C61, C71–C76, C81–C86, and O, is slightly tilted against the plane defined by the atoms Cr, C1, C3, C5, and C6 (15.4°). Within experimental error the Cr–CO(cis) distances are identical with the Cr–CO(trans) distance, implying that the σ-donor/π-acceptor ratio of the 2-azaallenylidene ligand in **3d** is roughly the same as that of CO. Crystals of [**3d**]BF_4 contain one molecule of CH_2Cl_2 per molecule of [**3d**]BF_4. However, the distances of the solvent molecules as well as of the anions from the cationic complex are too large to allow for any significant interaction.

Reactivity Studies. The reactions of [**4**]$AlBr_4$ with tetrahydrofuran, THF, to yield novel 2-azaallylidene complexes[1,38] and of [**3b**]$AlBr_4$ with THF to give a binuclear isocyanide complex[39] have already been reported.

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[**3d**]BF_4 reacts with an excess of $Me_3N^+{-}O^-$ to form xanthone, $O{=}C(C_6H_4)_2O$. No CO-containing complex was found among the reaction products. Very likely, the reaction is initiated by a nucleophilic attack of the oxygen atom of $Me_3N^+{-}O^-$ at the terminal carbon of the heterocumulene system (C61). On addition of Et_2O to solutions of [**3b**]BF_4 in CH_2Cl_2, the blue solution immediately turns colorless presumably due to addition of Et_2O to C61. When the solvent is removed, the blue colour of cation **3b** is restored again. Obviously, the addition of the ether is reversible.

Irradiation of CH_2Cl_2 solutions of [**3b**]BF_4 and [**3d**]BF_4 with light of wavelength $\lambda > 300$ nm yields the olefins $Ph_2C{=}CPh_2$ and $O(C_6H_4)_2C{=}C(C_6H_4)_2O$ in isolated yields of 34% and 29%, respectively. Earlier we proposed that the photoreaction is initiated by irradiation into the low-energy absorptions at 600–700 nm. However, a more detailed study shows that the strong mercury emission at 313 nm (which has not been completely filtered out by our filter solutions) is responsible for the photoreaction. The mechanistic aspects of this quite complicated reaction are currently being investigated.

Discussion and Conclusion

By reaction of Lewis acids with 2-azaallenyl complexes and $(CO)_5Cr{-}C{\equiv}N{-}CCl_3$, respectively, novel cationic metallaheterocumulene systems are accessible. In many respects these complexes are related to allenylidene complexes. An X-ray diffraction analysis performed with $[(CO)_5Cr{=}C{=}N{=}C(C_6H_4)_2O]BF_4{\cdot}CH_2Cl_2$ confirms the nearly linear, end-on bonding mode of the heterocumulene. IR, ^{13}C NMR, and electronic spectra reveal a high degree of electron delocalization within the M–C–N–C system. According to the X-ray analysis of [**3d**]$BF_4{\cdot}CH_2Cl_2$ both C–N distances differ strongly. Therefore, the complexes are best described as resonance hybrids of the two limiting structures A and B (eq 3). A similar situation applies to allenylidene complexes, for which the three resonance structures C–E (eq 4) have to be taken into account.

$$\underset{\underline{A}}{(CO)_5M{=}C{=}\overset{+}{N}{=}CR_2} \longleftrightarrow \underset{\underline{B}}{(CO)_5\overset{-}{M}{-}C{\equiv}\overset{+}{N}{-}\overset{+}{C}R_2} \qquad (3)$$

$$\underset{\underline{C}}{L_n\overset{-}{M}{-}C^1{\equiv}C^2{-}\overset{+}{C}{}^3R_2} \longleftrightarrow \underset{\underline{D}}{L_nM{=}C^1{=}C^2{=}C^3R_2} \longleftrightarrow \underset{\underline{E}}{L_n\overset{-}{M}{-}\overset{+}{C}{}^1{=}C^2{=}C^3R_2} \qquad (4)$$

Extended Hückel MO calculations indicate that increasing π-donor ability of R strengthens the C1–C2 bond and weakens the C2–C3 bond, thus increasing the difference in the C–C bond lengths.[34] In principle, we have obtained similar results from MO calculations performed with $[(CO)_5Cr{=}C{=}N{=}CH_2]^+$ and C-substituted derivatives thereof. Increasing π-donor ability of R stresses the importance of the resonance structure B relative to A. This agrees well with the influence exercised by different substituents R on the spectroscopic data: when increasing the π-donor ability of R the C–N–C vibration and the MLCT absorptions shift toward higher energy. Finally, an extreme form of this trend is observed in the radical complex $(CO)_5Cr{-}C{\equiv}N{-}C(2,4,6\text{-}C_6H_2Me_3)_2$ (**9**) which can be obtained by one-electron reduction of [**3e**]BF_4.[40] From the ESR spectrum of **9** it follows that the unpaired electron is mainly localized within the $CNCR_2$ ligand. The carbon atom C61 has nearly planar coordination, and the bond distances Cr–C, C–N, and N–C are those of typical isocyanide complexes.[40]

As might be expected from the MO calculations, increasing the π-donor ability of the metal–ligand fragment by exchange of $(CO)_5M$ for *trans*-$Br(CO)_4W^-$, giving *trans*-$Br(CO)_4W[CNCR_2]$ (**10**), results in a pronounced elongation of the C6–N bond and a slight shortening of the N–C61 bond.[1,38] In addition, however, the C6–N–C61 angle diminishes strongly to 135.4 (5)°. The W–C distance in **10** (R = Ph) is very short (187.8 (5) pm), comparable to that usually found in complexes with a formal tungsten–carbon triple bond. Therefore, these complexes of **10** can also be regarded as iminocarbyne complexes. A similarly drastic change has not been observed with allenylidene complexes when the π-donor properties of the metal–ligand fragment are increased. For organic 2-azaallenium cations $[R_2C{=}N{=}CR_2]^+$ a decreasing C–N–C bond angle with increasing donor properties of R has been predicted on the basis of ab initio calculations[36] and has been verified experimentally in several instances.[41]

There are still other differences between the allenylidene complexes $(CO)_5M{=}C{=}C{=}CR_2$ (M = Cr, W) and the 2-azaallenylidene complexes [**3**]BF_4 and [**4**]BF_4. Aryl-substituted 2-azaallenylidene complexes [**3a–e**]BF_4 and [**4a–e**]BF_4 are significantly more stable than the tert-butyl-substituted complexes [**3f**]BF_4 and [**4f**]BF_4. The reverse is true of allenylidene complexes.[30,31] Nucleophilic reagents add to allenylidene complexes either at C1 or C3, depending on the type of nucleophile and the type of allenylidene complex.[13] Until now, however, there are no indications for an attack of a nucleophile at the metal-bonded carbon C6 of 2-azaallenylidene complexes.

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Registry No. **1a**, 99807-65-5; **1b**, 54330-36-8; **1c**, 99807-66-6; **1d**, 94598-01-3; **1e**, 104130-64-5; **1f**, 99807-67-7; **2a**, 99807-68-8; **2b**, 90022-80-3; **2c**, 99807-69-9; **2d**, 99807-70-2; **2e**, 100813-81-8; **2f**, 99807-71-3; **3a**, 104130-42-9; **3b**, 104130-44-1; **3c**, 104130-46-3; **3d**·CH_2Cl_2, 104130-49-6; **3e**, 104130-51-0; **3f**, 104130-53-2; **3g**, 104130-55-4; **4a**, 104130-57-6; **4b**, 104155-40-0; **4c**, 104155-42-2; **4d**, 104130-59-8; **4e**, 104130-61-2; **4f**, 104130-63-4; $(CO)_5Cr{-}C{\equiv}N{-}CCl_3$, 68927-87-7; $O(C_6H_4)_2C{=}C(C_6H_4)_2O$, 517-45-3; xanthone, 90-47-1; tetraphenylethylene, 632-51-9.

Supplementary Material Available: Tables of crystal structure data, bond lengths and bond angles, temperature parameters, and atomic coordinates (19 pages); a table of structure factors (16 pages). Ordering information is given on any current masthead page.

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