Available online at www.sciencedirect.com
SCIENCE DIRECT®
Coordination Chemistry Reviews 248 (2004) 1659–1677
COORDINATION CHEMISTRY REVIEWS
www.elsevier.com/locate/ccr

Review

π-Donor-substituted metallacumulenes of chromium and tungsten

Helmut Fischer*, Normen Szesni

Fachbereich Chemie, Universität Konstanz, Fach M727, D-78457 Konstanz, Germany

Received 2 February 2004
Available online 24 June 2004

Contents

Abstract

The review describes the synthesis of π-donor-substituted carbonyl metallacumulenes $[(CO)_5M{=}(C{=}C{=})_xC(R^1)R^2]$ ($x = 1$: allenylidene complexes; $x = 2$: pentatetraenylidene complexes) of chromium and tungsten. The π-donating properties of the substituents at one end of the carbon chain have been varied through employing different combinations of R^1 (Ph, OR, NR_2) and R^2 (Ph, OR, NR_2). The back-bonding properties of the metal-ligand fragment at the other end of the chain have been changed by displacing carbonyl ligands by P-, As-, or Sb-donor ligands. The influence of varying these two parameters on the spectroscopic properties, the bonding within the metallacumulene chain, and the reactivity is evaluated. The reactivity of these metallacumulenes and the selectivity of reactions with various P-, N- and C-nucleophiles as well as the selectivity in reactions with ynamines are described. Examples for applying some of these reactions to the synthesis of heterocyclic ligands are given.

Keywords: Allenylidene complexes; Metallacumulenes; Pentatetraenylidene complexes; Substitution reactions; Insertion reactions

1. Introduction

The first planned synthesis of transition metal complexes containing a $M{=}C(sp^2)$ double bond was reported by Fischer and Maasböl in 1964 [1]. Since then, tremendous progress has been made in the chemistry of this class of organometallic compounds (carbene complexes, alkylidene complexes). Low-valent heteroatom-stabilized complexes, especially of the chromium triad such as e.g. $[(CO)_5M{=}C(XR)R']$ (Fischer-type carbene complexes), and low-valent Casey-type complexes ($[(CO)_5M{=}C(aryl)R]$, R = aryl, H, M = W, Cr [2]) as well as cationic iron carbene complexes, $[Cp(CO)(L)Fe{=}C(R^1)R^2]^+$ [3], have found wide-spread applications as stoichiometric reagents in organic chemistry for the synthesis of carbo- and heterocycles and other compounds [4]. High-valent molybdenum and tungsten alkylidene complexes (Schrock-type alkylidene complexes) [5], some titanium complexes [6], and $[Cl_2\{P(C_6H_{11})_3\}(L)Ru{=}C(R)H]$ (L $= P(C_6H_{11})_3$, N-heterocyclic carbenes: Grubbs catalysts) [7], in turn, have found wide-spread applications as catalysts in olefin metathesis [8] and other catalytic transformations [9].

---

* Corresponding author. Tel.: +49 7531 882783; fax: +49 7531 883136.
E-mail address: helmut.fischer@uni-konstanz.de (H. Fischer).

doi:10.1016/j.ccr.2004.05.006

Many different procedures for the synthesis of carbene complexes have been developed over the last three decades. Consequently, a large number of substitution patterns are now readily available. The influence of these substitution patterns on the reactivity and on the physico-chemical properties of these compounds has been studied in considerable detail.

Metallacumulenes may be regarded as unsaturated carbene complexes, e.g. allenylidene complexes being derived from carbene complexes by insertion of a C_2 unit into the metal–carbon double bond. The synthesis of the first allenylidene complexes was reported simultaneously and independently in 1976 by Fischer et al. [10] [$(CO)_5M{=}C{=}C{=}C(NMe_2)Ph$, M = Cr, W] and Berke [11] [$(Cp(CO)_2Mn{=}C{=}C{=}C(CMe_3)_2$]. In the last two decades a considerable number of allenylidene complexes of various transition metals have been synthesized and the reactivity as well as the spectroscopic and structural properties of these compounds have been investigated thoroughly [12].

Although two of the very first allenylidene complexes to be synthesized were aminoallenylidene complexes, the vast majority of allenylidene complexes studied until now are non-donor-substituted compounds carrying alkyl or aryl groups at the terminal carbon atom. Complexes of this type are readily accessible. They are usually prepared either (a) by reaction of suitable metal complexes with propargyl alcohol derivatives using a route introduced in 1982 by Selegue [13] or (b) by reaction of metal carbonyls with dilithio derivatives of substituted 2-propyn-1-ols followed by treatment with phosgene [14] or a base [15].

In contrast to heteroatom-substituted carbene complexes, the chemistry of π-donor-substituted allenylidene complexes is much less well developed, although these complexes are directly related to the classical Fischer-type d^6-metal carbene complexes.

In this account, we will concentrate on the synthesis, the spectroscopic and structural properties and the reactivity of π-donor-substituted allenylidene carbonyl complexes of chromium and tungsten, [$(CO)_5M{=}C{=}C{=}C(R^1)R^2$] (M = Cr, W) and on the relationship between these metallacumulenes and the corresponding carbene complexes. In addition, the chemistry of the higher homologues, pentatetraenylidene complexes [$(CO)_5M{=}C{=}C{=}C{=}C(R^1)R^2$], will also be summarized. The synthesis, spectroscopy, and electron transfer of another family of allenylidene d^6-metal complexes, cationic *trans*-[$Cl(L_2)_2Ru{=}C{=}C{=}C(R^1)R^2]^+$, is the subject of a second article in this journal.

2. Synthesis of π-donor-substituted allenylidene chromium and tungsten complexes

The first aminoallenylidene complexes were prepared by Lewis-acid induced elimination of ethanol from 3-dimethylamino-1-ethoxy-3-phenyl-propenylidene complexes (**1**) in the presence of a weak base (THF) (Scheme 1). The pentacarbonyl dimethylamino(phenyl)allenylidene complexes (**2**) were isolated in 30% (Cr) and 32% (W) yield, respectively [10].

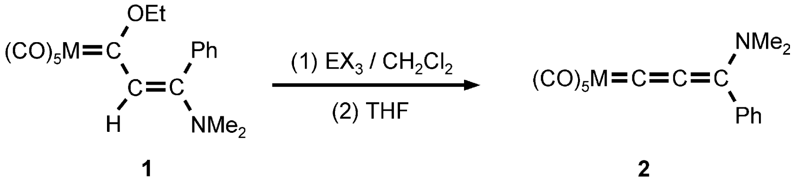
The starting carbene complexes **1** were obtained by Michael addition of dimethylamine to the CC triple bond of the corresponding ethoxy(phenylethinyl)carbene complexes (see Scheme 2: complex **3**, R = Ph) at −20 °C [10].

Later, Aumann et al. [16] demonstrated that also other amino(phenyl)allenylidene chromium complexes are accessible via this ethanol elimination route. In addition to dimethylamine, methylphenylamine, ethylphenylamine, and indoline were employed in the reaction with **1a**. Instead of boron trifluoride or the system triethylaluminum/CH_2Cl_2/THF, aluminium chloride in CS_2/CH_2Cl_2 was used.

A. de Meijere et al. [17,18] observed that, in addition to the Michael adduct, allenylidene complexes are formed as by-products when alkynyl(ethoxy)carbene chromium complexes having bulky tertiary substituents R at the acetylenic terminus are employed (Scheme 2).

The ratio **4**:**5** strongly depends on the steric requirement of R. When alkynylcarbene complexes **3** with less bulky substituents R are employed, allenylidene complexes **5** are not detected and the alkenylcarbene complexes **4** are the sole isolated products.

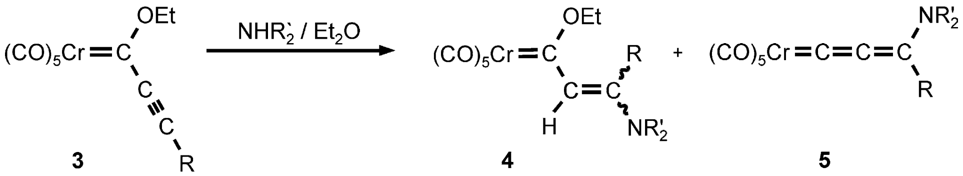
In addition to dimethylamine, the reaction of **3** with several other primary or secondary amines likewise affords aminoallenylidene complexes (in addition to **4**) [17–19] (Scheme 2).



(**a**) M = Cr, $EX_3 = BF_3$

(**b**) M = W, $EX_3 = AlEt_3$

Scheme 1.



R = C(C_2H_4)OEt, C(Me)$_2$OEt, $SiMe_3$, C(Me)$_2$OSiMe$_3$, ...

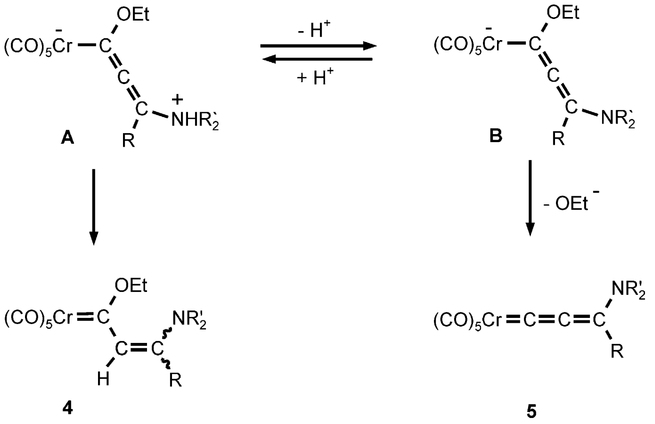
NR'$_2$ = NMe_2, NH_2, N(*i*-Pr)$_2$, N(CH_2Ph)$_2$, N(C_2H_5)$_2$, . . .

Scheme 2.

Even galactopyranosylamino-substituted allenylidene complexes of chromium and tungsten [20] and [(CO)$_5$Cr=C=C=C(NH_2)TMS] [17] are accessible via the route shown in Scheme 2 (R = Ph). Replacement of amines by lithium amides has turned out to be advantageous. In all reactions investigated, the yields of the corresponding allenylidene complexes were higher than with amines [19].

It seems reasonable to assume that the alkenylcarbene compounds **4** are intermediates in the formation of **5**. However, in a mechanistic study it was found that neither do alkenylcarbene complexes **4** react with amines to give **5** nor do allenylidene complexes react with ethanol to give **4** under the employed conditions [19]. No such conversion was observed even under more drastic conditions. From a series of experiments de Meijere et al. [19] concluded that the first step in the formation of both types of products (**4** and **5**) must be the addition of the amine to the C_γ atom of the alkynylcarbene complexes **3**. It was proposed that the resulting zwitterionic adduct **A** is in equilibrium through deprotonation and protonation with the allenylmetallate **B** (Scheme 3).

Isomerization of **A** gives rise to the formation of alkenylcarbene complexes **4**, ethoxide elimination from **B** yields allenylidene complexes **5**. A small change in the nature of the amine and the substitution pattern of the alkynylcarbene complexes **3** may cause a striking difference in the ratio of addition versus addition/elimination (formation of **4** versus **5**) [19]. Thus, the sensitivity to the substitution pattern and the reaction conditions somewhat reduce the synthetic utility of these reactions and the predictability of the yields to be expected.



Scheme 3.

Both synthetic approaches (Schemes 1 and 2) start out from alkynylcarbene complexes. This poses another restriction. Since alkynylcarbene complexes with a π-donor-substituent at C_γ are in general not accessible, bis(π-donor)-substituted allenylidene complexes cannot be prepared by these routes. Therefore, these syntheses have in general been confined to allenylidene complexes with N/C- or N/Si-substitution patterns (R = alkyl, aryl, and $SiMe_3$).

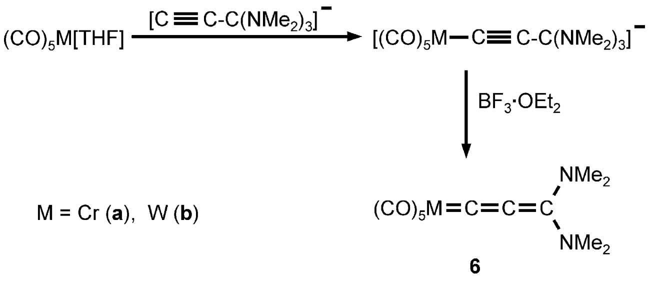
Substitution of EtO^- for $NHMe_2$ in the reaction with [(CO)$_5$M=C(OEt)–CC–Ph] (M = Cr, W) yields the O/C-substituted ethoxy(phenyl)allenylidene complexes [(CO)$_5$M=C=C=C(OEt)Ph]. The tungsten complex was isolated in small yield (10%), and the chromium complex proved to be very unstable and was neither isolated nor spectroscopically characterized [21].

For the synthesis of bis(π-donor)-substituted allenylidene complexes a different strategy has to be employed. The most common route to non-donor-substituted allenylidene complexes is to introduce a suitably substituted alkyne into the coordination sphere of a transition metal. Propargylic alcohols are the most convenient C_3 sources and have extensively been used for the synthesis of these allenylidene complexes [12]. This strategy could successfully be applied to the synthesis of bis(amino)allenylidene complexes of chromium and tungsten. Reaction of deprotonated 3,3,3-tris(dimethylamino)prop-1-yne with [(CO)$_5$M(THF)] (M = Cr, W) and subsequent BF_3 etherate promoted abstraction of one dimethylamido group from the alkynyl metallate intermediate affords the bis(dimethylamino)allenylidene complexes **6** in good yield (Scheme 4) [22].

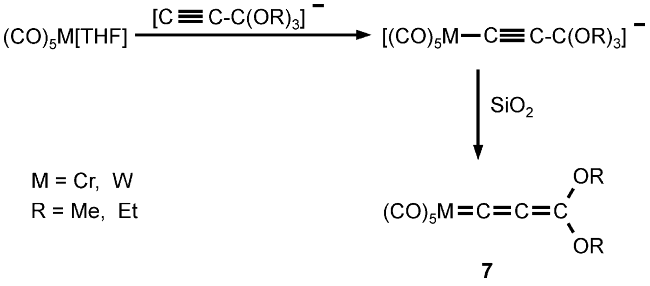
This method proved suitable for the synthesis of *O*,*O*-substituted allenylidene complexes (**7**) (Scheme 5) [22] and of higher homologues of bis(amino)allenylidene complexes [23].

The complexes **7** turned out to be quite labile and were not isolated in a pure form but were characterized spectroscopically and used as starting compounds for further transformations (see below).

When lithium 3,3,3-tris(dimethylamino)prop-1-ynide (Scheme 4) is replaced by lithium 5,5,5-tris(dimethylamino)penta-1,3-diynide in the reaction with [(CO)$_5$M(THF)] the



Scheme 4.



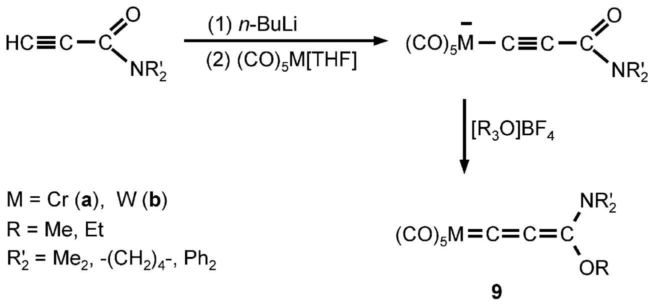
Scheme 5.

bis(dimethylamino)pentatetraenylidene complexes **8** are obtained [23].

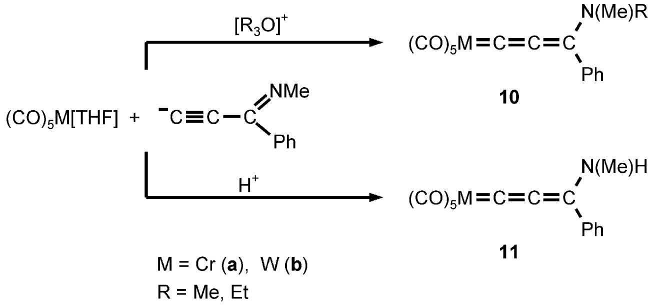
However, this method cannot be applied to the synthesis of allenylidene complexes bearing two different π-donor-substituents or only one π-donor group at the terminal carbon atom. Appropriate precursors are hitherto unknown. Additionally, the final step (abstraction of a dimethylamide) may be troublesome as amides are known to add to the γ-carbon atom of the allenylidene chain.

In part, these problems can be circumvented by using propynoic acid amides as the C_3 source. Thus, hitherto unknown amino(alkoxy)-substituted complexes can be prepared in a simple fashion. Sequential reaction of $[(CO)_5M(THF)]$ with deprotonated propynoic acid amides (to give an alkynyl metallate) and a Meerwein salt ($[R_3O]BF_4$) affords allenylidene complexes with an N/O-substitution pattern (**9**) in good to excellent yield (Scheme 6) [24]. In addition to Meerwein salts, other alkylating agents can likewise be used for the transformation of alkynyl metallates into **9**.

Through choice of the amide employed in the first reaction step, the electron richness (basicity) of the amines attached to the C_γ atom of the allenylidene complex can be varied.



Scheme 6.



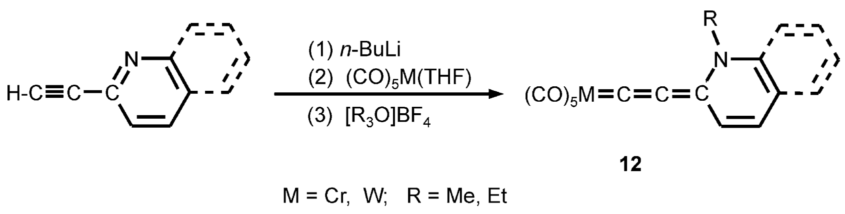
Scheme 7.

The same methodology is also applicable to the synthesis of N/C-substituted allenylidene complexes by using C-ethynylimines instead of propynoic acid amides as the C_3 source (Scheme 7) [24].

These reactions are easy to perform and produce the corresponding allenylidene complexes usually in good to excellent yields. Since *C*-ethynylimines are readily accessible, these routes offer facile access to a broad range of allenylidene complexes thus rendering them superior to those of Schemes 1 and 2.

Two non-interconverting isomers of **10** are formed in case of R $\neq$ Me, however, only one isomer of **11** can be detected. When the C=N double bond of the ethynylimine is part of an aromatic ring system like in 2-ethynyl pyridine or 2-ethinyl quinoline, allenylidene complexes (**12**) are obtained in which the terminal carbon atom of the chain is part of an *N*-heterocycle (Scheme 8).

O/C-, O/O-, and N/S-substituted allenylidene complexes can likewise be prepared by these reaction sequences shown in Schemes 6–8 starting from ethynyl ketones [HC≡C–C(=O)R′], propynoic acid esters [HC≡C–C(=O)OR′], and propynethioic acid amides [HC≡C–C(=S)NR′$_2$], respectively [25].



Scheme 8.

Thus, sequential reaction of $[(CO)_5M(THF)]$ with suitable deprotonated alkynes and an alkylating agent is the method of choice for the synthesis of π-donor-substituted allenylidene complexes rendering N/C-, O/C-, N/O-, N/S-, O/O-substitution patterns easily accessible. In addition, some of these complexes may also be transformed through substitution or insertion reactions into other allenylidene complexes (see below).

3. Spectroscopic properties

One of the most powerful tools for the investigation of the bonding in metal carbonyl complexes is IR spectroscopy. In allenylidene carbonyl complexes two types of stretching vibrations are especially interesting. The vibration of the CCC fragment offers clues on the bonding within the allenylidene ligand and the ν(CO) absorptions give information on the σ-donor/π-acceptor properties of the allenylidene ligand as a whole entity. Both, the ν(CCC) and the ν(CO) absorptions, are observed in the range 1850–2100 cm^{-1}. As a representative example Fig. 1 shows the spectrum of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$. Compared to carbene and other pentacarbonyl complexes, the A_1 absorption at higher wave numbers is of an unusually weak intensity indicating only weak coupling between the two ν(CO)-A_1 vibrations.

From the positions of the ν(CO) absorptions, it follows that these allenylidene ligands are strong donors comparable to the corresponding carbene ligands or to phosphanes. Therefore, π-donor-substituted allenylidene complexes are best described as hybrids of 1-metallabuta-1,2,3-trienes (**I**) and the zwitterionic complexes (**II–IV**). The zwitterionic resonance forms considerably contribute to the overall bonding situation.

The ν(CCC) absorptions in allenylidene pentacarbonyl complexes are found in the range 1960–2035 cm^{-1} the exact position depending on the substituents at C_γ. The cumulenylidene vibration of bis(aryl)-substituted allenylidene complexes (e.g. $[(CO)_5Cr{=}C{=}C{=}C(C_6H_4NMe_2)_2]$: 1963 cm^{-1} in THF) appears at wave numbers similar to those of organic allenes (≈1950 cm^{-1} [26]). Obviously, the metallabutatriene resonance form **I** dominates and the zwitterionic alkynyl structures (**II–IV**) are of only minor importance. Increasing the donor capacity of the substituents XR and YR′ leads to a shift of the ν(CCC) absorption towards higher energy. Finally, the position of the ν(CCC) band of bis(amino)allenylidene complexes such as e. g. **6a** (ν (CCC) = 2014 cm^{-1} in THF) or **13** (ν(CCC) = 2024 cm^{-1} in THF) is comparable to the ν(C≡C) vibration in alkynyl metallates ($Li[(CO)_5Cr{-}C{\equiv}C{-}C(NMe_2)_2Ph]$: 2037 cm^{-1} [27]; $[H_2NMe_2]^+[(CO)_5Cr{-}C{\equiv}C{-}C({=}NMe)Ph]^-$: 2020 cm^{-1} [25]).

With these complexes the polar resonance forms **II–IV** predominate.

In between these two extreme substitution patterns, there is a rather smooth transition between allenylidene and dipolar resonance forms. The ν(CCC) absorptions correlate rather well with the sum of the Hammett constant σ_p [28] of the substituents bonded to C_γ (see Fig. 2).

The deviation observed for the bis(dimethylamino)allenylidene complex **6a** is presumably due to unfavorable steric interaction between the NMe_2 groups which prevents coplanarity and thus optimal overlap of both *N*-lone pairs with the carbon chain. This assumption is confirmed by a shift of 10 cm^{-1} to higher energy when the amino substituents are incorporated into a five-membered ring system (**6a** → **13**) thereby enforcing coplanarity (Scheme 9).

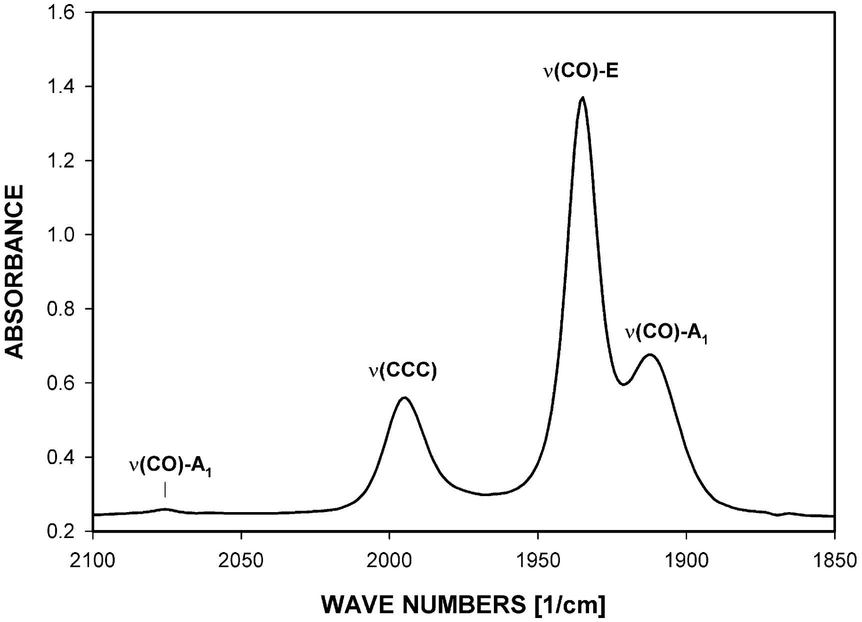


Fig. 1. IR spectrum of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ (**2a**) in THF in the range 1850–2100 cm^{-1}.

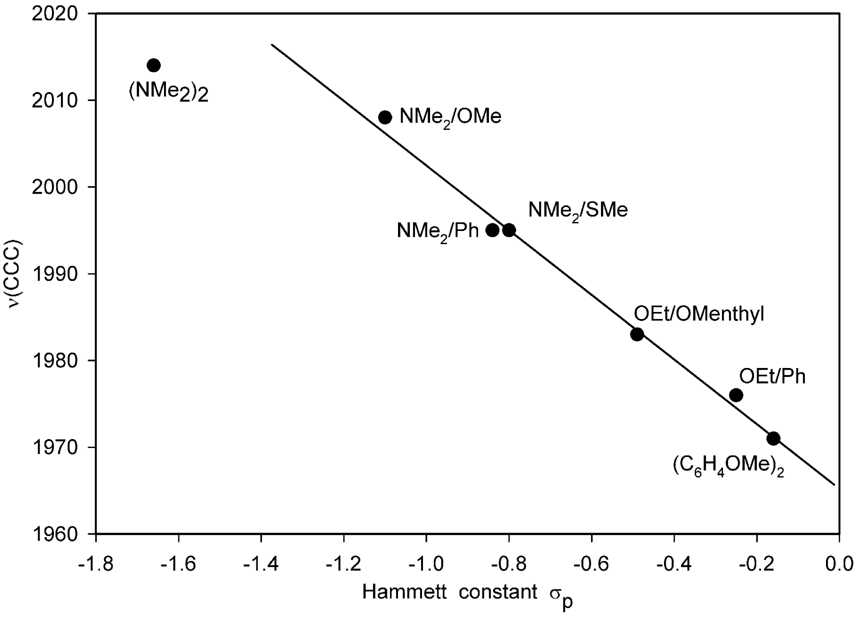
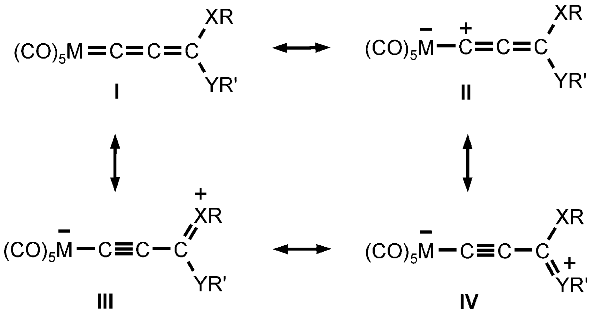


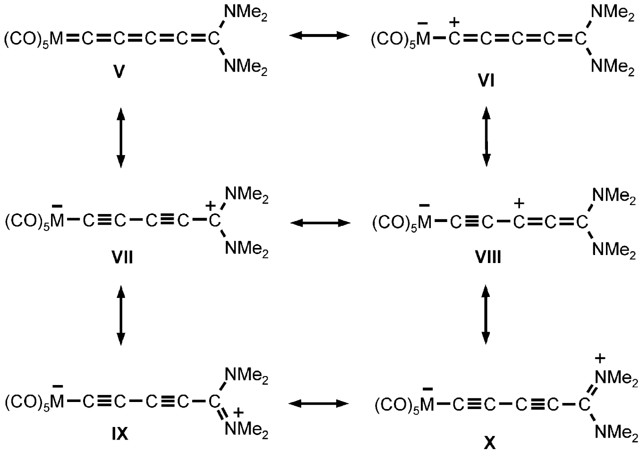
Fig. 2. Correlation between ν(CCC) and the sum of the Hammett constant σ_p of the C_γ-bonded substituents for various chromium complexes $[(CO)_5Cr{=}C{=}C{=}C(R^1)R^2]$.

Insertion of another C=C fragment into the M=C bond of allenylidene complexes (e.g. **6** → **8**) affords pentatetraenylidene complexes. The ν(CO) absorptions are comparable in position to those of the related allenylidene complexes. In contrast to allenylidene complexes the A_1 absorption at highest energy is of medium intensity and, instead of one, two ν(CCC) absorptions are observed. From the ν(CO) spectra, it follows that a pentatetraenylidene $C_5(NMe_2)_2$ ligand is a slightly better donor than the allenylidene $C_3(NMe_2)_2$ ligand. This is easily rationalized by an increase in the number of dipolar resonance forms and thus an enhanced electron transfer to the $(CO)_5M$ fragment (see Scheme 10).

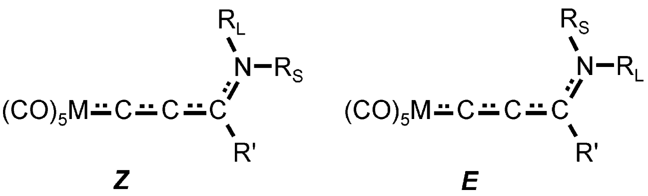
The NMR spectra support the conclusions drawn from the IR spectra. The ^{1}H- and ^{13}C-NMR spectra of mono-(amino)allenylidene complexes, $[(CO)_5M{=}C{=}C{=}C(NR^1R^2)R']$ (R′ = aryl, OR, SR), show two sets of resonances for the *N*-alkyl substituents ($R^1 = R^2$) confirming the double bond character of the C_γ–N bond as shown in Scheme 9 (resonance form **III**). In case of $R^1 \neq R^2$ this gives rise to *E*/*Z* regioisomers (Scheme 11). The *E*/*Z* ratio depends on the size of the substituents. In general, the *Z*-conformer with the sterically more demanding group oriented towards the metal moiety is preferred thus avoiding unfavorable steric interactions with the substituent R′ (Scheme 11) [24].



Scheme 9.



Scheme 10.



Scheme 11.

Upon warming solutions of mono(amino)allenylidene complexes to 120 °C, no coalescence of the signals of the *N*-bound groups is observed revealing a rather high barrier for the rotation around the C_γ–N bond ($\Delta G^{\neq} > 19\,\mathrm{kcal\,mol^{-1}}$) [24]. So far, there has been only one report of an experimentally determined rotational barrier in a d^6 mono(amino)allenylidene complex. The activation energy for the $E \rightarrow Z$ isomerization of $[(dppm)_2ClRu{=}C{=}C{=}C(N\{Me\}t\text{-}Bu)Me]^+$ was determined to be $86.4\,\mathrm{kJ\,mol^{-1}}$ and that for the $Z \rightarrow E$ isomerization to be $84.1\,\mathrm{kJ\,mol^{-1}}$, respectively [29].

In contrast to *mono*(amino)allenylidene complexes, the NMR spectra of the *bis*(amino)allenylidene complex **6a** and **6b** exhibit only one N–Me resonance. The signal neither broadens nor splits on cooling solutions down to −90 °C. This reveals a rather low rotational barrier ($\Delta G^{\neq} < 9\,\mathrm{kcal\,mol^{-1}}$) [23]. Comparable results have been found for the rotation around the partial C–N double bond in amides and related compounds. The activation energy for the rotation in tetramethyl urea ($O{=}C(NMe_2)_2$: $6.3\,\mathrm{kcal\,mol^{-1}}$ [30]) is markedly lower than in dimethyl carbamic acid methyl ester ($O{=}C(NMe_2)OMe$: $14.8\,\mathrm{kcal\,mol^{-1}}$) or dimethyl benzamide ($O{=}C(NMe_2)Ph$: $15.0\,\mathrm{kcal\,mol^{-1}}$) [30,31]). This was explained by steric interactions of the two dimethylamino groups which prevent a coplanar arrangement of the amino group with the π-system.

Analogously to the ν(CCC) absorptions, the resonance of the metal bound C_α atom depends on the substituents at C_γ. With increasing donor ability of the substituents the resonance of the C_α atom shifts towards higher field in accord with an increasing contribution of the resonance forms **III** and **IV** to the overall bonding. Like the ν(CCC) absorptions, the C_α resonances correlate reasonably well with the sum of the Hammett constant σ_p [28] of the C_γ substituents. Insertion of a C=C unit into the metal–carbon bond in $[(CO)_5M{=}(C{=}C{=})_xC(R^1)R^2]$ ($x = 0, 1, 2$: carbene → allenylidene → pentatetraenylidene complexes) causes a considerable high-field shift of the C_α resonance. The effect is even more pronounced than by variation of the C_γ substituents.

Like C_α, the C_β resonance is also substituent-dependent, however, only to a minor degree whereas the position of the C_γ resonance seems to be almost independent of the substitution pattern. These data again confirm the delocalization of the lone pair at nitrogen towards the metal center which considerably contributes to the stabilization of π-donor-substituted allenylidene complexes.

All donor-substituted allenylidene complexes as well as the pentatetraenylidene complexes exhibit a pronounced negative solvatochromic effect. The UV–vis absorption at lowest energy, which is assigned to a MLCT absorption, shifts towards shorter wavelengths when unpolar or weakly polar solvents are replaced by more polar ones. As an example Fig. 3 shows the UV–vis spectrum of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ in different solvents.

Increasing the donor capacity of the C_γ substituents increases: (a) the electron density at the metal center and concomitantly the energy of the predominantly metal-localized HOMO; and (b) simultaneously the energy of the mainly cumulenylidene ligand-localized LUMO. The influence on the LUMO is more pronounced than that on the HOMO. Therefore, the overall effect is an in-

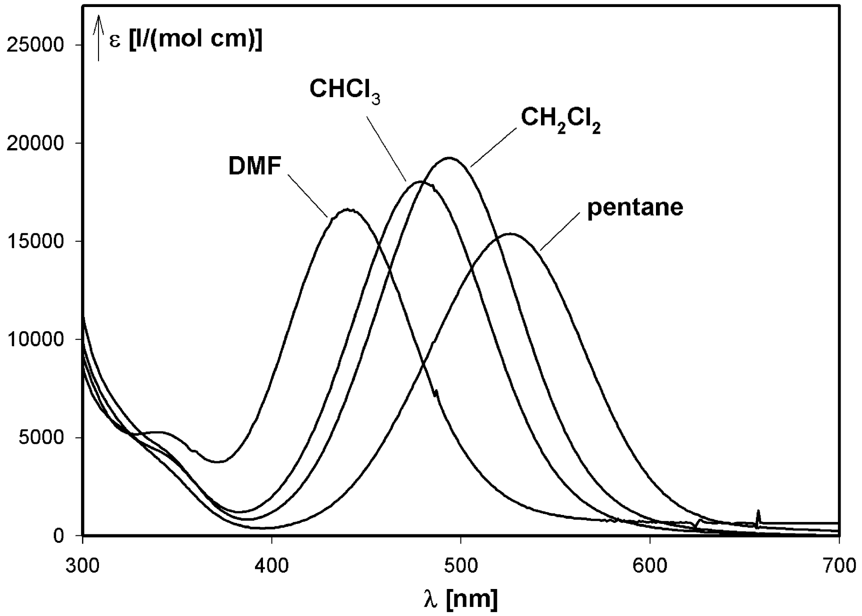


Fig. 3. UV–vis spectrum of $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ in different solvents.

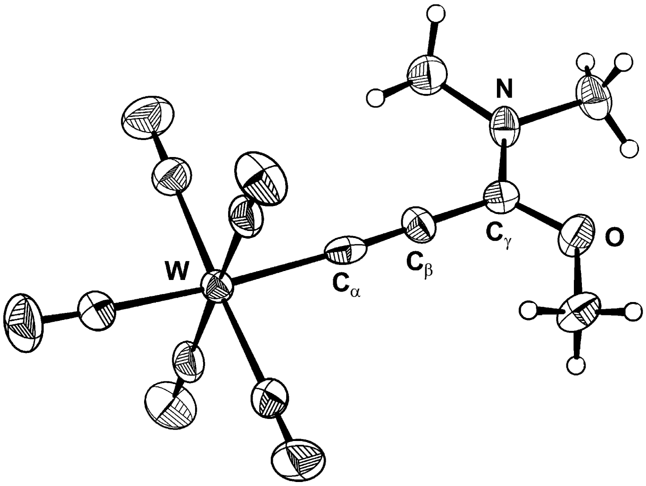


Fig. 4. Structure of [$(CO)_5W$=C=C=C(NMe_2)OMe] in the crystal.

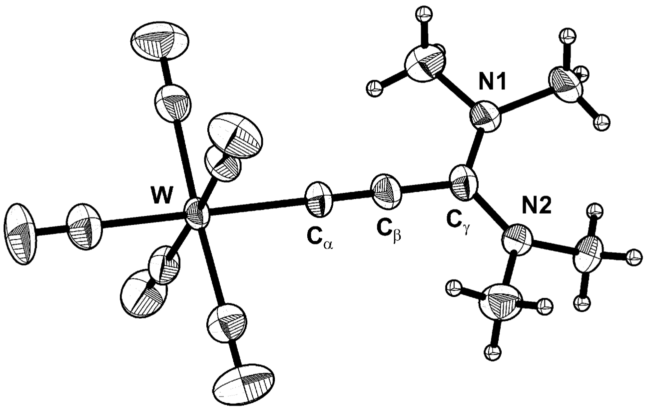


Fig. 5. Structure of [$(CO)_5W$=C=C=C$(NMe_2)_2$] (**6b**) in the crystal.

crease of the HOMO-LUMO gap. This causes a shift of the MLCT transition towards shorter wavelengths (e.g. λ_{max} of [$(CO)_5Cr$=C=C=C(NMe_2)R] in CH_2Cl_2: 478 nm (R = Ph), 400 nm (R = OMe), 394 nm (R = NMe_2)). Conversely, insertion of a C=C fragment into the M=C bond (**6** → **8**) leads to a considerable bathochromic shift of the MLCT absorption (λ_{max} = 394 nm (**6**), 474 nm (**8**), in CH_2Cl_2).

As expected on the basis of the dipolar character of these metallacumulenes, donor-substituted allenylidene and pentatetraenylidene complexes exhibit a pronounced non-linear optical response. The molar first hyperpolarizability β of **6** in DMF as determined by hyper-Rayleigh scattering experiments is in the range $(20–25) \times 10^{-30}$ esu and quadruples on insertion of a cumulated C_2 unit into the metallacumulene (**6** → **8**). Substitution of tungsten for chromium has only a minor effect on β [32].

The solid state structures of several aminoallenylidene and aminopentatetraenylidene complexes were determined. The structures of [$(CO)_5W$=C=C=C(NMe_2)OMe] [33], [$(CO)_5W$=C=C=C$(NMe_2)_2$] (**6b**) [23], and [$(CO)_5W$=C=C=C=C=C$(NMe_2)_2$] [**8b**] [23] are shown as representative examples in Figs. 4–6.

The results from the X-ray structural analyses confirm the conclusions drawn from the spectroscopic data. The MC_x (x = 3, 5) fragment is linear. The individual CC distances within the MC_x fragment differ markedly. The C_α=C_β bond in all complexes is considerably shorter than expected for a C(sp)=C(sp) bond and resembles an elongated carbon-carbon triple bond. Conversely, the C_β=C_γ bond in allenylidene complexes (C_δ=C_ε bond in pentatetraenylidene complex **8b**) is rather long compared to a standard C(sp)=C(sp^2) distance. As in donor-substituted allenylidene complexes, the C=C distances in the pentatetraenylidene complex **8b** strongly alternate (short/long/short/long). As expected on the basis of the spectroscopic data, the bond length alternation in these allenylidene complexes is slightly more pronounced than in [$(CO)_5Cr$=C=C=C$(Ph)_2$] [15].

The amino nitrogen atoms are planar coordinated. The C_γ–N bonds (C_ε–N bonds in **8**) are short and compare well with those usually observed for C(sp^2)–N(sp^2) bonds in push-pull systems confirming some double bond character of these C–N bonds (Schemes 9 and 10: resonance forms **III**/**IV** and **IX**/**X**, respectively).

Allenylidene as well as pentatetraenylidene ligands L exert a significant *trans* influence. The M–C(*trans*) bond in [$(CO)_5M$–L] complexes is shorter than the mean of the M–C(*cis*) bonds. As expected, this effect is most pronounced in bis(amino)-substituted complexes.

In addition to the spectroscopic studies, density functional calculations have been carried out on two series of metallacumulenes, [$(CO)_5Cr(=C)_nCH_2$] (n = 1–8) [34] and [$(CO)_5Cr(=C)_nCX_2$] (n = 1–7; X = F, SiH_3, CH=CH_2, NH_2, NO_2) [35], and on a series of donor-substituted allenylidene complexes, [$(CO)_5Cr$=C=C=C$(R^1)R^2$] (R^1 = Ph, R^2 = Ph, OMe, NMe_2; R^1 = OMe, R^2 = OMe, NMe_2; R^1 = NMe_2, R^2 = NMe_2) [36]. The calculated optimized geometries were found to be in good agreement with data determined by X-ray structural analyses. For the various allenylidene complexes the bond-length alternation was calculated to be more pronounced with complexes bearing substituents with high donor capacity.

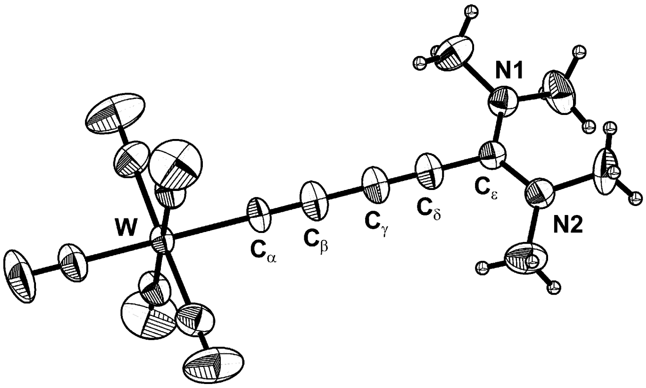


Fig. 6. Structure of [$(CO)_5W$=C=C=C=C=C$(NMe_2)_2$] (**8b**) in the crystal.

The most important results can be summarized as follows:

(a) In metallacumulenes with an odd number of carbon atoms, the LUMO is predominantly localized at the odd-numbered carbon atom (numbering starting at the metal: C_α and C_γ in allenylidene complexes, C_α, C_γ, and C_ε in pentatetraenylidene complexes). In turn, the metal and the even-numbered carbon atoms contribute most to the HOMO [34,35].

(b) Analysis of the electronic structure in terms of the synergistic σ donor π back-donation model reveals that the contribution from π back-donation is slightly higher than that from σ donation. The contribution from π back-donation was found to be much more sensitive to the nature of the substituents [34,35].

(c) The Cr=C bond dissociation energy for odd-numbered unsubstituted metallacumulenes (allenylidene and pentatetraenylidene complexes) is high and nearly independent of the chain length, however, decreases on introduction of amino substituents due to a reduction of the π-acceptor properties of the ligand [34,35].

(d) In unsubstituted metallacumulenes there are no significant charge differences among the various carbon atoms of the cumulene ligand indicating that charge distribution is not important in determining the regioselectivity of nucleophilic and electrophilic attack in these complexes [34]. An analysis of the MO energies in these metallacumulenes shows that the HOMOs are energetically relatively high-lying and the LUMOs low-lying. The HOMOs are quite isolated in energy from the other highest occupied MOs and the LUMOs are even better isolated from the other lowest unoccupied orbitals [34]. Therefore, the regioselectivity of nucleophilic and electrophilic attack is mainly determined by the frontier orbitals.

(e) The energy of the HOMO is almost independent of the chain length but increases when the H atoms in $[(CO)_5Cr{=}(C{=}C)_x{=}CH_2]$ are replaced by NH_2 groups [35]. In donor-substituted allenylidene complexes the energy of the HOMO rises in the series R^1/R^2 = Ph/Ph, Ph/OMe, $Ph/NMe_2 \approx$ OMe/OMe, $OMe/NMe_2 \approx NMe_2/NMe_2$ [36].

(f) The energy of the LUMO decreases on lengthening of the carbon chain and increases on replacing H by NH_2 [35]. In the series of allenylidene complexes, the LUMO energy increases along the series R^1/R^2 = Ph/Ph, Ph/OMe, $Ph/NMe_2 \approx$ OMe/OMe, OMe/NMe_2, NMe_2/NMe_2 [36].

(g) The analysis of the charge distribution within the carbon chain of donor-substituted allenylidene complexes reveals increasing positive charge at C_γ and, less pronounced, negative charge accumulation at C_β along the series R^1/R^2 = Ph/Ph, Ph/NMe_2, Ph/OMe, NMe_2/NMe_2, OMe/NMe_2, OMe/OMe. C_α bears almost no charge independent of the substitution pattern [36].

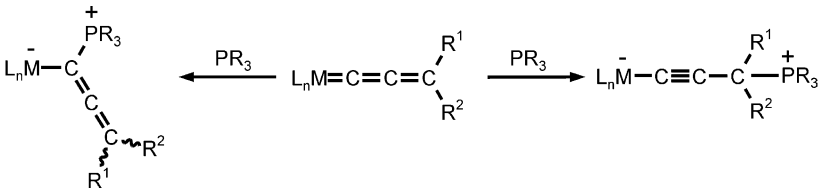
(h) The contribution of C_α and C_γ or of C_α, C_γ, and C_ε to the LUMO orbital of bis(amino)allenylidene or bis(amino)pentatetraenylidene complexes are similar, rendering the prediction of the site of a frontier-orbital controlled nucleophilic attack difficult [35]. However, when considering the effect of various substituents on the charge distribution as summarized in (g) an increasing tendency for C_γ attack of strong nucleophiles is to be expected.

4. Reactivity of donor-substituted allenylidene complexes

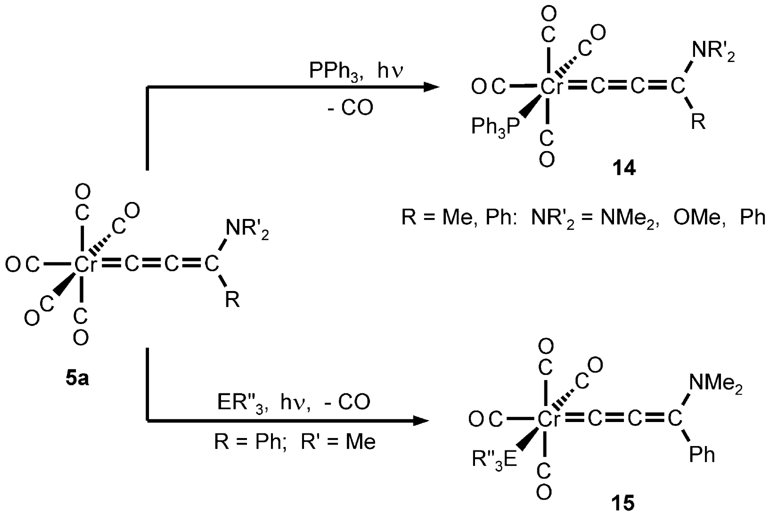
4.1. Reactivity towards P-nucleophiles

The carbon chain of allenylidene- and pentatetraenylidene complexes consists of an alternating array of electrophilic and nucleophilic sites. Therefore, electrophiles should preferably add to the C_β atom (or to C_δ in pentatetraenylidene complexes) and nucleophiles should add either to the C_α or C_γ atom (or the C_ε atom in pentatetraenylidene complexes) of the chain. Tertiary phosphanes are frequently used as nucleophiles to determine the site of attack. There are examples for the addition to C_α as well as to C_γ of allenylidene complexes [12,37] (Scheme 12). The selectivity depends on the nucleophilicity and the steric requirements of the phosphanes, the metal and its co-ligand sphere and on the substituents at the terminal carbon atom of the chain.

Bis(aryl)-substituted allenylidene pentacarbonyl chromium complexes like $[(CO)_5Cr{=}C{=}C{=}C(C_6H_4NMe_2\text{-}p)_2]$ as well as bis(*iso*-propyl)- and bis(*tert*-butyl)-substituted allenylidene complexes of chromium and tungsten add phosphanes to the C_α atom giving zwitterionic allenyl phosphane complexes [37a,38]. When secondary or primary phosphanes are employed, phosphane addition to the C_α atom of $[(CO)_5Cr{=}C{=}C{=}C(C_6H_4NMe_2\text{-}p)_2]$ is followed by rearrangement to give allenylphosphane complexes or their dimers (secondary phosphanes) or alkynylphosphane complexes (primary phosphanes) [38].



Scheme 12.



R = Me, Ph: NR'$_2$ = NMe$_2$, OMe, Ph

ER''$_3$ = P(i-Pr)$_3$, PMe$_3$, P(OMe)$_3$, AsPh$_3$, SbPh$_3$
P(C$_6$H$_4$R-p)$_3$ (R = OMe, Me, F, Cl, CN)

Scheme 13.

The reactivity of amino-substituted allenylidene complexes deviates from this reaction pattern. Tertiary phosphanes do not add to the allenylidene chain of aminoallenylidene complexes even at elevated temperatures. This agrees well with the expected lowering of the reactivity on introduction of π-donor-substituents due to the increase in the energy of the LUMO. However, upon irradiation the phosphane displaces one CO ligand to give *cis*-allenylidene tetracarbonyl phosphane complexes **14** (Scheme 13) [39].

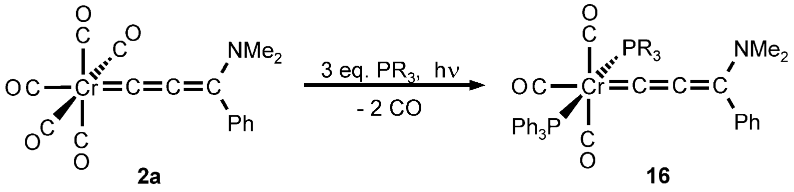
Similar to bis(alkyl)- and bis(aryl)-substituted allenylidene pentacarbonyl complexes but in contrast to aminoallenylidene complexes, Fischer-type alkoxycarbene complexes of chromium and tungsten, [(CO)$_5$M=C(OR)R$'$] (M = Cr, W; R = Me, Et; R$'$ = alkyl, aryl) add secondary and tertiary phosphanes at low temperature to the metal-bound carbene carbon atom [40]. The addition is reversible, the addition-dissociation equilibrium depending on the solvent, the temperature, and strongly on the substituents [41]. The substitution products, carbene tetracarbonyl phosphane complexes, are irreversibly formed on photolysis at low temperature or on thermolysis at elevated temperatures of [(CO)$_5$M=C(OR)R$'$]/PR$_3$ mixtures [42].

The ligand exchange reactions, as shown in Scheme 13, offer facile access to a series of aminoallenylidene tetracarbonyl complexes (**15**) with different co-ligands of various donor propensity. Thus, it is possible to subtly modify on purpose the back-bonding properties of the metal-ligand fragment.

The IR spectra confirm the *cis* conformation of the complexes. There is no indication for the formation of the *trans* isomer. In contrast, the corresponding carbene phosphane complexes *cis*-[(CO)$_4$(PR$_3''$)M=C(OR)R$'$] isomerize until an equilibrium is established [42,43].

Replacing a CO acceptor ligand by a P-, As- or Sb-donor leads to a shift of the ν(CCC) vibration towards lower energy (1948–1971 cm^{-1}) indicating enhanced contribution of the metallabutatriene resonance form **I** (Scheme 9) to the overall bond description when compared to the pentacarbonyl complexes. As expected, the strongest effect is observed for phosphanes with high donor capacity (P(i-Pr)$_3$).

Replacement of two carbonyl ligands in aminoallenylidene pentacarbonyl complexes by two rather electron-poor P-donor ligands such as P(OMe)$_3$, P(C$_6$H$_4$F-p)$_3$ or P(C$_6$H$_4$Cl-p)$_3$ is possible through photolysis of the complexes in the presence of a three-fold excess of PR$_3$. In the resulting *mer*-allenylidene tricarbonyl bisphosphane complexes **16** (Scheme 14) the ν(CCC) absorption appears in the range 1921–1935 cm^{-1}. Its position is at even lower energy than in bis(aryl)-substituted allenylidene pentacarbonyl complexes and is comparable to that in allenes (e.g.



R = C$_6$H$_4$F-p, C$_6$H$_4$Cl-p, OMe

Scheme 14.

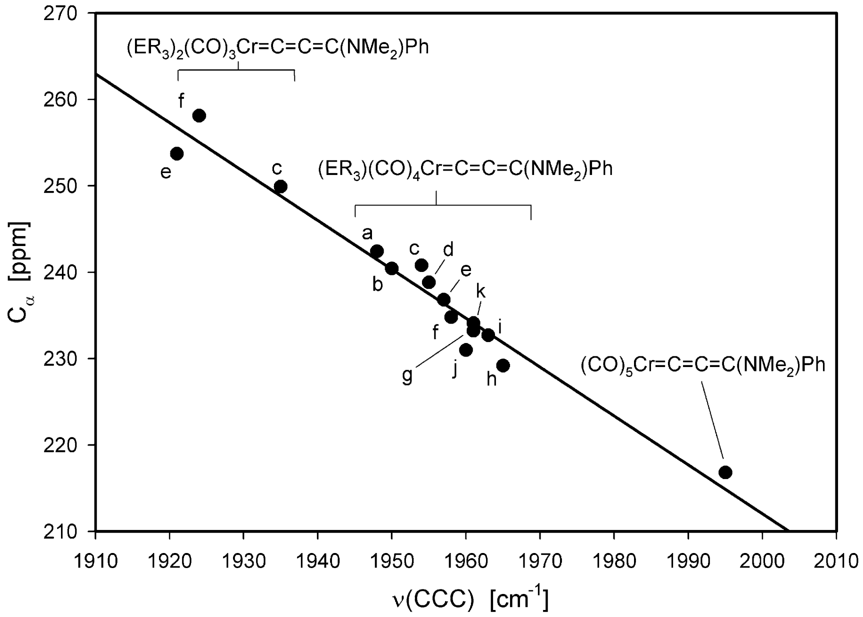


Fig. 7. $^{13}C_\alpha$ resonance vs. ν(CCC) absorption for various chromium complexes $[(ER_3)_x(CO)_{5-x}Cr=C=C=C(NMe_2)Ph]$ (x = 0–2): $ER_3 = P(i\text{-}Pr)_3$ (a), PMe_3 (b), $P(C_6H_4R'\text{-}p)_3$ (R′ = OMe (c), Me (d), H (e), F (f), Cl (g), CN (h)), $P(OMe)_3$ (i), $SbPh_3$ (j), $AsPh_3$ (k)).

$H_2C=C=CD_2$: ν(CCC) = 1941 cm^{-1} [44], $H_2C=C=CPh_2$: ν(CCC) = 1934 cm^{-1} [45]). A CO/PR$_3$ exchange gives rise to a shift of the ν(CCC) absorption of about 28–37 cm^{-1} and the effect seems to be cumulative.

The influence of the various ligands on the electron distribution within the allenylidene chain also shows up in the ^{13}C-NMR resonance of the metal bound C_α atom. Increasing the back-bonding capacity of the metal-ligand fragment by CO/PR$_3$ exchange induces a shift towards lower field. The low-field shift correlates well with that of the ν(CCC) absorption to lower energy. Conversely, increasing the donor properties of the substituents at the terminal carbon atom of the chain causes a high-field shift of the C_α resonance and a shift towards higher energy of the ν(CCC) absorption (Fig. 7).

The diminishing importance of dipolar structures in the series of allenylidene penta-, tetra-, and tricarbonyl complexes is also evident in the resonances of the N–Me groups. In accord with a pronounced double bond character of the C_γ–N bond the penta- and tetracarbonyl amino allenylidene complexes exhibit two N–Me resonances in the ^{1}H- and ^{13}C-NMR spectra whereas only one signal is observed for the tricarbonyl complexes indicating a rather low rotational barrier.

Thus, through choice of the substituents and the ligand sphere, the polarity of the bonding in allenylidene complexes can easily be enhanced or reduced.

4.2. Reactivity towards N-nucleophiles

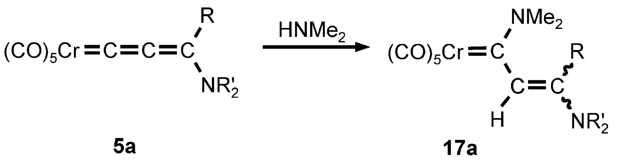
There is only one report about an addition of an amine to the C_γ atom, namely that of ammonia to the rhenium allenylidene complex $[(triphos)(CO)_2Re=C=C=C(Ph)_2]^+$ [46]. Usually, allenylidene complexes add amines to the C_α atom.

Analogous to bis(aryl)-substituted allenylidene pentacarbonyl complexes, $[(CO)_5M=C=C=C(aryl)_2]$ [47], mono(amino)allenylidene complexes of chromium (**5a**) and tungsten (**5b**) add amines across the C_α–C_β bond to give alkenyl(amino)carbene complexes (**17a**, **17b**) [19,25] (Scheme 15).

Since aminoallenylidene complexes are less reactive than bis(aryl)allenylidene complexes the additions proceed more slowly when analogous conditions (equimolar amounts, temperature, solvent, concentration) are applied (Schemes 16–21).

Addition of dimethylamine in large excess gives rise to the formation of the demethylated allenylidene complex $[(CO)_5Cr=C=C=C\{N(H)Me\}Ph]$ (**11a**) (Scheme 16) (the mechanism of the formation will be discussed later, see Scheme 22).

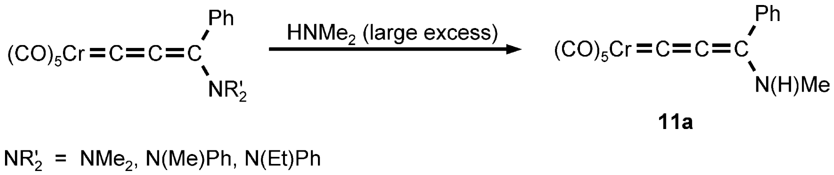
In case of $NR'_2 = N(R^*)H$ (R* = 2-galactopyranosyl), the reaction with NEt$_3$ did not give a C_α adduct but rather a stable isolable iminoalkynyl derivative by reversible depro-



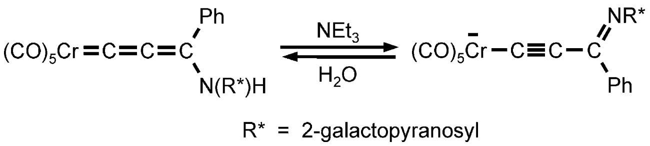
R = Ph: $NR'_2 = NMe_2$, NEt_2, $N(i\text{-}Pr)_2$, N(Me)Ph, N(Et)Ph

R = CMe_2OEt: $NR'_2 = N(CH_2Ph)_2$

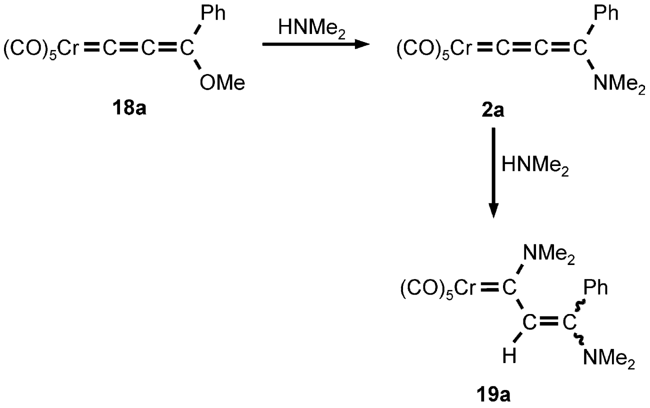
Scheme 15.



Scheme 16.



Scheme 17.

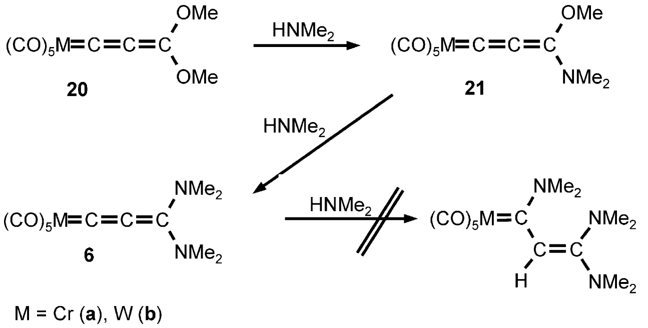


Scheme 18.

tonation of the amino substituent. Reprotonation is achieved by water [20]. Other monoalkylamino(phenyl)allenylidene complexes are also readily deprotonated with bases and may subsequently be reprotonated or alkylated (see Scheme 7) [34].

When solutions of the alkoxy-substituted complex [(CO)$_5$Cr=C=C=C(OMe)Ph] (**18a**) are treated with one equivalent of dimethylamine, likewise a C_α–C_β adduct is not obtained. Instead, complex **2a** constitutes the major reaction product formed by substitution of the methoxy group [48]. Obviously, substitution is much faster than C_α–C_β addition.

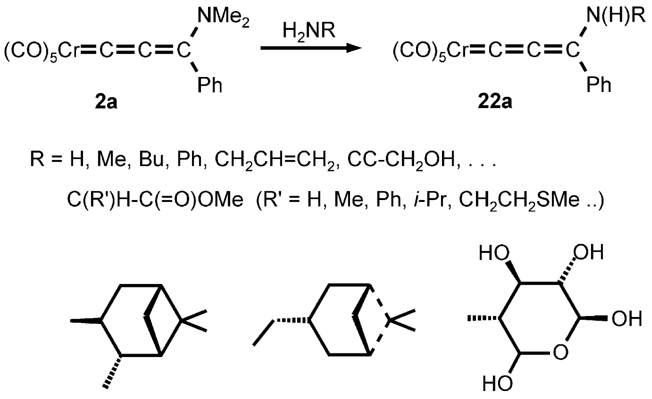
The substitution reaction presumably proceeds by addition of dimethylamine to the C_γ atom followed by elimination of methanol and is the “allenylidene version” of the aminolysis of alkoxycarbene complexes [49]. Ammonia, primary and secondary amines readily react with alkoxy(organyl)carbene complexes to yield amino(organyl)carbene complexes and the corresponding alcohol [4,49]. The mechanism of this reaction has been studied in great detail. In decane, the reaction follows a fourth order rate law, first order in the concentration of the complex and third order in the concentration of the amine [50]. This aminolysis is characterized by a negative Arrhenius activation energy, i.e. the reaction rate increases with decreasing temperature. A step-wise mechanism has been proposed. At present it is unknown whether the “aminolysis” of alkoxy(organyl)allenylidene complexes follows the same step-wise mechanism or not.



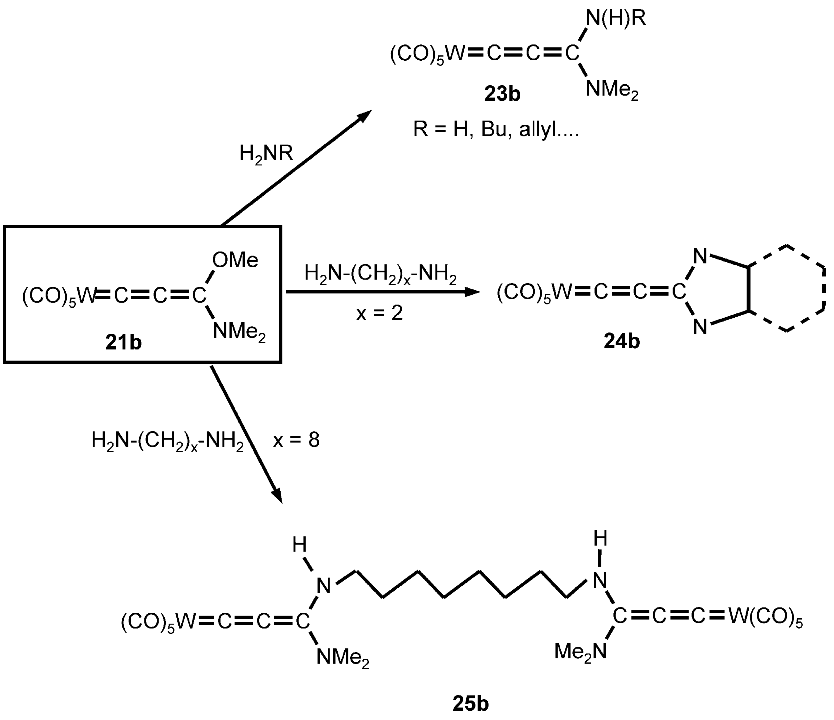
Scheme 19.

In addition to **2a**, small amounts of the alkenyl(amino)carbene complex [(CO)$_5$Cr=C(NMe$_2$)CH=C(NMe$_2$)Ph] (**19a**) are formed by C_α–C_β addition of another molecule of dimethylamine to **2a**. Complex **19a** constitutes the exclusive product when excess dimethylamine is used. A large excess of dimethyl amine finally leads to the formation of [(CO)$_5$Cr=C=C=C{N(H)Me}Ph] (**11a**, see also Scheme 16) [48] very likely by a sequence related to that shown in Scheme 22 (see below).

Bis(alkoxy)allenylidene complexes [(CO)$_5$M=C=C=C(OR)$_2$] (M = Cr, W; R = Me, Et) such as **20** likewise exhibit a C_γ preference in the reaction with *N*-nucleophiles. With dimethylamine alkoxy(dimethylamino)allenylidene complexes [(CO)$_5$M=C=C=C(NMe$_2$)OR] are formed by an addition/elimination sequence. These complexes add excess dimethylamine to finally give bis(amino)allenylidene complexes **6** in small yields (Scheme 19) [51]. Neither



Scheme 20.



Scheme 21.

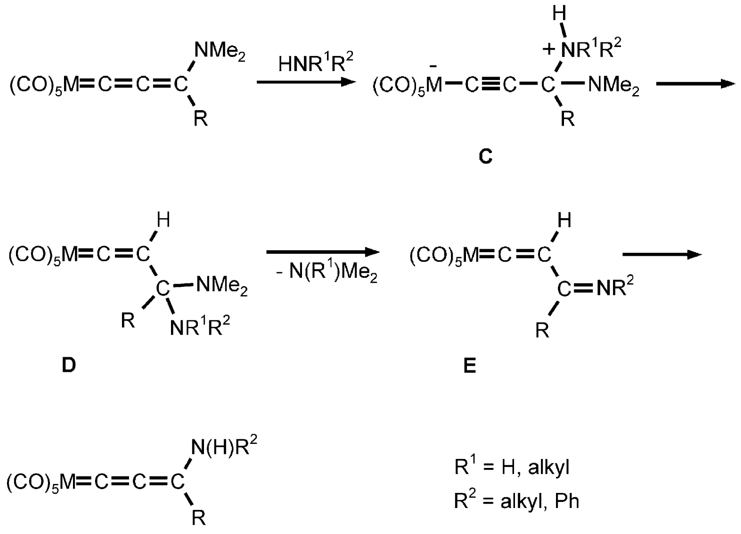
in the starting bis(alkoxy)allenylidene nor in the product alkoxy(dimethylamino)allenylidene and bis(amino)allenylidene complexes can the formation of C_α–C_β adducts (alkenyl(amino)carbene complexes) be observed [48].

If *N*,*N*′-dimethyl ethylene diamine is used instead of dimethylamine in the reaction with $[(CO)_5Cr{=}C{=}C{=}C(OMe)_2]$ (**20a**) a metallacumulene with a terminating bis-*N*-heterocycle (**13**) is formed [48].

Likewise, the bis(dimethylamino)allenylidene complex **6** is not inert towards addition of secondary amines to the C_γ atom although the reaction is slow due to the two strong π-donor-substituents. Displacement of a dimethylamino group yields mixed bis(amino)allenylidene complexes.

Replacing one dimethylamino by the less basic diphenylamino group already leads to a significantly enhanced reactivity. In contrast to $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)_2]$ the initially formed mixed bis(amino)allenylidene complex $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)NPh_2]$ adds dimethylamine to form an amino[bis(amino)ethenyl)carbene complex, $[(CO)_5Cr{=}C(NMe_2)CH{=}C(NMe_2)NPh_2]$ (related to **19a** in Scheme 18).

Contrary to dimethylamine (see Scheme 18), neither ammonia nor primary amines, H_2NR, add to the C_α–C_β



Scheme 22.

bond of the mono(dimethylamino)allenylidene complex $[(CO)_5Cr{=}C{=}C{=}C(NMe_2)Ph]$ (**2a**). Instead, the dimethylamino group is replaced by N(H)R (Scheme 20). This substitution reaction has turned out to be a very efficient method for the derivatization of allenylidene complexes. A series of alkyl, aryl, or acyl amines, functionalized amines such as allyl or propargyl amines, and chiral amines like amino acids, terpenes or amino sugars can easily be introduced into the γ-position of allenylidene complexes [48].

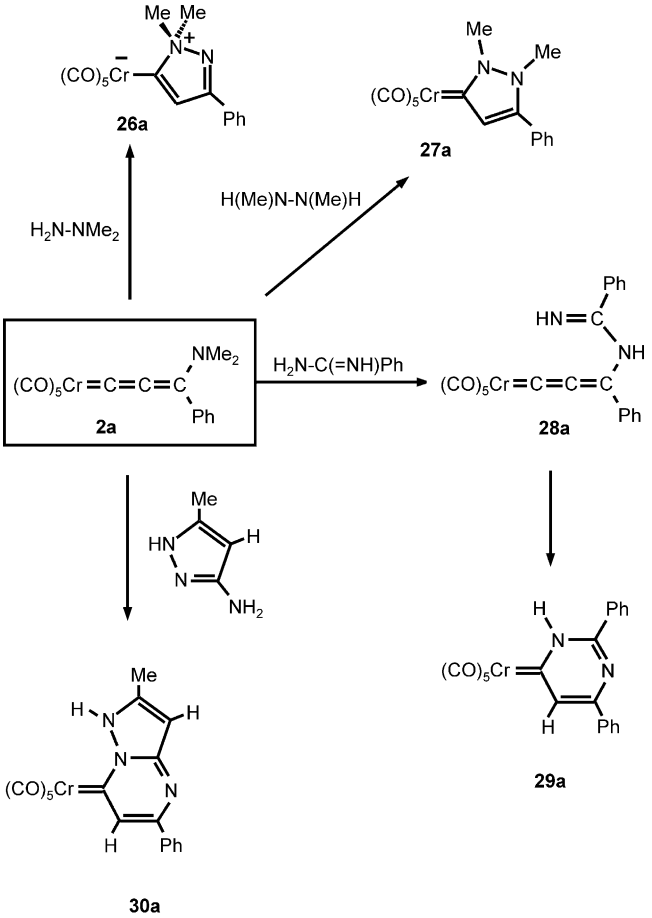
Dimethylamino(alkoxy)allenylidene complexes (e.g. **21b**, Scheme 19) are also excellent starting compounds for the introduction of various amino groups and functional groups into the allenylidene ligand. As expected, in reactions with ammonia and primary amines, the alkoxy group is replaced first thus giving access to allenylidene complexes with two different amino substituents (**23b**) (Scheme 21). When the amine is used in excess, the NMe_2 group is displaced as well. The reaction of **21b** with α,ω-diamines affords either allenylidene complexes with a heterocyclic end-group (**24b**) or dinuclear bisallenylidene complexes (**25b**) depending on the number of CH_2 spacers in the diamine (Scheme 21) [48].

These substitution reactions presumably proceed by a sequence of steps as shown in Scheme 22. The addition of dimethylamine to the C_γ atom of the allenylidene complex, to give a zwitterionic alkynyl complex (**C**), is followed by rearrangement of **C** into the vinylidene intermediate **D**. By subsequent elimination of $HNMe_2$ from **D**, the iminovinylidene complex **E** is formed. Proton shift (comparable to keto-enol tautomerization) finally affords the substitution product.

Through proper choice of bifunctional *N*-nucleophiles, substitution at C_γ and addition to the C_α–C_β bond may be combined. This opens up a route to *N*-heterocyclic ligands. Thus, the reaction of the dimethylamino(phenyl)allenylidene complex **2a** with (a) 1,1-dimethyl hydrazine affords the zwitterionic *N*-methylated pyrazolyl complex **26a**, and with (b) 1,2-dimethyl hydrazine the dimethyl dihydropyrazolidene complex **27a** (Scheme 23) [48].

In contrast, bis(aryl)allenylidene complexes add hydrazines to the C_α atom. The resulting alkenyl(hydrazino)carbene complexes obtained from bis(aryl)allenylidene complexes and 1,1-dimethyl hydrazine rapidly rearrange to give nitrile complexes and dimethylamine [47]. The addition of 1,2-disubstituted hydrazines to bis(aryl)allenylidene complexes yields *E*/*Z* mixtures of isolable alkenyl(hydrazino)carbene complexes. On heating, some of these adducts rearrange to give acrylamidine complexes. Acid-catalyzed, some of the *E* isomers are transformed by intramolecular cyclization into pyrazolidinylidene complexes [52].

As observed in the previous reactions, the amino group of benzamidine displaces the dimethylamino substituent in **2a** to form the amino(phenyl)allenylidene complex **28a** (Scheme 23). Although the allenylidene ligand in compound **28a** quickly cyclizes to give the pyrimidine-4-ylidene complex **29a**, intermediate **28a** can be detected by spectroscopic means [48]. The product obtained by substitution of benzamidine for the methoxy group in the dimethylamino(methoxy)allenylidene complex **21a** in almost quantitative yield is an isolable species. Cyclization is catalyzed by acids [53].

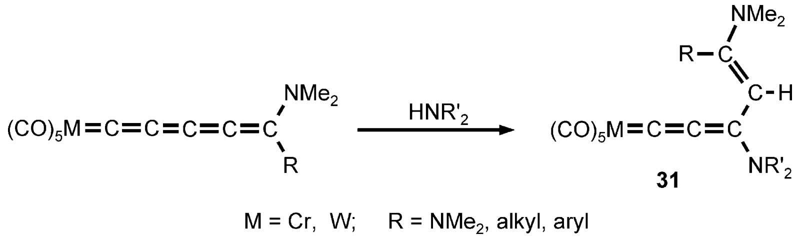


Scheme 23.

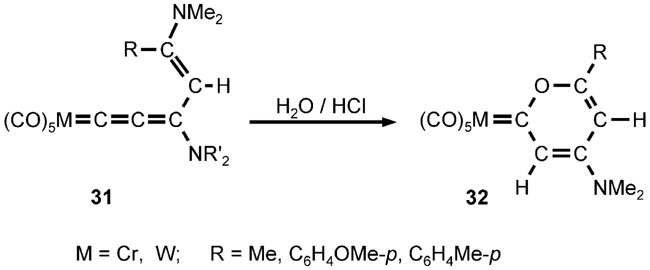
The formation of the pyrazolopyrimidin-7-ylidene complex **30a** (Scheme 23) from **2a** and dimethyl-(5-methyl-1*H*-pyrazol-3-yl)-amine presumably likewise starts with a nucleophilic addition of the heterocycle to the C_γ atom of **2a** followed by substitution of NMe_2 and intramolecular cyclization [51].

All these reactions are characterized by an initial attack of the *N*-nucleophile at the C_γ atom of the amino- or alkoxyallenylidene complexes whereas, in bis(aryl)allenylidene complexes, N–H compounds usually add to the C_α–C_β bond giving alkenyl(amino)carbene complexes. Obviously, replacing aryl group(s) by π-donor-substituents not only changes the bonding properties within the allenylidene moiety but also the regioselectivity of nucleophilic additions.

From DFT calculations, it follows that on extending the cumulene chain the energy of the LUMO decreases. Consequently, an increase in the nucleophilicity of the metallacumulenes is to be expected. The expectation is confirmed by the experimental results. When considering the distribution of the orbital coefficients the ad-



Scheme 24.



Scheme 25.

dition either to C_α, C_γ, or C_ε is to be expected. The orbital coefficients are very similar in extent. Whereas the bis(dimethylamino)allenylidene complexes **6a** and **6b** do not react with secondary amines, monoamino- as well as bis(dimethylamino)pentatetraenylidene complexes rapidly add HNR'_2 even at low temperature to give alkenyl(amino)allenylidene complexes (**31**) (Scheme 24) [23,27]. Until now, only compounds derived from a nucleophilic attack of the amine at the C_γ atom have been detected. Only C_γ–C_δ addition products have been isolated. The reaction is highly stereoselective. When dimethylamino(organyl)pentatetraenylidene complexes are employed, the formation of only the *E* isomer of **31** is observed (Scheme 24) [27].

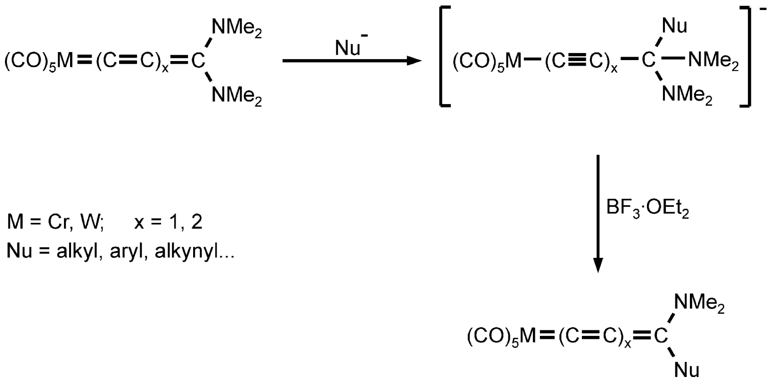
Addition of H_2O/HCl to solutions of **31** ($R' = Me$) affords the 4-amino-pyran-2-ylidene complexes **32** (Scheme 25) presumably by a sequence involving: (a) protonation of the C_β atom of the chain and formation of a cationic vinylidene complex; (b) addition of water to the C_α atom; (c) dimethylamine elimination; (d) cyclization, and deprotonation [27].

Heptahexaenylidene complexes, the higher homologues of pentatetraenylidene complexes, are even more reactive than pentatetraenylidene or allenylidene complexes. Complex $[(CO)_5W{=}C{=}C{=}C{=}C{=}C{=}C(NMe_2)_2]$ could only be generated in situ but could neither be isolated nor detected by spectroscopic means. Very likely, this was due to the rapid addition of dimethylamine, present in the reaction solution, to the C_ε atom. However, the follow-up product, alkenyl(dimethylamino)pentatetraenylidene complex **33**, was isolated in good yield [54].

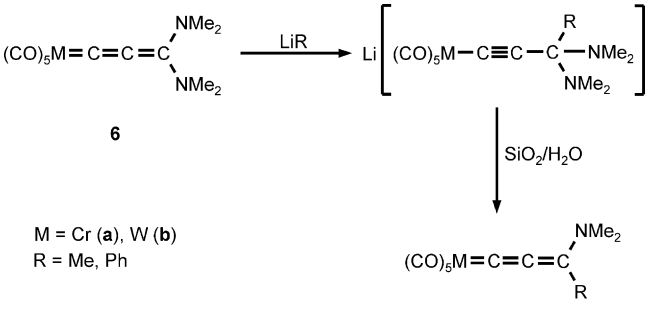
4.3. Reactivity towards C-nucleophiles

Anionic carbon nucleophiles readily add to the terminal carbon atom of **6** or **8** forming alkynylmetallates and diynylmetallates, respectively. These complexes can spectroscopically be detected. Treatment of the metallates with $BF_3\cdot OEt_2$ or SiO_2/H_2O effects the abstraction of one dimethylamido group (Scheme 26).

The overall sequence corresponds to the substitution of an organyl group for NMe_2. Such a transformation of an already existing cumulene ligand offers facile access to a great variety of N/C-substituted allenylidene as well as pentatetraenylidene complexes. Thus, also substitution patterns can be realized that are only difficult to obtain by other synthetic routes. In addition to aryl and alkyl groups, alkynyl fragments may also be introduced into the terminal position of the cumulene ligand [27], e.g. the reaction of **6** with methyllithium or phenyllithium followed by chromathography on silica yields dimethylamino(organyl)allenylidene complexes (Scheme 27).



Scheme 26.



Scheme 27.

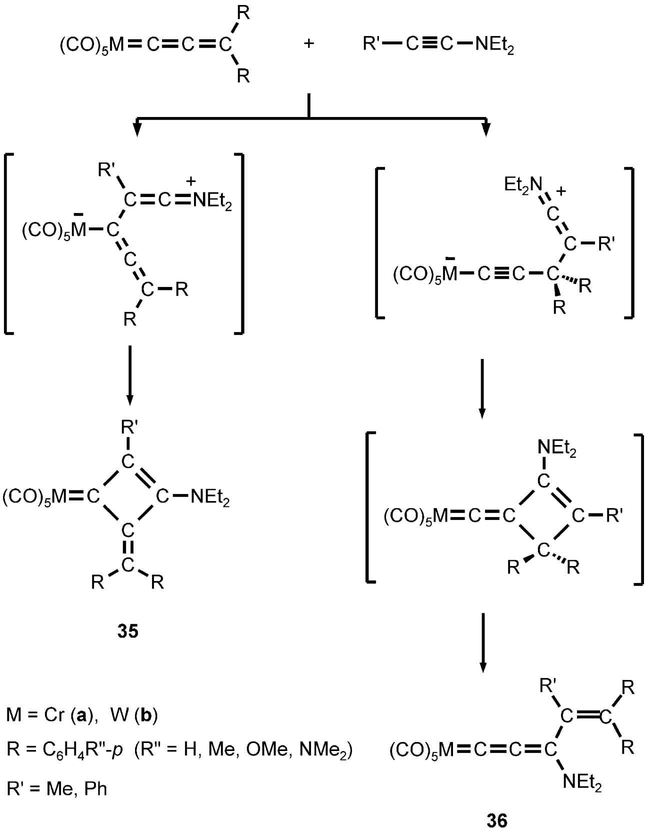
The analogous reaction sequence starting from bis(dimethylamino)pentatetraenylidene chromium and tungsten (**8**) and various organyl lithium compounds affords the mono(amino)pentatetraenylidene complexes **34** (Scheme 28). Until now, there are no other routes available for the synthesis of complexes of type **34** [27].

The addition of carbanions to the C_α atom (or the C_γ atom in pentatetraenylidene complexes) has not been observed.

Fischer type alkoxy(aryl)carbene pentacarbonyl complexes of chromium and tungsten add carbanions to the carbene carbon atom to give α-alkoxyalkyl or α-alkoxyaryl derivatives. On subsequent treatment of these metallates with acids or SiO_2/H_2O, bis(aryl)carbene complexes are formed by alcohol elimination [55,56]. In contrast, amino(aryl)carbene complexes do not add carbanions due to the reduced electrophilicity of the carbene carbon atom.

4.4. Derivatization by insertion of the CC triple bond of an ynamine into the C_β–C_γ (C_δ–C_ε) bond

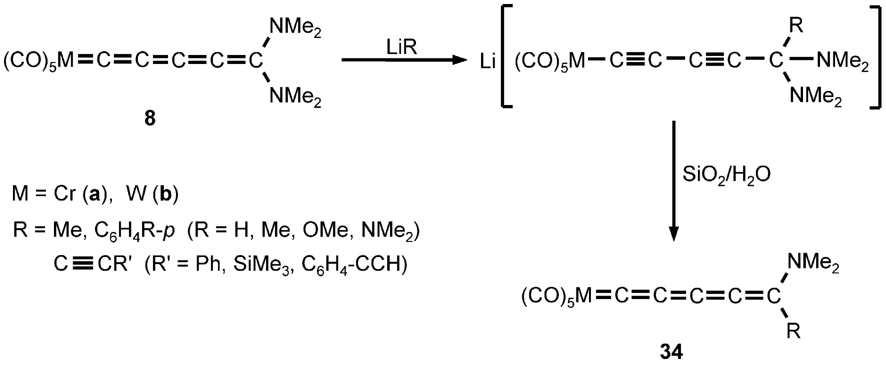
Fischer type carbene complexes of chromium and tungsten react with diethylaminopropyne by insertion of the CC triple bond into the metal-carbene bond and redistribution of the π-electrons to give alkenyl(amino)carbene complexes [57]. Based on a detailed kinetic study, a mechanism involving initial rate-determining nucleophilic attack of the ynamine at the carbene carbon atom was proposed [58].



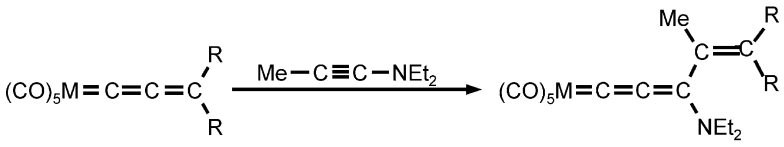
Scheme 29.

The reaction of bis(aryl)allenylidene complexes with diethylaminopropyne yields two products: cyclobutenylidene complexes (**35**) and alkenyl(amino)allenylidene complexes (**36**) (Scheme 29) [59]. The complexes **35** are formed by regiospecific cycloaddition of the ynamine to the C_α–C_β bond of the allenylidene ligand. Cycloaddition of the ynamine to the C_β–C_γ bond followed by cycloreversion afford the alkenyl(amino)allenylidene complexes **36**. The product ratio strongly depends on the solvent and the substituents R and R′. The ratio **36**/**35** increases with increasing donor propensity of R.

In contrast to bis(aryl)allenylidene complexes, only alkenyl(amino)allenylidene complexes are formed in the reactions of π-donor-substituted allenylidene complexes with ynamines (Scheme 30). Products derived from ad-



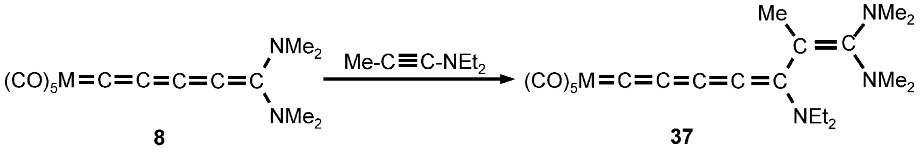
Scheme 28.



M = Cr, W

CR_2 = $C(NMe_2)Ph$, $C(NMe_2)OMe$, $C(NMe_2)_2$, C(OEt)Omenthyl

Scheme 30.



M = Cr (**a**), W (**b**)

Scheme 31.

dition to the C_α–C_β or M=C_α bond cannot be detected [48]. This is in accord with the observed shift towards formation of alkenyl(amino)allenylidene complexes when the electron-releasing properties of the substituents R in bis(aryl)allenylidene complexes are enhanced.

Like the reactions of π-donor-substituted allenylidene complexes with ynamines, those of aminopentatetraenylidene complexes also yield only one product formed via regioselective [2+2] cycloaddition of the CC triple bond to the C_δ–C_ε bond of the metallacumulene and subsequent cycloreversion (see e.g. Scheme 31) [32].

From the IR spectra, it follows that displacing one dimethylamino substituent in **8** by the $C(Me)=C(NMe_2)_2$ group in **37** leads to a pentatetraenylidene ligand with slightly enhanced donor properties. In accord with the conclusion the MLCT transition in the UV–vis spectrum of **37** is at higher energy than in **8** and the non-linear optical response increases by about 20% [32].

5. Summary

A broad spectrum of substitution patterns is now available for allenylidene carbonyl complexes of chromium and tungsten. Several strategies for the synthesis of such complexes have been developed. Through variation of the substituents at one end of the carbon chain and of the co-ligands of the metal carbonyl fragment, the bonding within the chain can be manipulated. Increasing the π-donor properties of the substituents gives rise to enhanced dipolarity of the complexes and to an increasing contribution of zwitterionic resonance forms to the overall bonding. In turn, increasing the back-bonding properties of the metal-ligand fragment through displacement of carbonyl ligands by phosphanes or by other donor ligands reduces the dipolarity and leads to increasing importance of the metallabutatriene resonance form of allenylidene complexes (or of the metallahexapentaene form of pentatetraenylidene complexes).

The thermal stability of these metallacumulenes increases with increasing tendency to transfer electron density to the metal-ligand fragment since the first reaction step in the decomposition of carbonyl complexes is usually the dissociation of a carbonyl ligand. The thermally most stable complexes are the bis(amino)- and aminoalkenyl(amino)-substituted metallacumulenes. This is true despite the results of DFT calculations indicating that the Cr=C bond dissociation energy decreases on introduction of amino substituents into $[(CO)_5Cr=(C=C=)_xCH_2]$.

The reactivity of these metallacumulenes decreases with increasing π-donor propensity of the substituents. The preferred site of attack in these metallacumulenes is the terminal carbon atom of the chain. Adducts may be obtained with many C-, N-, and P-nucleophiles. Depending on the nucleophile, follow-up reactions can lead to substitution products or to the formation of heterocyclic ligands thus considerably enlarge the scope of metallacumulenes available and the applicability of metallacumulenes for the synthesis of other complexes and of heterocyclic compounds.

References

[1] E.O. Fischer, A. Maasböl, Angew. Chem. 76 (1964) 645;
E.O. Fischer, A. Maasböl, Angew. Chem. Int. Ed. Engl. 3 (1964) 580.

[2] (a) C.P. Casey, T.J. Burkhardt, J. Am. Chem. Soc. 95 (1973) 5833;
(b) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, J. Am. Chem. Soc. 99 (1977) 2127;
(c) E.O. Fischer, W. Held, F.R. Kreißl, A. Frank, G. Huttner, Chem. Ber. 110 (1977) 656;
(d) C.P. Casey, S.W. Polichnowski, J. Am. Chem. Soc. 99 (1977) 6097;
(e) H. Fischer, S. Zeuner, K. Ackermann, J. Chem. Soc., Chem. Commun. (1984) 684.

[3] W. Petz, Iron Carbene Complexes, Springer-Verlag, 1993.

[4] (a) Selected reviews: K.H. Dötz, H. Fischer, P. Hofmann, F.R. Kreissl, U. Schubert, K. Weiss (Eds.), Transition Metal Carbene Complexes, Verlag Chemie, 1983. pp. 1.;
(b) K.H. Dötz, Angew. Chem. 96 (1984) 573;
K.H. Dötz, Angew. Chem. Int. Ed. Engl. 23 (1984) 587;
(c) M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411;
(d) D.F. Harvey, D.M. Sigano, Chem. Rev. 96 (1996) 271;
(e) L.S. Hegedus, Tetrahedron 53 (1997) 4105;
(f) R. Aumann, H. Nienaber, Adv. Organomet. Chem. 41 (1997) 163;
(g) W.D. Wulff, Organometallics 17 (1998) 3116;
(h) K.H. Dötz, P. Tomuschat, Chem. Soc. Rev. 28 (1999) 187;
(i) A. Meijere de, H. Schirmer, M. Duetsch, Angew. Chem. 112 (2000) 4124;
(j) A. Meijere de, H. Schirmer, M. Duetsch, Angew. Chem. Int. Ed. 39 (2000) 3964.
[5] R.R. Schrock, Dalton Trans. 18 (2001) 2541. Review.
[6] (a) For reviews see e.g.: R.H. Grubbs, in: K.H. Dötz, W. Hoffmann (Eds.), Organic Synthesis via Organometallics, vol. 3, Vieweg, 1991, pp. 1.;
(b) R. Beckhaus, C. Santamaría, J. Organomet. Chem. 617/618 (2001) 81.
[7] (a) S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 114 (1992) S3974;
(b) P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100;
(c) T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. 110 (1998) 2631;
T. Weskamp, W.C. Schattenmann, M. Spiegler, W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 37 (1998) 2490;
(d) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674;
(e) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 993.
[8] (a) M. Schuster, S. Blechert, Angew. Chem. 109 (1997) 2124;
(b) M. Schuster, S. Blechert, Angew. Chem. Int. Ed. Engl. 36 (1997) 2036;
(c) R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) 4413;
(d) R.H. Grubbs, S. Chang, Tetrahedron 54 (1998) S4413;
(e) S.K. Armstrong, J. Chem. Soc., Perkin Trans. 1 (1998) 371;
(f) R.R. Schrock, Tetrahedron 55 (1999) 8141;
(g) A. Fürstner, Angew. Chem. 112 (2000) 3140;
(h) A. Fürstner, Angew. Chem. Int. Ed. Engl. 39 (2000) 3012;
(i) M. Buchmeiser, Chem. Rev. 100 (2000) 1565;
(j) A.H. Hoveyda, R.R. Schrock, Chem. Eur. J. 7 (2001) 945;
(k) T.M. Trnka, R.H. Grubbs, Acc. Chem. Res. 34 (2001) 18;
(l) R.R. Schrock, A.H. Hoveyda, Angew. Chem. 115 (2003) 4740;
(m) R.R. Schrock, A.H. Hoveyda, Angew. Chem. Int. Ed. 42 (2003) 4592;
(n) S.J. Connon, S. Blechert, Angew. Chem. 115 (2003) 1944;
(o) S.J. Connon, S. Blechert, Angew. Chem. Int. Ed. 42 (2003) 1900. For reviews see e.g..
[9] B. Alcaide, P. Almendros, Chem. Eur. J. 9 (2003) 1259. Review.
[10] (a) E.O. Fischer, H.-J. Kalder, A. Frank, F. Herwig Köhler, G. Huttner, Angew. Chem. 88 (1976) 683;
E.O. Fischer, H.-J. Kalder, A. Frank, F. Herwig Köhler, G. Huttner, Angew. Chem. Int. Ed. Engl. 15 (1976) 623.
[11] (a) H. Berke, Angew. Chem. 88 (1976) 684;
H. Berke, Angew. Chem. Int. Ed. Engl. 15 (1976) 624.
[12] (a) M.I. Bruce, A.G. Swincer, Adv. Organomet. Chem. 22 (1983) 59;
(b) M.I. Bruce, Chem. Rev. 91 (1991) 197;
(c) M.I. Bruce, Chem. Rev. 98 (1998) 2797. For reviews see;
(d) V. Cadierno, M. Pilar Gamasa, J. Gimeno, Eur. J. Inorg. Chem. (2001) 571.
[13] J.P. Selegue, Organometallics 1 (1982) 217.
[14] H. Berke, P. Härter, G. Huttner, L. Zsolnai, Chem. Ber. 115 (1982) 695.
[15] H. Fischer, D. Reindl, G. Roth, Z. Naturforsch. 49b (1994) 1207.
[16] R. Aumann, B. Jasper, R. Fröhlich, Organometallics 14 (1995) 3173.
[17] M. Duetsch, F. Stein, R. Lackmann, E. Pohl, R. Herbst-Irmer, A. de Meijere, Chem. Ber. 125 (1992) 2051.
[18] F. Stein, M. Duetsch, M. Noltemeyer, A. de Meijere, Syn. Lett. (1993) 486.
[19] F. Stein, M. Duetsch, E. Pohl, R. Herbst-Irmer, A. de Meijere, Organometallics 12 (1993) 2556.
[20] R. Aumann, Chem. Ber. 127 (1994) 725.
[21] R. Aumann, Chem. Ber. 125 (1992) 2773.
[22] G. Roth, H. Fischer, unpublished results.
[23] G. Roth, H. Fischer, Organometallics 15 (1996) 1139.
[24] H. Fischer, N. Szesni, G. Roth, N. Burzlaff, B. Weibert, J. Organomet. Chem. 683 (2003) 301.
[25] N. Szesni, A. Weyh, H. Fischer, unpublished results.
[26] J.W. Munson, in: S. Patai (Ed.), The Chemistry of Ketenes, Allenes, and Related Compounds, Wiley, Chichester, 1980.
[27] M. Dede, H. Fischer, unpublished results.
[28] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165. The Hammett constants σ_p were taken from.
[29] R.F. Winter, S. Hartmann, S. Zális, K.W. Klinkhammer, Dalton Trans. (2003) 2342.
[30] M. Oki, Application of Dynamic NMR Spectroscopy to Organic Chemistry, VCH, Deerfield Beach, 1985.
[31] L.M. Jackman, F.A. Cotton (Eds.), Dynamic Nuclear Magnetic Resonance Spectroscopy, Academic Press, New York, 1975.
[32] G. Roth, H. Fischer, T. Meyer-Friedrichsen, J. Heck, S. Houbrechts, A. Persoons, Organometallics 17 (1998) 1511.
[33] N. Szesni, B. Weibert, H. Fischer, unpublished results.
[34] N. Re, A. Sgamellotti, C. Floriani, Organometallics 19 (2000) 1115.
[35] A. Marrone, N. Re, Organometallics 21 (2002) 3562.
[36] E. Hübner, H. Fischer, unpublished results.
[37] (a) H. Berke, P. Härter, G. Huttner, L. Zsolnai, Z. Naturforsch. 36 (1981) 929;
(b) V. Cadierno, M.P. Gamasa, J. Gimeno, M.C. López-Gonzáles, J. Borge, S. García-Granda, Organometallics 16 (1997) 4453;
(c) M.A. Esteruelas, F.J. Lahoz, M. Martin, E. Onate, L.A. Oro, Organometallics 16 (1997) 4572;
(d) M.A. Esteruelas, A.V. Gómez, A.M. López, J. Modrego, E. Onate, Organometallics 17 (1998) 5434;
(e) M.I. Bruce, B.W. Skelton, A.H. White, N.N. Zaitseva, J. Chem. Soc., Dalton Trans. (2000) 881.;
(f) B. Weberndörfer, H. Werner, Dalton Trans. (2002) 1479;
(g) M. Peruzzini, P. Barbaro, V. Bertolasi, C. Bianchini, I. Rios de los, N. Mantovani, L. Martelli, R. Rossi, Dalton Trans. 21 (2003) 4121. Representative examples include.
[38] H. Fischer, D. Reindl, C. Troll, F. Leroux, J. Organomet. Chem. 490 (1995) 221.
[39] N. Szesni, B. Weibert, H. Fischer, Inorg. Chim. Acta 357 (2004) 1789
[40] (a) F.R. Kreißl, C.G. Kreiter, E.O. Fischer, Angew. Chem. 84 (1972) 679;
F.R. Kreißl, C.G. Kreiter, E.O. Fischer, Angew. Chem. Int. Ed. Engl. 11 (1972) 643;
(b) F.R. Kreißl, E.O. Fischer, C.G. Kreiter, H. Fischer, Chem. Ber. 106 (1973) 1262;
(c) H. Fischer, E.O. Fischer, C.G. Kreiter, Chem. Ber. 107 (1974) 2459.
[41] H. Fischer, J. Organomet. Chem. 170 (1979) 309.
[42] (a) H. Werner, H. Rascher, Inorg. Chim. Acta 2 (1968) 181;
(b) E.O. Fischer, H. Fischer, H. Werner, Angew. Chem. 84 (1972) 682;
E.O. Fischer, H. Fischer, H. Werner, Angew. Chem. Int. Ed. Engl. 11 (1972) 644;
(c) E.O. Fischer, H. Fischer, Chem. Ber. 107 (1974) 657.
[43] (a) H. Fischer, E.O. Fischer, Chem. Ber. 107 (1974) 673;
(b) H. Fischer, E.O. Fischer, H. Werner, J. Organomet. Chem. 73 (1974) 331.

[44] J.C. Evans, J.K. Wilmhurst, H.J. Bernstein, Can. J. Chem. 34 (1956) 1139.
[45] P. Langer, M. Döring, D. Seyferth, H. Görls, Chem. Eur. J. 7 (2001) 573.
[46] N. Mantovani, L. Marvelli, R. Rossi, V. Bertolasi, C. Bianchini, I. de los Rios, M. Peruzzini, Organometallics 21 (2002) 2382.
[47] H. Fischer, G. Roth, D. Reindl, C. Troll, J. Organomet. Chem. 454 (1993) 133.
[48] N. Szesni, H. Fischer, unpublished results.
[49] U. Klabunde, E.O. Fischer, J. Am. Chem. Soc. 89 (1967) 7141.
[50] H. Werner, E.O. Fischer, B. Heckl, C.G. Kreiter, J. Organomet. Chem. 28 (1971) 367.
[51] G. Roth, N. Szesni, H. Fischer, unpublished results.
[52] H. Fischer, G. Roth, J. Organomet. Chem. 490 (1995) 329.
[53] M. Drexler, H. Fischer, unpublished results.
[54] G. Roth, H. Fischer, Organometallics 15 (1996) 5766.
[55] (a) C.P. Casey, T.J. Burkhardt, J. Am. Chem. Soc. 95 (1973) 5833; (b) C.P. Casey, T.J. Burkhardt, C.A. Bunnell, J.C. Calabrese, J. Am. Chem. Soc. 99 (1977) 2127.
[56] (a) E.O. Fischer, W. Held, F.R. Kreißl, A. Frank, G. Huttner, Chem. Ber. 110 (1977) 656;
(b) E.O. Fischer, W. Held, F.R. Kreißl, Chem. Ber. 110 (1977) 3842.
[57] (a) K.H. Dötz, C.G. Kreiter, J. Organomet. Chem. 99 (1975) 309;
(b) K.H. Dötz, Chem. Ber. 110 (1977) 78. First reports.
[58] H. Fischer, K.H. Dötz, Chem. Ber. 113 (1980) 193.
[59] G. Roth, D. Reindl, M. Gockel, C. Troll, H. Fischer, Organometallics 17 (1998) 1393.