16-electron complex and would be capable of binding a bis(trimethylsilyl)acetylene.

$$(\eta\text{-}C_5H_5)Co(\eta^2\text{-}B_6H_{10}) + R_2C_2 \rightarrow (\eta\text{-}C_5H_5)Co(\eta^2\text{-}B_6H_{10})(\eta^2\text{-}R_2C_2)$$

Fusion of the coordinated hexaborane(10) and acetylene groups accompanied by the loss of 2 equiv of H_2 could then yield compounds II and III.

It was indeed surprising that the major product of the reaction, compound I, did not have a single cage structure but instead adopted the unique diborane–metallacarborane structure (Figure 1). At first glance it is difficult to understand how such a structure could be derived from hexaborane(10); however, as shown in Figure 2 the reaction can be envisioned as occurring in much the same way as that proposed for the formation of II and III. Thus, the fusion of an acetylene to the open face of the hexaborane cage generates a pentagonal ring, composed of the two carbons and borons 4, 5, and 6, suitable for bonding to a $(\eta\text{-}C_5H_5)Co$ atom. If, as the cobalt atom bonds to this ring, the B4–bridging hydrogen and B6–bridging hydrogen bonds are cleaved, then a $-B_2H_5$ unit can be extrued from the cobaltaborane cage as shown in the figure. Thus, the driving force leading to this unique bridged structure may result from the favored formation of the cobaltaborane sandwich, $1\text{-}(\eta\text{-}C_5H_5)Co\text{-}2,3\text{-}(Me_3Si)_2C_2B_4H_3$-complex.

Acknowledgment. We thank the National Science Foundation and the Army Research Office for the support of this work.

Supplementary Material Available: Tables of general temperature factors, molecular planes, and observed and calculated structure factors (32 pages). Ordering formation is given on any current masthead page.

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Spontaneous Rearrangement of Aminochlorocarbene into Chloro Aminocarbyne Complexes. Synthesis of Aminocarbene and Aminocarbyne Complexes and Kinetics and Mechanism of the Rearrangement Reaction[†1]

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Received August 13, 1984

The reaction of $(CO)_5Cr[C(OEt)NR_2]$ (NR_2 = NMe_2, NC_5H_{10}, NEt_2) (**3a–c**) with BCl_3 gives $[(CO)_5Cr{\equiv}CNR_2]^+$ (**4a–c**). The corresponding cationic NPh_2 and N-*i*-Pr_2 compounds (**4d** and **4e**) can be prepared from $(CO)_5Cr[C(NR_2]N{=}C(OMe)Ph]$ (R = Ph, *i*-Pr) and excess BCl_3. **4c** exchanges ^{13}CO for CO at 0 °C with a rate constant of $(2.5 \pm 0.8) \times 10^{-4}\ s^{-1}$. No stereochemical preference for ligand exchange cis or trans to the carbyne ligand could be detected. In solution the cations **4a–d** add Cl^- rapidly to the carbyne carbon to give $(CO)_5Cr[C(Cl)NR_2]$ (**6a–d**). When solutions of **6a–d** are heated, the carbene complexes spontaneously rearrange with extrusion of one CO ligand and neutral carbyne complexes *trans*-$Cl(CO)_4Cr{\equiv}CNR_2$ (**7a–d**) are formed. The reaction of **4e** with Cl^- at −60 °C immediately affords *trans*-$Cl(CO)_4Cr{\equiv}CN$-*i*-Pr_2 instead of $(CO)_5Cr[C(Cl)N$-*i*-$Pr_2]$. The rearrangement of **6a–d** into **7a–d** with elimination of a CO group follows a first-order rate law. The reaction rate is not influenced by the presence of Cl^-, radical initiators, radical inhibitors, PPh_3, or CO (up to a CO pressure of 78 atm) in the solution. The activation entropy is low. The solvent influence is small. Increasing the bulk of the amino substituent, however, strongly enhances the reaction rate. These results suggest that the rearrangement is an intramolecular process involving concerted Cr–CO dissociation and C/Cr migration of Cl. The mechanistic conclusions are discussed with respect to the mechanism for the general synthesis of carbyne complexes by reaction of carbene complexes with halides of group 13 elements.

Introduction

Metal-bound alkylidene (carbene) and alkylidyne (carbyne) groups are believed to play a pivotal role in several catalytic reactions.[2] Complexes in low oxidation states containing a terminally bonded carbene and carbyne ligand, respectively, are closely interrelated: carbene complexes can be transformed into carbyne complexes and vice versa. For instance, the most common method for the preparation of carbyne complexes employs the abstraction of an alkoxy, alkylthio or amino group from a carbene ligand by halides of group 13 elements to give cationic carbyne complexes (eq 1) or, with simultaneous CO/X^-

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[†] The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

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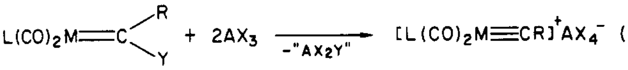
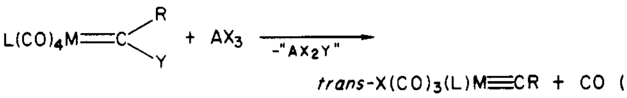
exchange, neutral trans halo carbyne complexes (eq 2).[3]



$$L(CO)_2M{=}C(R)(Y) + 2AX_3 \xrightarrow[-\text{"}AX_2Y\text{"}]{} [L(CO)_2M{\equiv}CR]^+AX_4^- \quad (1)$$

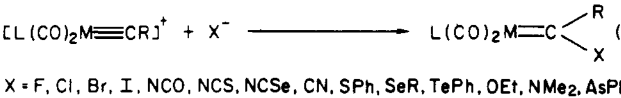
L = η^6-$C_6H_{6-n}Me_n$, η^5-C_5H_4Me, η^5-C_5H_5, $[(CO)_5Re(CO)_2]$, *trans*-$(PR_3)(CO)_2$...; R = alkyl, aryl, SiR_3, NR_2; Y = OMe, OEt; AX_3 = BF_3, BCl_3, BBr_3



$$L(CO)_4M{=}C(R)(Y) + AX_3 \xrightarrow[-\text{"}AX_2Y\text{"}]{} trans\text{-}X(CO)_3(L)M{\equiv}CR + CO \quad (2)$$

L = *cis*-PR_3, CO; R = aryl, alkyl, SiR_3, NR_2, ...; Y = OR, SR, NR_2; A = B, Al, Ga; X = Cl, Br, I

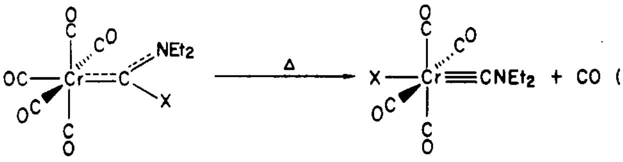
In turn, a great number of different nucleophiles can add to the carbyne carbon atom of cationic carbyne complexes to give neutral carbene complexes (eq 3).[4] This method is useful for the synthesis of carbene complexes that cannot be prepared by other routes.



$$[L(CO)_2M{\equiv}CR]^+ + X^- \longrightarrow L(CO)_2M{=}C(R)(X) \quad (3)$$

X = F, Cl, Br, I, NCO, NCS, NCSe, CN, SPh, SeR, TePh, OEt, NMe_2, $AsPh_2$, $SnPh_3$, $PbPh_3$, Me, $(CO)_5M[C({=}O)R]$ (M = Cr, W), ...

With some (aminocarbene)pentacarbonylchromium complexes, the transformation of carbene into carbyne complexes occurs spontaneously. When they are heated, $(CO)_5Cr[C(X)NEt_2]$ rearranges with C, Cr migration of the group X and loss of one CO ligand to give *trans*-X-$(CO)_4Cr{\equiv}CNEt_2$ (eq 4).[4]



(4)

1 2

X = Cl, Br, I, SeR, TePh, $SnPh_3$, $PbPh_3$

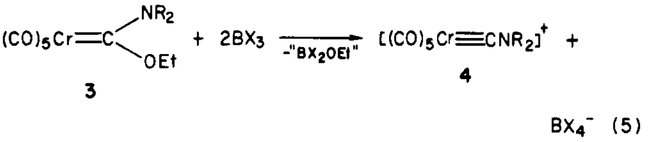
In other cases (X = F, $SiPh_3$, OEt, NCS, NCO, CN), no rearrangement according to eq 4 could be observed. However, these carbene complexes are generally thermally more stable than those which do rearrange. Therefore, it is still unclear whether these complexes do not rearrange at all or whether the decomposition of the resulting carbyne complexes is essentially faster than their formation. (The thermal stability of these carbyne complexes is expected to be much lower than that of **2**.) On the basis of the results of several kinetic studies of the rearrangement reaction, a mechanism has been deduced which involves simultaneous migration of X from the carbene carbon to the metal and Cr–CO dissociation.[5] If X = Cl, SeR, TePh, $SnPh_3$, and $PbPh_3$ (eq 4), the reaction rate is remarkably insensitive to variations of the migrating group X. At 40 °C in 1,1,2-trichloroethane, the rate ratio is $k(PbPh_3)$:k-$(SnPh_3)$:k(SePh):k(Cl):k(TePh) = 1:1.8:2.9:3.9:8.1. Variation of R with X = SeR does not influence the rate very much either (R = p-C_6H_4R'): $k(R' = CF_3)$:$k(R' = Br)$:$k(R' = F)$:$k(R' = H)$:$k(R' = Me)$:$k(R' = OMe)$ = 1.12:0.83:0.67:1.0:0.84:0.63. If R = Ph is replaced by R = 1-naphthyl, the rate drops only by 50%.[5d] In the case where tungsten is the metal, until now only two complexes related to **1** could be synthesized from $[(CO)_5W{\equiv}CNEt_2]^+$ and a nucleophile, X^- (X = p-$SeC_6H_4CF_3$, $AsPh_2$).[6,7] For both of these carbene complexes no rearrangement analogous to reaction 4 could be detected.

X-ray studies of several (diethylamino)carbene complexes of chromium **1** (X = Me,[8a] H,[8b,c] Cl,[8d] Br,[8e] NCO,[8f] NCS,[8f] SePh,[8g] $SnPh_3$[8c]) reveal that (1) the Cr–C–N angle is significantly enlarged [ranging from 129.4° (X = Me) to 136.5° (X = Br)] and (2) the Cr–C–X angle is smaller than 120°. Increasing the bulk of the amino group NR_2 should further enlarge the Cr–C–N angle, thus pushing X even closer to the $(CO)_5Cr$ fragment. Since a considerable effect on the rearrangement rate can be expected, we undertook a detailed investigation of the influence of different amino substituents on the reactivity of these carbene complexes.

We report here (a) the first synthesis and characterization of various new cationic aminocarbyne complexes, aminochlorocarbene complexes, and neutral trans chloro aminocarbyne complexes and (b) the results of the kinetic study of their carbene/carbyne rearrangement.

Results

Synthesis of Complexes. (1) Cationic Carbyne Complexes. $(CO)_5Cr[C(OEt)NMe_2]$ (**3a**)[9] and $(CO)_5Cr$-$[C(OEt)NC_5H_{10}]$ (**3b**), accessible from $(CO)_6Cr$ via successive reaction with $[NC_5H_{10}]^-$ and $EtOSO_2F$ (see Experimental Section), react rapidly in dichloromethane already at −100 °C with BCl_3 and BF_3, respectively, to form the cations **4a** and **4b**, respectively. These can be isolated in the form of the corresponding BF_4^- or BCl_4^- salts. The analogous reaction of $(CO)_5Cr[C(OEt)NEt_2]$ (**3c**)[10] with BCl_3 gives $[(CO)_5Cr{\equiv}CNEt_2]BCl_4$ (**4c–BCl$_4$**).



$$(CO)_5Cr{=}C(NR_2)(OEt) + 2BX_3 \xrightarrow[-\text{"}BX_2OEt\text{"}]{} [(CO)_5Cr{\equiv}CNR_2]^+ + BX_4^- \quad (5)$$

3 4

a, NR_2 = NMe_2; b, NR_2 = NC_5H_{10}; c, NR_2 = NEt_2

Since it has so far been impossible to prepare (diarylamino)ethoxycarbene complexes (**3**, R = aryl), obviously due to too low nucleophilicity of the amide anion in lithium diarylamides, this method (eq 5) cannot be employed for the preparation of (diarylamino)carbyne complexes. Therefore, a new route (eq 6) has been developed.[11] With 3 equiv of boron trichloride $(CO)_5Cr[C(NPh_2)N{=}C$-$(OMe)Ph]$ (**5d**)[1] produces in a Lewis acid induced fragmentation reaction the desired carbyne cation **4d** in very high yield. The analogous reaction of **5e** with BCl_3 affords

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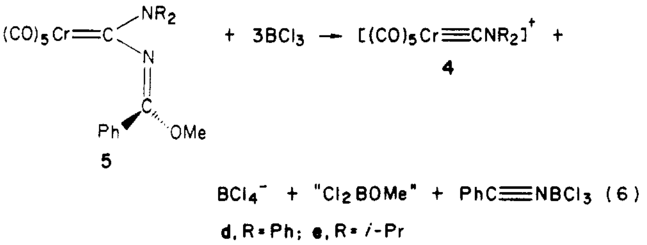
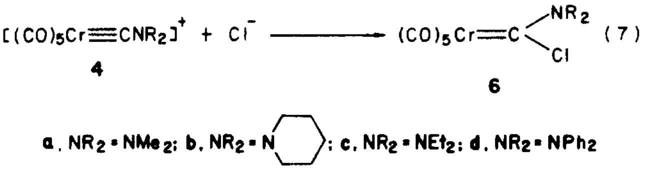


4e. The BCl_4^- salts of **4d** and **4e** can be converted with $SbCl_5$ into the more stable $SbCl_6^-$ salts and with $AgBF_4$ into the BF_4^- salts, respectively.[11]

The BCl_4^- salts of 4 (**4-BCl$_4$**) are very thermally labile (vide infra). The BF_4^- salts (**4-BF$_4$**), however, are substantially more stable. At −30 °C, **4-BF$_4$** may be stored for months in a nitrogen atmosphere. The IR spectrum of **4a–e** shows in the ν(CO) region one weak and one very strong, broad absorption (Table I). The X-ray analysis of **4c-BF$_4$** reveals that the $Cr–CO_{trans}$ distance is significantly longer than the mean of the $Cr–CO_{cis}$ distances.[12] Therefore, the weak band at higher wavenumber can be ascribed to the A_1 absorption of the trans CO group.

The ^1H NMR spectra (acetone-d_6, −50 °C, chemical shifts (δ) in ppm downfield from Me_4Si) show for **4a–BCl$_4$** one singlet at δ 3.63 and for **4c-BCl$_4$** a triplet at δ 1.6 and a quartet at δ 4.1 (ratio 3/2), indicating that both *N*-alkyl groups are magnetically equivalent. The Cr≡C(carbyne)—N fragment is, therefore, linear. Similar observations have been made earlier with **4a-BF$_4$**[13] and **4c-BF$_4$**.[14] The ^{13}C NMR spectrum of **4c-BCl$_4$** (dichloromethane-d_2, −50 °C) shows resonances at δ 282.34 ($C_{carbyne}$), 206.98 (CO_{cis}), 202.94 (CO_{trans}), 49.10 (NCH_2), and 13.28 (NCH_2CH_3), in agreement with the cationic nature of **4c-BCl$_4$**. The cations **4d** and **4e** have already been described elsewere.[11]

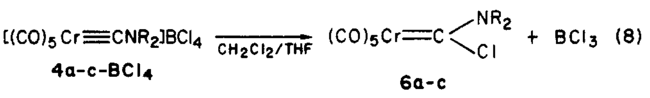
(2) Aminochlorocarbene Complexes. In CH_2Cl_2/THF (1:1) at temperatures below −40 °C, the cations **4a–d** add the chloride ion from $[NEt_4]Cl$ and $[(Ph_3P)_2N]Cl$, respectively, to give the neutral aminochlorocarbene pentacarbonyl complexes **6a–d** in 63–77% yield. **6a-c** is also obtained when solutions of **4a–c-BCl$_4$** in CH_2Cl_2 are warmed to 0 °C. The addition of small amounts of THF or acetone accelerates this reaction. Finally, in pure THF or acetone the formation of **6a–c** proceeds rapidly already at −30 °C.



$$[(CO)_5Cr{\equiv}CNR_2]^+ + Cl^- \longrightarrow (CO)_5Cr{=}C(NR_2)Cl \quad (7)$$

4 6

a, NR2 = NMe2; b, NR2 = N(ring); c, NR2 = NEt2; d, NR2 = NPh2



$$[(CO)_5Cr{\equiv}CNR_2]BCl_4 \xrightarrow[CH_2Cl_2/THF]{} (CO)_5Cr{=}C(NR_2)Cl + BCl_3 \quad (8)$$

4a-c-BCl4 6a-c

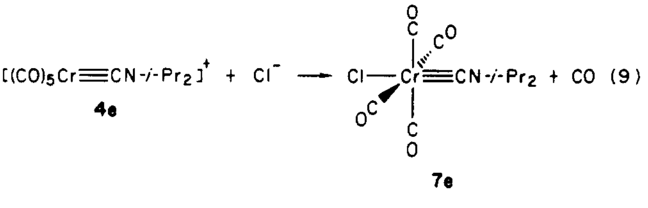
Obviously, THF (or acetone) displaces a chloride from BCl_4^-. The chloride then adds to the carbyne carbon atom of **4a–c**. The complexes **6a–d** form yellow, diamagnetic crystals which readily dissolve in polar solvents such as diethyl ether, acetone, or dichloromethane. In hexane they are poorly soluble. According to their IR spectra (Table I), the aminochlorocarbene ligand in **6a–c** has a somewhat lower σ-donor/π-acceptor ratio than the aminoethoxycarbene ligand in the corresponding complexes **3a–c**.

Table I. IR Spectra (cm^{-1}) of 4a-c-BCl$_4$, 6a-d, and 7a-e in the ν(CO) Region

compd	medium	ν(CO)
4a-BCl$_4$	THF	2137 (w) (A_1^1), 2020 (vs) (A_1^2, E)
4b-BCl$_4$	CH_2Cl_2	2139 (w) (A_1^1), 2033 (vs) (A_1^2, E)
4c-BCl$_4$	CH_2Cl_2	2136 (w) (A_1^1), 2032 (vs) (A_1^2, E)
6a	1,1,2-trichloroethane	2063 (m), 1986 (w), 1939 (vs), 1915 (w, sh)
6b	1,1,2-trichloroethane	2062 (m), 1986 (w), 1939 (vs), 1910 (w, sh)
6c	1,1,2-trichloroethane	2063 (m), 1986 (w), 1939 (vs), 1910 (w, sh)
6d	hexane	2065 (m), 1989 (w), 1954 (s), 1946 (s)
7a	1,1,2-trichloroethane	2102 (w), 2046 (w, sh), 2027 (s), 1995 (vs)
7b	1,1,2-trichloroethane	2102 (w), 2044 (w, sh), 2020 (s), 1993 (vs)
7c	1,1,2-trichloroethane	2103 (w), 2042 (w, sh), 2020 (s), 1995 (vs)
7d	1,1,2-trichloroethane	2107 (w), 2058 (w, sh), 2040 (s), 2010 (vs)
7e	1,1,2-trichloroethane	2100 (w), 2040 (w, sh), 2020 (s), 1993 (vs)

Analogous to **3a** and **3b**, the rotation about the C(carbene)–N bond in **6a** and **6b** is restricted, giving rise to two sets of *N*-alkyl resonances according to their *E* and *Z* positions. Compared to **3**, the $N–CH_3$ and $N–CH_2$ hydrogen atoms in **6** are deshielded as expected. Similarly, in the ^{13}C NMR spectrum of **6a** the resonance of the carbene carbon atom is observed at lower field compared to that of **3a**.

(3) Neutral Trans Chloro Aminocarbyne Complexes. When $[(CO)_5Cr{\equiv}CN\text{-}i\text{-}Pr_2]^+$ (**4e**) was treated with chloride at −60 °C in dichloromethane, the neutral trans chloro (diisopropylamino)carbyne complex **7e** was obtained instead of the chloro(diisopropylamino)carbene complex $(CO)_5Cr[C(Cl)N\text{-}i\text{-}Pr_2]$ (**6e**). The formation of **6e** even as an intermediate could not be detected by IR or ^1H NMR spectroscopy. However, **6e** is very likely an intermediate in the formation of **7e**.



Neutral trans chloro aminocarbyne complexes also are formed when solutions of **6a–d** are heated. The carbene complexes **6a–d** rearrange with extrusion of a CO ligand to yield **7a–d**. The temperature required for this rearrangement strongly depends on the amino substituent and increases in the series NR_2 = NPh_2, NEt_2, NC_5H_{10}, and NMe_2.

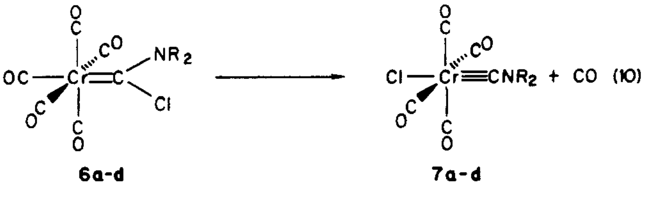


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Table II. ^{1}H NMR Spectral Data

compd	medium	^{1}H, δ	T, °C
4a-BCl_4	acetone-d_6	3.63 (s, CH_3)	−70
4c-BCl_4	acetone-d_6	4.1 (q, NCH_2), 1.6 (t, CH_3)	−50
6a	acetone-d_6	3.97 (s, CH_3, Z), 3.65 (s, CH_3, E)	−10
6b	acetone-d_6	4.71 (m), 4.47 (m), 1.64 (m)	−10
6c	CD_2Cl_2	4.29 (q, NCH_2, E), 4.01 (q, NCH_2, Z), 1.48 (t, CH_3, E), 1.34 (t, CH_3, Z)	−20
6d	CD_2Cl_2	6.8 (m)	−50
7c[14b]	CD_2Cl_2	3.36 (q, NCH_2), 1.38 (t, CH_3)	−20
7d	CD_2Cl_2	6.8 (m)	−50
7e	CD_2Cl_2	3.19 (m, NCH), 1.32 (d, CH_3)	−50

In a succeeding, slower reaction step, the neutral carbyne complexes **7a–e** decompose, initiated by loss of a CO ligand. The thermal stability of **7** is influenced by the group NR_2, increasing in the series NR_2 = NPh_2, NMe_2, NC_5H_{10} ≈ NEt_2, and N-*i*-Pr_2. The complexes **7c–e** were isolated; complexes **7a,b** were identified by the similarity of their IR spectra to those of **7c–e**. The compound **7c** has already been described elsewere.[14b] In contrast to *trans*-X-$(CO)_4M{\equiv}CR$ complexes (X = Cl, Br, I; M = Cr, Mo, W; R = aryl, alkyl), which show two ν(CO) bands, for the compounds **7a–e** four ν(CO) absorptions are observed. Therefore, a strong deviation of the carbonyl metal fragment from D_{4h} or C_{4v} symmetry can be assumed. The intensity ratio of the four ν(CO) absorptions is almost independent of the amino substituent. Analogous to the cations **4**, both N–R groups in the ^{1}H NMR spectra of **7** are magnetically equivalent (Table II).

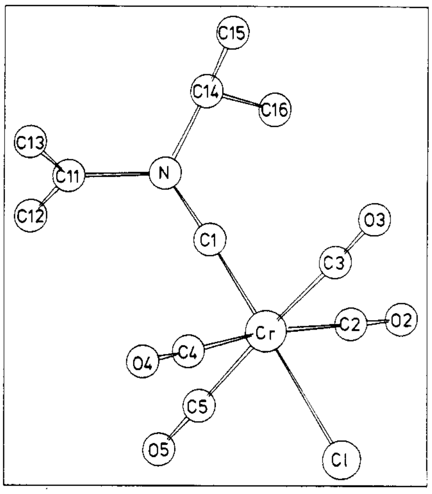

Figure 1. Molecular structure (ball and stick model) of **7e**.

The structure of **7e** was additionally confirmed by an X-ray diffraction study (Figure 1). Final position parameters and bond distances and angles are given in Tables III and IV, respectively. The N–C11–C14 plane is eclipsed to the cis CO groups. The Cr–C(carbyne) distance is 1.747 (5) Å, somewhat longer than that in *trans*-$Cl(CO)_4Cr{\equiv}CPh$ (**8**), 1.68 (1) Å,[15] and close to that in *trans*-$Br(CO)_4Cr{\equiv}$

Table III. Positional and Thermal Parameters of **7e**[a]

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cr	0.21836 (11)	0.15926 (5)	0.22711 (4)	O4	0.6613 (6)	0.2172 (3)	0.3163 (3)
Cl	0.1681 (2)	0.09130 (9)	0.34934 (6)	O5	0.0364 (6)	0.3601 (3)	0.2703 (2)
C1	0.2517 (7)	0.2109 (4)	0.1389 (3)	H11	0.477	0.368	0.130
N	0.2819 (7)	0.2523 (3)	0.0752 (2)	H14	0.213	0.252	−0.046
C11	0.3930 (12)	0.3514 (5)	0.0779 (5)	H121	0.292	0.488	0.040
C12	0.2662 (12)	0.4373 (5)	0.0791 (5)	H122	0.304	0.472	0.128
C13	0.5987 (13)	0.3466 (6)	0.0805 (9)	H123	0.123	0.423	0.066
C14	0.2060 (8)	0.2047 (5)	−0.0035 (3)	H131	0.610	0.347	0.015
C15	0.3507 (12)	0.1274 (6)	−0.0191 (4)	H132	0.669	0.284	0.091
C16	−0.0023 (12)	0.1690 (11)	−0.0141 (4)	H133	0.689	0.402	0.094
C2	−0.0615 (8)	0.1150 (4)	0.1834 (3)	H151	0.385	0.081	0.022
C3	0.3337 (7)	0.0307 (4)	0.2054 (3)	H152	0.483	0.162	−0.023
C4	0.4975 (9)	0.1959 (4)	0.2844 (3)	H153	0.301	0.093	−0.068
C5	0.1034 (7)	0.2851 (4)	0.2547 (3)	H161	−0.097	0.225	−0.004
O2	−0.2292 (6)	0.0895 (3)	0.1564 (2)	H162	−0.021	0.116	0.019
O3	0.4035 (6)	−0.0433 (3)	0.1906 (2)	H163	−0.060	0.150	−0.068

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cr	2.46 (3)	1.66 (3)	2.38 (3)	−0.15 (3)	0.78 (2)	−0.18 (3)
Cl	4.58 (7)	2.65 (6)	2.49 (5)	0.25 (6)	1.10 (5)	0.19 (5)
C1	2.6 (2)	1.9 (2)	3.8 (2)	−0.1 (2)	1.2 (2)	−0.4 (2)
N	4.7 (2)	2.5 (2)	4.0 (2)	0.1 (2)	2.6 (2)	0.6 (2)
C11	8.8 (5)	2.0 (3)	11.2 (5)	−0.7 (3)	7.0 (4)	0.3 (3)
C12	8.5 (5)	3.3 (4)	10.5 (5)	1.0 (3)	1.4 (4)	−1.3 (3)
C13	4.8 (4)	3.6 (4)	35.9 (17)	−1.4 (4)	0.9 (7)	−3.9 (7)
C14	3.8 (3)	5.2 (3)	3.2 (2)	1.0 (3)	1.2 (2)	1.3 (2)
C15	7.7 (4)	7.1 (5)	7.0 (4)	2.5 (4)	−2.5 (3)	−4.3 (3)
C16	5.6 (4)	35.7 (16)	3.7 (3)	−5.5 (7)	0.5 (3)	−2.1 (6)
C2	3.4 (3)	2.6 (2)	2.9 (2)	−0.4 (2)	1.2 (2)	−0.2 (2)
C3	3.0 (2)	2.5 (2)	2.9 (2)	−0.6 (2)	1.2 (2)	0.0 (2)
C4	3.2 (3)	2.5 (2)	4.1 (3)	0.3 (2)	0.7 (2)	−0.2 (2)
C5	2.9 (2)	2.6 (3)	3.0 (2)	−0.0 (2)	0.9 (2)	0.2 (2)
O2	3.3 (2)	4.8 (2)	4.5 (2)	−1.0 (2)	0.5 (1)	−0.4 (2)
O3	5.1 (2)	2.4 (2)	6.7 (2)	0.0 (2)	2.8 (2)	−0.7 (2)
O4	3.4 (2)	4.2 (2)	7.3 (2)	−0.1 (2)	−0.4 (2)	−0.5 (2)
O5	5.3 (2)	2.7 (2)	5.3 (2)	0.9 (2)	1.5 (2)	−0.5 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-{}^1/_4(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. B = 3.5 Å^2 for hydrogen atoms.

Table IV. Selected Bond Lengths (Å) and Bond Angles (deg) of 7e

Cr-C1	1.747 (5)	N-C11	1.490 (8)
Cr-C2	1.912 (5)	N-C14	1.494 (7)
Cr-C3	1.927 (5)	C2-O2	1.145 (7)
Cr-C4	1.938 (6)	C3-O3	1.132 (7)
Cr-C5	1.927 (5)	C4-O4	1.129 (7)
Cr-Cl	2.412 (1)	C5-O5	1.140 (7)
C1-N	1.297 (6)		

Bond Angles

Cl-Cr-C1	178.7 (2)	C2-Cr-C4	172.3 (2)
Cl-Cr-C2	86.1 (2)	C2-Cr-C5	88.2 (2)
Cl-Cr-C3	89.3 (2)	C3-Cr-C4	87.4 (2)
Cl-Cr-C4	86.3 (2)	C3-Cr-C5	176.8 (2)
Cl-Cr-C5	87.5 (2)	C4-Cr-C5	91.9 (2)
C2-Cr-C3	92.1 (2)	Cr-C1-N	177.4 (4)

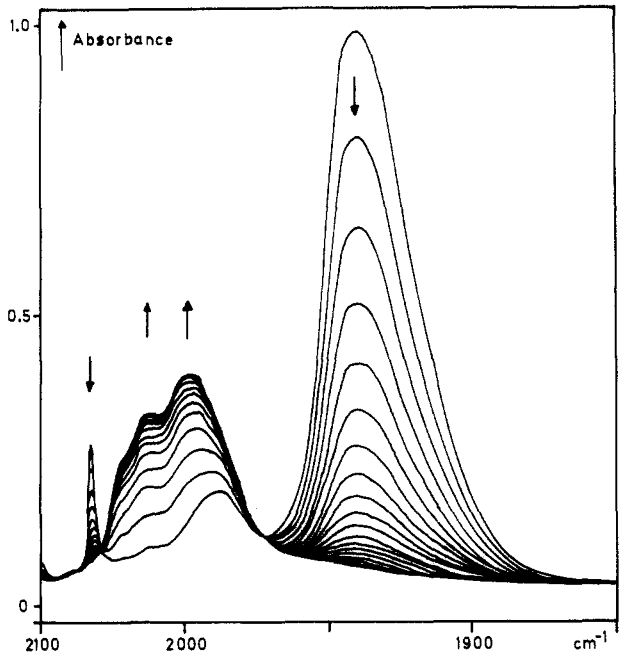

Figure 2. Change of the IR spectrum of **6c** in 1,1,2-trichloroethane in the range 2100–1850 cm^{-1} at 47.4 °C (Δt = 60 s).

C-NEt$_2$ (**9**), 1.720 (10) Å.[16] The Cr–C(carbyne)–N fragment is almost linear (177.4 (4)° and 180° in **8**, 178.7° in **9**). All CO ligands are bent away from the aminocarbyne group. However, the Cl–Cr–CO(cis) angles vary only slightly between 86.1 and 89.3 (2)°. The variation in the Cl–Cr–CO(cis) angles in *trans*-Br(CO)$_4$Cr$\equiv$CC$_6$H$_4$CF$_3$-*p*[17] which in solution shows only two ν(CO) absorptions, is larger: 82.3–91.2(8)°. Thus, no hints can be deduced from the solid-state structure of **7e** concerning an explanation of the unusual ν(CO) spectra of **7** in solution. The observation of four ν(CO) bands in solution for **7** is, however, in agreement with C_{2v} symmetry of the carbonyl–metal fragment; this can possibly be explained by restricted rotation about the Cr–C(carbyne) bond.

Table V. First-Order Rate Constants *k* for the Rearrangement Reaction of **6a–d** in 1,1,2-Trichloroethane and Nitromethane

	NR$_2$	solv[a]	10^3[6], M	temp,[b] °C	10^3*k*, s^{-1}
6a	NMe$_2$	T	10	49.0	0.354
				54.2	0.702
				58.2	1.21
				62.6	2.04
				64.0	2.35
				67.7	3.50
6a	NMe$_2$	N	10	40.6	0.520
				45.3	0.900
				51.5	2.05
				55.9	3.36
				63.3	7.50
6b	NC$_5$H$_{10}$	T	10	40.2	0.387
				46.6	0.915
				53.8	2.14
				60.5	4.38
				66.6	8.46
6b	NC$_5$H$_{10}$	N	10	33.2	1.22
				37.0	2.02
				41.5	3.55
				46.4	6.38
6c	NEt$_2$	T	10	31.5	0.593
				35.7	1.05
				37.7	1.33
			1	40.0	1.97
			2	40.0	1.97
			5	40.0	1.90
			10	40.0	1.92
			10	44.3	2.95
			5	47.4	4.54
			10	47.4	4.53
			1	48.4	4.83
			10	48.4	4.90
			10	55.5	11.0
6c	NEt$_2$	N	5	17.0	0.568
			5	25.3	1.80
			2.5	30.6	3.59
			5	30.6	3.75
			10	30.6	3.65
			25	30.6	3.50
			40	30.6	3.46
			5	35.7	6.80
			5	41.2	13.5
6d	NPh$_2$	T	1	8.5	0.312
				13.2	0.593
				18.5	1.09
				25.3	2.29
				29.0	3.58

[a] T = 1,1,2-trichloroethane; N = nitromethane. [b] ±0.1 °C.

Table VI. First-Order Rate Constants *k* for the Rearrangement Reaction of **6c** in Different Solvents at 39.9 °C ([**6c**]$_0$ = 0.010 M)

solvent	20[a]	10^3*k*, s^{-1}
octane	1.95	0.239
toluene	2.39	0.251
trichloroethylene	3.41	0.318
1,2-dibromoethane	4.81	0.471
n-butyl bromide	7.07	0.302
1,1,2-trichloroethane	7.52	1.92
1,1,2,2-tetrachloroethane	8.20	5.67
1,2-dichloroethane	10.65	1.47
nitromethane	37.5	11.5
hexamethylphosphoric triamide	43.3	0.275

[a] Dielectric constant at 20 °C.

Kinetic Investigations. The conversion of **6c** into **7c** is a clean reaction. The IR spectrum in the ν(CO) region (Figure 2) shows two isosbestic points (2059 and 1973 cm^{-1}). Whereas the carbyne complexes **7c** and **7e** are stable under the conditions employed, the complexes **7a,b** and **7d** slowly decompose during the course of the reaction by loss of a CO ligand. This dissociation is, however, significantly slower and does not influence the accuracy of the rate constants. The rates of the rearrangement reaction **10** were determined in different solvents by measuring the rate of disappearance of the carbene com-

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Table VII. Rate Constants k for the Rearrangement Reaction of **6c** without and in the Presence of Different Addends to the Solutions ($[\mathbf{6c}]_0$ = 5.0 mmol/L)

solvent	10^3k, s^{-1}
1,1,2-trichloroethane	4.54[a]
1,1,2-trichloroethane + 5.35 mmol/L $[NBu_4]Cl$	4.54[a]
1,1,2-trichloroethane + 10.7 mmol/L $[NBu_4]Cl$	4.59[a]
nitromethane	3.87[b]
nitromethane + 5.0 mmol/L azobis(isobutyronitrile)	3.75[b]
nitromethane + 5.0 mmol/L hydroquinone	3.90[b]
nitromethane + 50 mmol/L $[NBu_4]Cl$	3.93[b]
octane	0.239[c]
octane + 100 mmol/L PPh_3	0.237[c]

[a] At 47.3 °C. [b] At 31.2 °C. [c] At 39.9 °C, $[\mathbf{6c}]_0$ = 10 mmol/L.

Table VIII. Activation Parameter of the Rearrangement Reaction of **6a–d** in 1,1,2-Trichloroethane and Nitromethane and Rate Constants at 40 °C in 1,1,2-Trichloroethane

NR_2	10^3k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	(a) In 1,1,2-Trichloroethane		
NMe_2	0.109	26.2 ± 0.5	7.0 ± 1.5
NC_5H_{10}	0.394	23.9 ± 0.4	2.0 ± 1.2
NEt_2	1.80	23.7 ± 0.3	4.4 ± 1.1
NPh_2	11.3	19.3 ± 0.3	−6.1 ± 1.1
	(b) In Nitromethane		
NMe_2	0.478	24.2 ± 0.3	3.5 ± 0.9
NC_5H_{10}	2.93	23.7 ± 0.2	5.5 ± 0.8
NEt_2	11.6	23.1 ± 0.1	6.2 ± 0.2

plexes **6**. The plots of ln $(A - A_\infty)$ vs. t were linear for at least 3 half-lives. The results of the measurements, summarized in Tables V and VI, show that the rearrangement follows a first-order rate law: $-d[\mathbf{6}]/dt = k[\mathbf{6}]$.

The reaction rate of **6c** increases with increasing polarity of the solvent. However, the solvent influence is comparatively small and almost independent of the group NR_2. At 40 °C, the ratio of the rate constants in nitromethane (k^N) and 1,1,2-trichloroethane (k^T) is k^N:k^T = 4.39 (NMe_2), 7.44 (NC_5H_{10}), and 6.44 (NEt_2). The plots of ln (k/T) vs. $1/T$ give good straight lines (correlation coefficient −0.999). The values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the various systems calculated from the plots are summarized in Table VII. With all compounds, the activation entropy is small, slightly positive for the (dialkylamino)carbene complexes and slightly negative for **6d**. Not included in Table V are the rearrangement rates of the (diisopropylamino)carbene complex **6e**. Even at −60 °C **7e** is formed immediately upon addition of Cl^- to solutions of the precursor **4e**. Although **6e** could not be observed as an intermediate, **7e** must be formed via **6e**, since the first step in the alternative path (eq 11) is at least 1000 times slower than formation

$$\mathbf{4e} \xrightarrow[-CO]{} [(CO)_4Cr{\equiv}C\text{-}N\text{-}i\text{-}Pr_2]^+ \xrightarrow{+Cl^-} \mathbf{7e} \qquad (11)$$

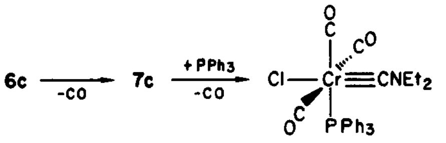
of **7e** from **4e** and Cl^-. At 20.8 °C in 1,1,2-trichloroethane, the half-life of the exchange of trans CO for PPh_3 in **4e** to give *trans*-$[(PPh_3)(CO)_4Cr{\equiv}CN\text{-}i\text{-}Pr_2]^+$ is 120 s. This reaction follows a dissociative path, Cr–CO bond rupture being rate determining. As a representative example, the rearrangement of **6c** was investigated in more detail (Table VI).

(a) The presence of free chloride ions in the solvent does not influence the reaction rate.

(b) The presence of free CO does not influence the rate either. There is no significant decrease in the reaction rate, at least not up to a CO pressure of 78 atm ($[\mathbf{6c}]_0$ = 5.0 mmol/L; [CO] ≈ 300 mmol/L; room temperature; 1,1,2-trichloroethane as solvent).

(c) Neither radical initiators [azobis(isobutyronitrile)] nor radical inhibitors (hydroquinone) influence the reaction rate.

(d) The addition of a 10 M excess of PPh_3 to the reaction solution does not influence the rate. However, instead of **7c**, *mer*-$Cl(PPh_3)(CO)_3Cr{\equiv}NEt_2$ (**10**)[18] is obtained exclusively. Since CO/PPh_3 exchange in **7c** is faster than the formation of **10** from **6c** by a factor of at least 100,[18] **10** must be produced via **7c**.



10

(12)

CO/^{13}CO Exchange with 4c. To clarify whether a cis or a trans CO group is eliminated from **6**, attempts were made to produce stereospecifically labeled **6c**. From kinetic experiments it follows that CO dissociation from **6c** is not faster than the rearrangement (eq 10). Therefore, we tried to produce labeled **4c** which can then be converted into **6c** via addition of Cl^- to the carbyne carbon atom of **4c**. Solutions of **4c-BF$_4$** in CH_2Cl_2 were stirred rapidly at 0 °C in a ^{13}CO atmosphere (90 atom % ^{13}CO). The rate of ^{13}CO incorporation into the trans position of **4c** was determined by IR analysis of aliquots taken from the reactor by measuring the intensity of the A_1 (trans) absorption of $[(^{12}CO)_5Cr{\equiv}CNEt_2]^+$ at 2136 cm^{-1}. At 0 °C, the rate constant is $(2.5 \pm 0.8) \times 10^{-4}\ s^{-1}$. To determine the rate of ^{13}CO incorporation into the cis position of **4c**, the aliquots taken from the reactor were added to solutions of Cl^- in CH_2Cl_2, thus converting **4c** into **6c**. After removal of the solvent, the IR spectrum of **6c** was recorded in methylcyclohexane. The $\nu(CO)$ spectrum was then analyzed with respect to the relative amounts of $(^{12}CO)_5Cr[C(Cl)NEt_2]$ and $(^{13}CO)_n(^{12}CO)_{5-n}Cr[C(Cl)NEt_2]$ using for the different species data which have been calculated from the absorption of $(^{12}CO)_5Cr[C(Cl)NEt_2]$ and secular equations given by Braterman.[19] From the decrease of the A_1(cis) absorption of $(^{12}CO)_5Cr[C(Cl)NEt_2]$ in the initial reaction period, the rate constant for ^{13}CO incorporation into the cis position of **4c** was calculated to be $(2.5 \pm 1.0) \times 10^{-4}\ s^{-1}$. In neither case was an induction period for the incorporation into the cis or the trans position observed. Both rate constants are of the same order of magnitude as the rate constant for the exchange of one CO ligand for PPh_3 in **4c-BF$_4$** to given *trans*-$[(PPh_3)(CO)_4Cr{\equiv}CNEt_2]^+$ which follows a dissociative path ($k = (3.2 \pm 0.3) \times 10^{-4}\ s^{-1}$, 0 °C, CH_2Cl_2 as the solvent).

The principle of microscopic reversibility requires that the stereochemistry of the substitution product mirrors the site of initial Cr–CO bond breaking. Therefore, the results mean that either the coordination octahedron in **4c** is fluxional or that the rate constant k for Cr–CO(trans) dissociation in **4c** is only approximately 4 times that of Cr–CO(cis) dissociation. Considering the significant difference in the Cr–CO(cis) and the Cr–CO(trans) distance observed in the solid-state structure of **4c-BF$_4$**,[12] the latter

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Table IX. Comparison of the Activation Enthalpy for the Rearrangement Reaction and the Bond Energy of Ph-X Compounds

X	$\Delta H^{\ddagger}$, kcal/mol	ref	D(Ph-X), kcal/mol	ref
Cl	23.7 ± 0.3	*a*	94	20
SePh	24.4 ± 0.1	5d	70.2 ± 3.0	21
$SiPh_3$	*b*	5e	84.5 ± 2.4	22
$SnPh_3$	24.4 ± 0.2	5c	61.3 ± 1.4	22
$PbPh_3$	24.6 ± 0.2	5e	48.9 ± 3.6	22

[a] This work. [b] No rearrangement observed.

interpretation seems unlikely. At any case, stereospecifically labeled **6c** cannot be produced by this route.

Discussion and Conclusions

The rearrangement of all aminochlorocarbene complexes **6** follows first-order kinetics. The reaction rate is influenced neither by the presence of free CO nor by the addition of Cl^- or triphenylphosphine to the solution. Similar results also were obtained with other aminocarbene complexes, $(CO)_5Cr[C(X)NEt_2]$ (**1**) (X = SeR, TePh, $SnPh_3$, $PbPh_3$).[5] Although the reaction rate of **6** increases with increasing polarity of the solvent, the solvent effect is only small. If an aryl group is bonded to the migrating atom, the solvent effect is almost negligible: k(in nitromethane):k(in 1,1,2-trichloroethane) = 6.4 (X = Cl), 1.5 (SePh), 1.5 (TePh), 1.3 ($PbPh_3$), 1.2 ($SnPb_3$).

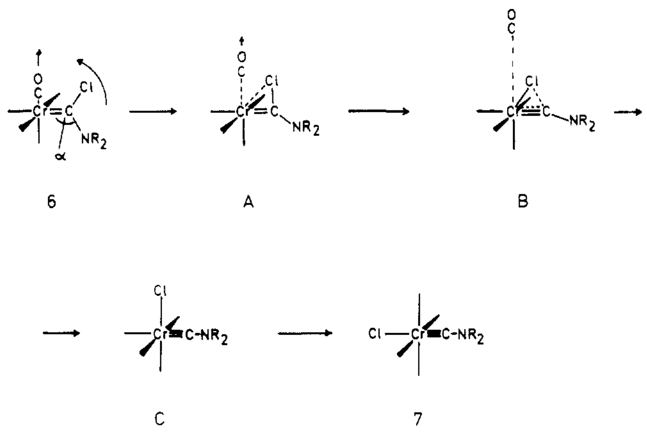
The addition of a radical inhibitor or a radical initiator does not influence the reaction rate either. Furthermore, in a series of complexes **1** no linear correlation between the activation enthalpy and the bond energy for the different carbon–X bonds is observed (Table IX). Thus a mechanism which involves a rate-determining homolytic C(carbene)–X bond rupture can be excluded. Mechanisms with rate-limiting (reversible) C(carbene)–Cl and Cr–CO dissociation also are not in agreement with the kinetic results since neither Cl^- nor CO in the solution alter the reaction rate. In the rearrangement of the complexes **1** there also was no indication of a stepwise mechanism. All observations are in agreement with a concerted Cr–CO dissociation and C/Cr migration of X.

The activation entropy is slightly positive for **6a–c** and slightly negative for **6d**. However, all $\Delta S^{\ddagger}$ values are small as expected for an intramolecular process. The reaction rate for **1** is almost independent of the type of migrating group, but a striking acceleration of the rate in the series **6a–d** was observed.

The diphenylamino-substituted compound **6d** already reacts 103 times faster than the dimethylamino complex **6a**. Taking into account that the half-life of the diisopropylamine compound **6e** at −60 °C is less than 2 s, the rate constant at 40 °C can be estimated to be at least 10^3 s^{-1}, i.e., **6e** rearranges at least 10^7 times faster than **6a**. This clearly demonstrates that the reaction rate is dominated by the bulk of the NR_2 substituent. In contrast, if the rearrangement is mainly determined by the electronic properties of the amino substituent, **6d** would have been expected to react slower than **6a**.

Since stereospecifically labeled **6c** could not be synthesized, the question whether a cis or a trans CO group is eliminated from the complex cannot be answered with certainty. However, the X-ray diffraction study of **6c**[8d] shows the Cr–CO(trans) distance to be shorter than the Cr–CO(cis) distances. This indicates that the cis CO ligands in **6c** are more weakly bonded than the trans CO group. The photolytic substitution of a CO ligand for PPh_3 in pentacarbonyl carbene complexes at temperatures below −10 °C results in the exclusive formation of cis tetracarbonyl carbene triphenylphosphine complexes[23] which subsequently isomerize above 30 °C to afford a mixture of the cis and trans isomers.[24,25] Selective thermally induced exchange of ^{13}CO into the cis position was observed for $(CO)_5M[C(Ph)OMe]$ complexes (M = Cr, Mo, W).[26] Generally, in $(CO)_5ML$ complexes (L being a donor ligand) the trans CO ligand is more strongly bonded to the metal than the cis CO groups. If L is a π-donor ligand or carries at least a substituent which is capable to π donate electron density into an empty metal d orbital of $(CO)_4ML$ created by dissociation of a cis CO ligand, a M–CO(cis) bond rupture is further facilitated ("cis labilization").[27] Therefore, with **6** the elimination of a cis CO group also can be assumed. The removal of a cis CO ligand from the complex produces an acceptor orbital on the metal directed somewhat away from the plane of the cis CO ligands toward the carbene ligand.[28] Interaction with lone-pair electrons of Cl draws Cl closer to the metal and increases the angle α (Scheme I). The interaction is further facilitated by bulky amino substituents at the carbene carbon which, because of steric crowding around the carbene carbon, increase the angle α, thus moving the migrating group closer to the plane of the cis carbonyl ligands. This is clearly reflected in the stepwise decrease of the reaction enthalpy with increasing steric requirements of the amino substituent in the series NR_2 = NMe_2 > NC_5H_{10} ≈ NEt_2 > NPh_2.

Scheme I



CO dissociation and Cl migration are concerted processes. Final C(carbene)–Cl bond rupture gives a cis aminocarbyne tetracarbonyl (X) complex which then rapidly isomerizes either by a Bailar[29] or a Ray–Dutt type mechanism[30] to form the trans isomer. Such isomerizations of octahedral complexes by an intramolecular, non-bond-breaking mechanism are well documented.[25,31]

Whereas the reaction rate drastically increases with increasing bulk of the NR_2 group (**6a–e**), the ν(CO) absorptions of **6a–d** are almost unaffected by the NR_2 substituent. This indicates that the NR_2 effect is mainly due to

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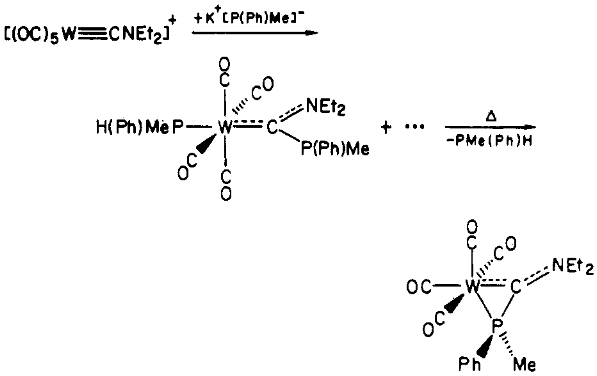
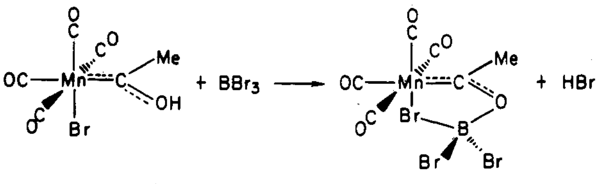
[31] See, e.g.: (a) Dombek, B. D.; Angelici, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4110. (b) Darensbourg, D. J. *Inorg. Chem.* **1979**, *18*, 14. (c) Darensbourg, D. J. *J. Organomet. Chem.* **1981**, *209*, C37.

a lowering of the energy of the transition state for rearrangement.

If complexes 1 (X = $SnPh_3$, $PbPh_3$) are employed, no lone-pair electrons at the migrating group X are available for interaction with the acceptor orbital at the metal. With these compounds the C(carbene)–X bonding electrons interact with the acceptor orbital. For several complexes 1 no rearrangement has been observed despite a significantly enlarged Cr–C(carbene)–N angle. Obviously, besides the bulk of the NR_2 group other factors also decisively influence the rearrangement rate. Other important factors seem to be the availability of energetically suitable lone-pair electrons or C(carbene)–X bonding electrons for the interaction with Cr–CO and Cr acceptor orbitals and the difference in stability of the Cr–X and the C(carbene)–X bond. The importance of the latter factor is confirmed by the isolation of a complex related to B in Scheme I although prepared by a slightly different route. The reaction of the tungsten analogue of **4c** with K[P(Me)Ph] in tetrahydrofuran at –60 °C yields among other products a trans carbene tetracarbonyl phosphine complex which upon thermolysis eliminates the trans phosphine ligand to give a metallacyclic carbene complex (eq 13)[32] which contains a tungsten–C(carbene)–P ring.[33] The carbene/carbyne complex rearrangement can be regarded as a possible step of the mechanism for the general synthesis of carbyne complexes by reaction of alkoxy-, (alkylthio)-, or aminocarbene complexes with halides of group 13 elements, AX_3 (eq 2). The first step in the reaction sequence of the latter reaction involves an electrophilic attack of the Lewis acid at the heteroatom bonded to the carbene carbon. A metallacyclic carbene complex closely related to such an adduct could be isolated from the reaction of *cis*-$Br(CO)_4Mn[C(Me)OH]$ with BBr_3 (eq 14).[3a]



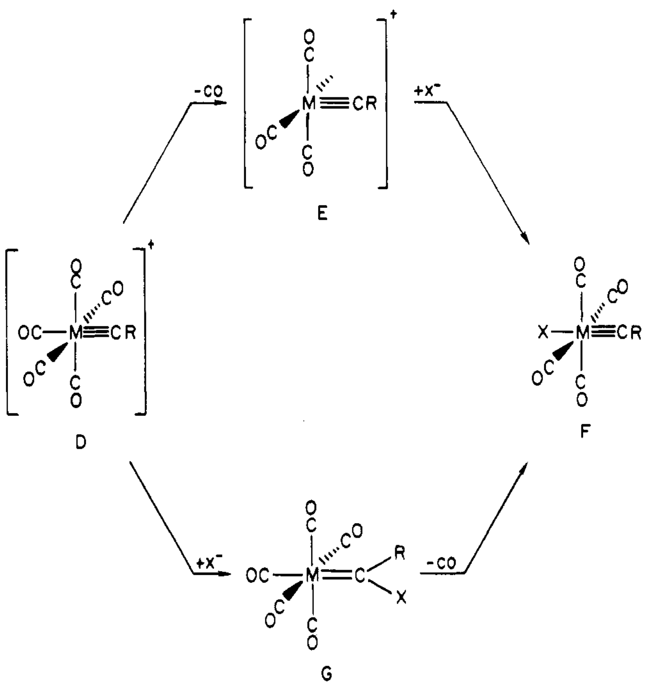
(13)



(14)

In general, however, the carbene–oxygen bond in these adducts is strongly labilized and a heteropolar dissociation of this bond can be expected to occur in a fast subsequent step. The resulting carbyne complexes can be isolated if the carbyne carbon carries a strong π-donor group such as NR_2 or if the trans position is blocked by strong donor ligands (see eq 1). For instance, *cis*-$(PPh_3)(CO)_4Cr[C(Me)OMe]$ reacts with BBr_3 to give *mer*-$Br(PPh_3)(CO)_3Cr\equiv CMe$ (Br trans to the carbyne ligand).[34] The trans complex *trans*-$(PPh_3)(CO)_4Cr[C(Me)OMe]$, on the other hand, gives isolable *trans*-$[(PPh_3)(CO)_4Cr\equiv CMe]^+$ on reaction with BBr_3.[35]

Scheme II



For the next steps in the formation of neutral carbyne complexes, two different reaction sequences are conceivable, one almost as likely as the other (Scheme II). In the first sequence, first a CO ligand is eliminated from the cation and the resulting pentacoordinated intermediate rapidly adds X^- to give the neutral complex F (D–E–F). In an alternative sequence, X^- is first added to the electrophilic carbyne carbon yielding a new halocarbene complex (G). Subsequent CO elimination, migration of X from the carbene carbon to the metal and isomerization finally also give F. When cationic aminocarbyne complexes of chromium (**6**) are employed, the first step in the associative path (D → G) is fast, faster than CO elimination from the cation (D → E; at least if $[4] \approx [X^-] > 10^{-5}$ mol/L). The reverse is true for the analogous tungsten complexes. When anionic nucleophiles X^- are added to solutions of $[(CO)_5W\equiv CNEt_2]^+$, instead of addition of the nucleophile to the carbyne carbon, exchange of one CO ligand for the nucleophile is generally observed, giving immediately neutral carbyne complexes F. Only in the cases of X = $AsPh_2$ and $SeC_6H_4CF_3$-*p* were the corresponding pentacarbonyl (diethylamino)(X)carbene complexes isolated.[6,7] In the reaction of $[(CO)_5W\equiv CNEt_2]^+$ with $[SeC_6H_4CF_3]^-$ in tetrahydrofuran at –30 °C, both the neutral carbyne complex *trans*-$(CF_3C_6H_4Se)(CO)_4W\equiv CNEt_2$ (**11**) and the neutral carbene complex $(CO)_5W[C(SeC_6H_4CF_3)NEt_2]$ are formed simultaneously, the carbyne complex constituting the main product. Since the carbene complex does not rearrange to form the corresponding carbyne complex even at +65 °C, **11** cannot be formed via the sequence D–G–F but must be formed via the dissociative path D–E–F of Scheme II. The same conclusion very likely also applies to the reaction of $[(CO)_5W\equiv CNEt_2]^+$ with other nucleophiles and is in line with the observation that cationic aminocarbyne complexes of tungsten are thermally more

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labile than their chromium analogues. In turn, the carbyne carbon in the tungsten complexes is less electrophilic than that in the chromium complexes.

The second step in the associative path (G → F) of Scheme II is slow for chromium complexes and even slower for the tungsten compounds. The rate of this step is increased by increasing the bulk of the NR_2 substituent. Replacement of the π-donor substituent NR_2 by a poorer donor group (D in Scheme II, R = alkyl or aryl) should simultaneously accelerate the first step in both the associative and the dissociative paths and, in the case of small substituents (R = Me, Et, Ph in G, Scheme II), should decrease the rate of the rearrangement step (G → F). Thus, if the associative path D–G–F is the preferred reaction sequence, we would expect that in the reaction of aryl- and alkylalkoxycarbene complexes with halides of group 13 elements (see eq 2) aryl- and alkylhalocarbene complexes, respectively, are isolatable or at least observable intermediates. However, so far such halocarbene complexes could not be detected in the reaction of eq 2 (R = aryl, alkyl). The results obtained by studying the rearrangement of aminocarbene complexes leads to the conclusion that carbyne complexes generally are formed via the dissociative sequence D–E–F. Only for a limited number of special carbene complexes with strong π-donor substituents (R = NR_2) the formation of the neutral carbyne complexes follows the associative path D–G–F.

Experimental Section

General Remarks. All manipulations were carried out under a purified nitrogen atmosphere using conventional Schlenk techniques. The silica gel used for chromatography (No. 60, 0.062–0.2 mm, Merck) was N_2 saturated. The yields refer to analytically pure compounds and are not optimized.

Pentane, hexane, octane and toluene were distilled under N_2 from sodium benzophenone ketyl. 1,2-Dichloroethane, 1,2-dibromoethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, trichloroethylene, *n*-butyl bromide, nitromethane, and hexamethylphosphoric triamide were dried by passing them through a column filled with molecular sieves 4A. Dichloromethane was distilled under nitrogen twice from P_4O_{10} and then once from sodium–lead alloy. Tetrahydrofuran was distilled from Na–K alloy. All solvents were stored under nitrogen over 4A molecular sieves.

$(CO)_5Cr[C(OEt)NEt_2]$ (**3c**),[10] $(CO)_5Cr[C(NPh_2)N{=}C(OMe)Ph]$ (**5d**),[1] $(CO)_5Cr[C(N\text{-}i\text{-}Pr_2)N{=}C(OMe)Ph]$ (**5e**),[1] $[(CO)_5Cr{\equiv}CNPh_2]SbCl_6$ (**4d-SbCl$_6$**),[11] $[(CO)_5Cr{\equiv}CN\text{-}i\text{-}Pr_2]SbCl_6$ (**4e-SbCl$_6$**),[11] $[(CO)_5Cr{\equiv}CN\text{-}i\text{-}Pr_2]BCl_4$ (**4e-BCl$_4$**),[11] $[(Ph_3P)_2N]Cl$,[36] $LiNMe_2$,[37] $LiNC_5H_{10}$,[38] and $[Et_3O]BF_4$[39] were prepared by literature methods. ^{13}CO (90 atom % ^{13}C) was a product of Merck, Sharp and Dohme. All other chemicals were commercial products of the highest quality available and were used without further purification.

Spectroscopic Methods. IR spectra were recorded on a Perkin-Elmer spectrometer 580. ^1H NMR spectra were recorded on a JEOL PMX-60; chemical shifts are reported in acetone-d_6 and dichloromethane solutions, if not otherwise specified, relative to CD_2HCOCD_3 (2.1 ppm) and $CDHCl_2$ (5.4 ppm), respectively. ^{13}C NMR spectra were recorded in acetone-d_6 and dichloromethane solutions on a JEOL FX 60; chemical shifts are reported relative to CD_3COCD_3 (206.5 ppm) and CD_2Cl_2 (54.2 ppm), respectively. UV–vis spectra were recorded on a Cary 17D spectrometer; mass spectra were recorded on a Varian MAT 311A instrument.

Preparation of $(CO)_5Cr[C(OEt)NMe_2]$ (3a). This complex was prepared by a modification of the method described by Fischer et al.[9] Instead of $[Et_3O]BF_4$, $EtOSO_2F$ was used in the alkylation of $(CO)_5Cr[C(OLi)NMe_2]\cdot 2Et_2O$: yield 17%; IR (1,1,2-trichloroethane) 2063 (m), 1986 (w), 1939 (vs), 1915 (w, sh); ^1H NMR (acetone-d_6) δ 4.3 (q, OCH_2), 2.9 (s, NCH_3, *Z*), 2.2 (s, NCH_3, *E*), 0.9 (t, CH_3); ^{13}C NMR (acetone-d_6) δ 239.94 ($C_{carbene}$), 222.36 (CO_{trans}), 217.34 (CO_{cis}), 71.00 (OCH_2), 45.15 (NCH_3, E), 38.74 (NCH_3, Z), 15.65 (CH_3).

Preparation of $(CO)_5Cr[C(OEt)NC_5H_{10}]$ (3b). This complex was prepared according to the method described by Fischer et al. for the synthesis of **3a**:[9] yellow-green crystals; yield 2%; mp 82 °C dec; IR (hexane) ν(CO) 2058 (m), 1926 (vs); ^1H NMR (acetone-d_6) δ 4.7 (q), 4.0 (m), 3.5 (m), 1.7 (m), 1.4 (t); MS, *m/e* 333 (M^+) and peaks for $[M - n(CO)]^+$, *n* = 1–5. Anal. Calcd for $C_{13}H_{15}CrNO_6$ (333.28): C, 46.85; H, 4.54; Cr, 15.60; N, 4.20; O, 28.80. Found: C, 46.97; H, 4.61; Cr, 15.75; N, 4.04; O, 28.50.

Preparation of $[(CO)_5Cr{\equiv}CNMe_2]BCl_4$ (4a-BCl$_4$). At −100 °C, to a solution of 1.47 g (5 mmol) of **3a** in 50 mL of CH_2Cl_2 was added BCl_3 until the color of the solution turned from yellow to orange. The solvent was removed in vacuo at −40 °C, and the residue was washed several times with Et_2O at −78 °C. The product was recrystallized several times from CH_2Cl_2/Et_2O: Orange-red crystals: yield 1.6 g (80%). Anal. Calcd for $C_8H_8BCl_4CrNO_5$ (400.76): C, 23.98; H, 1.51; N, 3.50. Found: C, 24.05; H, 1.81; N, 3.38.

Preparation of $[(CO)_5Cr{\equiv}CNMe_2]BF_4$ (4a-BF$_4$). To a solution of 300 mg (1 mmol) of **3a** in 10 mL of CH_2Cl_2 was added BF_3 at −100 °C. After removal of the solvent in vacuo at −30 °C, the residue was washed with Et_2O. The product was dissolved in THF and chromatographed at −40 °C on silica gel. Byproducts were removed by employing first CH_2Cl_2 and then Et_2O. **4a-BF$_4$** was finally eluted with MeOH. Removal of the solvent and recrystallization from THF/Et_2O gave **4a-BF$_4$** in the form of an orange powder: yield 190 mg (54%).

Preparation of $[(CO)_5Cr{\equiv}CNC_5H_{10}]BCl_4$ (4b-BCl$_4$). This complex was prepared by the same method as **4a-BCl$_4$**, starting with 330 mg (1 mmol) of **3b** and BCl_3: yield 277 mg (63%). Anal. Calcd for $C_{11}H_{10}BCl_4CrNO_5$ (440.82): C, 29.97; H, 2.29. Found: C, 28.88; H, 2.31.

Preparation of $[(CO)_5Cr{\equiv}CNC_5H_{10}]BF_4$ (4b-BF$_4$). This complex was prepared analogous to the method of **4a-BF$_4$**: yield 43%. Identification was by IR and ^1H NMR spectra and by addition of Cl^- to give **6b**.

Preparation of $[(CO)_5Cr{\equiv}CNEt_2]BCl_4$ (4c-BCl$_4$). The complex was prepared by the same route as **4a-BCl$_4$**: red powder; yield 52%. Anal. Calcd for $C_{11}H_{10}BCl_4CrNO_5$ (428.81): C, 28.01; H, 2.35; B, 2.52; Cr, 12.13; N, 3.27. Found: C, 28.00; H, 2.36; B, 2.70; Cr, 12.41; N, 3.19.

Preparation of $(CO)_5Cr[C(Cl)NMe_2]$ (6a). A 800-mg (2-mmol) sample of **4a-BCl$_4$** were dissolved in 20 mL of THF/CH_2Cl_2 (3:1) at −40 °C. This solution then was slowly warmed to +5 °C. The color of the solution changed from red to yellow. After removal of the solvent in vacuo, the residue was washed several times with pentane of −40 °C. Further purification was effected by column chromatography (silica gel, −30 °C). First orange **7a** was eluted with CH_2Cl_2/THF (1:1), and then **6a** was eluted by employing Et_2O as eluant. Recrystallization from Et_2O/pentane (1:1) yielded **6a** as slightly yellow crystals: mp 63 °C dec; yield 400 mg (70%); ^{13}C NMR (acetone-d_6) δ 246.78 ($C_{carbene}$), 223.39 (CO_{trans}), 217.22 (CO_{cis}), 51.38 (NCH_3, *E*), 47.15 (NCH_3, *Z*). Anal. Calcd for $C_8H_6ClCrNO_5$ (283.60): C, 33.88; H, 2.13; Cl, 12.50; Cr, 18.34; N, 4.94; O, 28.21. Found: C, 33.67; H, 2.20; Cl, 12.40; Cr, 17.99; N, 4.65; O., 28.60.

Preparation of $(CO)_5Cr[C(Cl)NC_5H_{10}]$ (6b). This complex was prepared by the same method as **6a**: yellow crystals; mp 62 °C dec; MS, *m/e* 323 (M^+) and peaks for $[M - n(CO)]^+$, *n* = 1–5, as well as 288 $[M - Cl]^+$ and $[M - Cl - n(CO)]^+$, *n* = 1–5. yield 77%. Anal. Calcd for $C_{11}H_{10}ClCrNO_5$ (323.66): C, 40.82; H, 3.11; Cl, 10.95; Cr, 16.07; N, 4.33; O, 24.72. Found: C, 40.95; H, 3.16; Cl, 10.60; Cr, 15.72; N, 4.12; O, 24.80.

Preparation of $(CO)_5Cr[C(Cl)NPh_2]$ (6d). At −60 °C, a solution of 2.30 g (3.25 mmol) of $[(CO)_5Cr{\equiv}CNPh_2]SbCl_6$ and 1.86 g (3.25 mmol) of $[(Ph_3P)_2N]Cl$ was stirred for 1 h. The solvent was removed in vacuo at −60 °C. The residue was washed twice at −60 °C with 100 mL of Et_2O. The resulting yellow solution was filtered. After removal of the solvent in vacuo and recrystallization from pentane/Et_2O (1:1), **6d** was obtained as lemon-

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yellow needles: yield 840 mg (63%). Anal. Calcd for $C_{18}H_{10}ClCrNO_5$ (407.73): C, 53.02; H, 2.47; Cl, 8.70; Cr, 12.75; N, 3.44; O, 19.62. Found: C, 52.91; H, 2.51; Cl, 8.75; Cr, 12.56; N, 3.39; O, 19.54.

Preparation of $(CO)_5Cr[C(Cl)NEt_2]$ (6c). Preparation was analogous to that of **6d**. Identification was by comparison with published spectroscopic data of **6c**:[40] yield 65%.

Preparation of *trans*-$Cl(CO)_4Cr{\equiv}CNPh_2$ (7d). A solution of 800 mg (1.96 mmol) of **6d** in 50 mL of CH_2Cl_2 was stirred for ca. 1 h at 0 °C. The solution then was column chromatographed (silica gel, −30 °C). With pentane/Et_2O (1:1) **7d** was eluted, whereas unreacted **6d** stayed on top of the column. After removal of the solvent in vacuo at −40 °C, the residue was recrystallized from pentane/Et_2O (1:1): light yellow crystals; yield ca. 200 mg (14%) of **7d** which is, however, still contaminated with some $Cr(CO)_6$; identification by IR and ^1H NMR spectra.

Preparation of *trans*-$Cl(CO)_4Cr{\equiv}CN$-*i*-Pr_2 (7e). To a solution of 1.95 g (3.06 mmol) of $[(CO)_5Cr{\equiv}CN\text{-}i\text{-}Pr_2]SbCl_6$ in 30 ml of CH_2Cl_2 at −60 °C was added 1.79 g (3.06 mmol) of $[(PPh_3)_2N]Cl$. An immediate gas evolution was observed. After 2 h, the volume of the solution was reduced in vacuo at −25 °C to ca. 10 mL, and then the residue was purified by column chromatography (silica gel, −25 °C, pentane). With Et_2O a light red **7e** was eluted. The solvent was removed in vacuo at −40 °C and the residue recrystallized from Et_2O: red crystals; mp 57 °C dec; yield 610 mg (64%). Anal. Calcd for $C_{11}H_{14}ClCrNO_4$ (311.69): C, 42.39; H, 4.53; Cl, 11.37; Cr, 16.68; N, 4.49; O, 20.53. Found: C, 42.37; H, 4.58; Cl, 11.59; Cr, 16.53; N, 4.37; O, 20.45.

Kinetic Measurements. The rearrangement reaction was followed by IR spectroscopy (**6a–c**) or by UV–vis spectroscopy (**6d**). Samples of **6** were dissolved in the calculated amount of the thermostated solvent or in solutions of $[NBu_4]Cl$ in 1,1,2-trichloroethane, azobis(isobutyronitrile), hydroquinone, or $[NBu_4]Cl$ in nitromethane, or PPh_3 in octane, respectively. Solutions of **6a–c** then were rapidly transferred into the thermostated IR cuvette (RIIC FH 01, 0.1–1.0-mm path length depending on the concentration of the solution); solutions of **6d** were transferred into a 10-mm quartz cuvette. The disappearance of the $\nu(CO)$ absorption band at 1939 cm^{-1} (**6a–c**) or of the UV absorption band at 390 nm (**6d**) was then monitored continuously for 8–10 half-lives. The data were collected with a desk-top computer (HP 9825S) connected with the spectrometer via a system voltmeter (HP 3437A). The time was taken from a real-time clock (HP 98035A). The temperature was measured during (**6a–c**) or after (**6d**) the kinetic runs with thermistors which have been calibrated before (accuracy ±0.1 °C). Plots of $\ln (A - A_\infty)$ vs. time were linear for more than 3 half-lives, and k was determined from the slope of these lines by the least-squares method using the data of the first 3 half-lives. The correlation coefficient of the least-squares lines was at least 0.9993. The rate constants for different kinetic runs under identical conditions were reproducible to at least 5%. The rate constants given in Tables V and VI are means of at least two runs under the same conditions.

Rearrangement under CO Pressure. A 4 mL sample of a solution containing 0.005 mol/L **6c** in 1,1,2-trichloroethane were divided into two aliquots. One aliquot was kept in the dark in a Schlenk tube under 1 atm of CO. The second aliquot was placed into an autoclave, and a CO pressure of 78 atm was applied. After 160 min (ca. 2 half-lives) at ambient temperature, the CO pressure was removed. Both aliquots then were simultaneously cooled to −78 °C, and the $\nu(CO)$ spectra were taken. The **6c**/**7c** ratio was finally determined from the $\nu(CO)$ absorptions of **6c** and **7c**.

^{13}CO Exchange Experiments. The exchange experiments were carried out in a 30-mL round-bottomed flask fitted with a stopcock and capped with a rubber septum. The flask was evacuated and then charged with 760 mm of CO (90 atom % ^{13}CO). The pressure was kept constant during the experiments. By syringe 4 mL of a 0.015 M solution of **4c-BF_4** in dichloromethane was injected through the rubber septum. Efficient gas–liquid equilibration was achieved by stirring the solution rapidly with a magnetic stirring bar. Vigorous splashing and swirling of the solution resulted. The temperature of the solution was kept at 0 °C with a water–ice bath. Portions (0.25 mL) of the reaction solution were taken by syringe. In one series of experiments (a) these samples were immediately transferred to a cooled IR cuvette and the IR spectrum in the range 2150–2000 cm^{-1} was measured. In another series of experiments (b) the samples were added to a solution of $[NBu_4]Cl$ in dichloromethane, thus converting the cation **4c** into **6c**. The solvent was removed in vacuo. The residue was extracted with 0.5 mL of methylcyclohexane, and the IR spectrum of the solution was recorded in the range 2150–1850 cm^{-1}. From the decrease of the A_1 (trans) absorption of **4c** at 2136 cm^{-1} (series a) the rate for the exchange of the trans CO group was calculated. From the decrease of the A_1 (cis) absorption of **6c** at 2063 cm^{-1} (series b) the rate constant of cis $CO/^{13}CO$ exchange was calculated.

X-ray Crystallography of 7e. $C_{11}H_{14}ClCrNO_4$ (mol wt 311.69): monoclinic, $P2_1/c$, a = 6.555 (2) Å, b = 13.171 (4) Å, c = 17.522 (5) Å, β = 103.07 (2)°, V = 1474 Å^3, Z = 4, ρ(calcd) = 1.41 g cm^{-3}. Crystals suitable for X-ray measurements were obtained by slow diffusion of pentane into a dichloromethane solution of **7e** at −30 °C. The measurements were made at −40 °C with a crystal of appropriate dimensions, 0.3 × 0.3 × 0.2 mm, mounted in a glass capillary on a Syntex $P2_1$ diffractometer using graphite-monochromated Mo $K\bar{\alpha}$ radiation (λ = 0.71069 Å). Intensity data ($1° \leq \theta \leq 24°$) were collected by the ω scan technique ($\Delta\omega$ = 1.1°; scan rate 1.1–29.3°/min). Lorentz–polarization effects but no absorption effects were corrected (μ = 9.9 cm^{-1}).

After equivalent reflections were averaged, a total of 2264 independent reflections was obtained of which the 1777 reflections with $I(hkl) > 1.96\sigma(I(hkl))$ were used in the subsequent calculations. The structure was solved by Patterson methods and completed by Fourier syntheses. Full-matrix least-squares refinement (non H atoms anisotropically, H atoms constant at idealized calculated positions, 163 refined parameters, 1771 F_0) converged at R = 0.053, R_w = 0.048, and $w = 1/\sigma^2 (F_0)$. The refinement was severely hampered by disorder of both isopropyl groups resulting in abnormally large thermal parameters of some carbon atoms and distorted geometries. Although difference maps revealed several positions for most of the isopropyl carbon atoms, all attempts to refine alternative structural models failed. All calculations were done on a Nova 1200 computer using the Syntex XTL program package.

Acknowledgment. The support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Prof. Dr. E. O. Fischer for his support, J. Riede for the X-ray measurements, Dr. G. Müller for valuable discussions concerning the X-ray analysis, and U. Graf and M. Barth for the elemental analyses.

Supplementary Material Available: Tables listing bond lengths and bond angles, anisotropic temperature parameters, atomic coordinates, and structure factors (14 pages). Ordering information is given on any current masthead page.

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