ELSEVIER

Journal of Organometallic Chemistry 491 (1995) 47–55

Journal of Organometallic Chemistry

Chromium–carbon multiple bonds: aminocarbyne complexes of chromium bearing isocyanide ligands

Alexander C. Filippou *, Christian Mehnert, Klaus M.A. Wanninger, Matthias Kleine

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Received 12 July 1994; in revised form 31 August 1994

Abstract

High yield syntheses of neutral and cationic aminocarbyne complexes of chromium-bearing isocyanide ligands are reported. Neutral complexes of the type $Br(CO)_2(RNC)_2Cr{\equiv}CN^iPr_2$($R = Et$ (**3a**); $R = {}^tBu$ (**3b**)) are obtained from $Br(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (**2**) (pic = γ-picoline) by exchange of the γ-picoline ligands with RNC. Complex **3b** reacts with ^tBuNC in toluene at 60°C to give the monocarbonyl derivative $Br(CO)(^tBuNC)_3Cr{\equiv}CN^iPr_2$ (**4b**). Formation of cationic aminocarbyne complexes is favoured in polar solvents as demonstrated by the reaction of **3a** or **3b** with RNC in refluxing CH_2Cl_2, which leads exclusively to $[(RNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ ($R = Et$ (**5a**); $R = {}^tBu$ (**5b**)). Thermal decarbonylation of **5b** with ^tBuNC in refluxing tetrahydrofuran (THF) affords the cationic aminocarbyne complex $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ (**7b**). Similarly, **3b** is converted with $TlPF_6$ and ^tBuNC to $[(^tBuNC)_3(CO)_2Cr{\equiv}CN^iPr_2]PF_6$ (**6b**), which reacts with ^tBuNC in refluxing THF to give $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]PF_6$ (**7b'**).

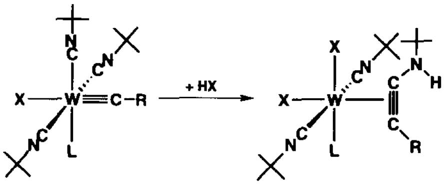
Keywords: Chromium; Aminocarbyne complexes; Isocyanides; Multiple bonds

---

1. Introduction

Carbyne–isocyanide coupling was first observed by Fischer and coworkers [1] in the reaction of the low valent manganese carbyne complex $[Cp(CO)_2Mn{\equiv}CPh]BCl_4$ with ^tBuNC to give the ketene iminyl complex $[Cp(CO)_2Mn[C(CN^tBu)Ph]]BCl_4$. Later, Green and coworkers [2] demonstrated coupling of a carbyne ligand with two isocyanides in the reactions of the low valent molybdenum carbyne complexes $Cp[P(OMe)_3]_2Mo{\equiv}CCH_2R$ ($R = CMe_3$ or $CHMe_2$) with 2,6-xylyl isocyanide to afford the bis(imino)allyl complexes $Cp(R'NC)_2Mo[R'NCC(CH_2R)CNR']$ ($R' = 2,6\text{-}C_6H_3Me_2$).

We have recently shown that low valent molybdenum and tungsten carbyne complexes of the type $X(CO)_n(^tBuNC)_{4-n}M{\equiv}CR$ (X = Br or I; $n = 0$–2; R = Ph or NEt_2) and $[(RNC)_5M{\equiv}CN(R)Et]BF_4$ (R = Et or ^tBu) undergo with Brönsted acids HX a carbyne–isocyanide coupling reaction to afford the aminoalkyne complexes $(X)_2(CO)_n(^tBuNC)_{3-n}M[\eta^2-RC{\equiv}CN(H)^tBu]$ and $[X(RNC)_4M[\eta^2-Et(R)NC{\equiv}CN(H)R]]BF_4$ respectively [3]:



(1)

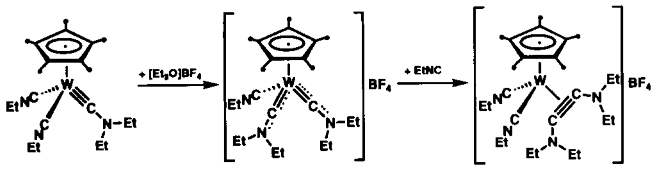
X = Br, I; R = Ph, NEt_2; L = CO, ^tBuNC

The reverse of this reaction, i.e. base-induced cleavage of an aminoalkyne to a carbyne and an isocyanide ligand, could be also demonstrated [4]. Subsequent studies revealed that the acid-induced carbyne–isocyanide coupling reaction follows a different pathway from the well-known nucleophile- or photochemical-induced carbyne–carbonyl coupling reaction of low valent metal carbyne complexes to form η^2-ketenyl complexes [5]. In the first step, protonation of the carbyne complex occurs at the carbyne-carbon to give a carbene complex [6]. Proton transfer is then assumed to

---

[*] Corresponding author. Present address: Institut für Anorganische und Allgemeine Chemie, Humboldt-Universität zu Berlin, Hessische Straße 1-2, D-10115 Berlin, Germany.

SSDI 0022-328X(94)05208-5



Scheme 1.

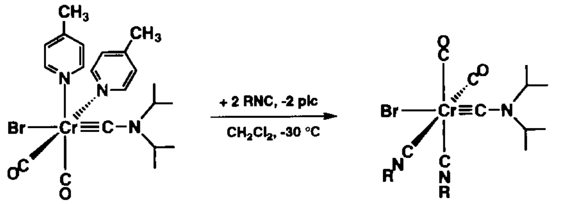
occur from the carbene–carbon to the nitrogen atom of an adjacent isocyanide ligand to afford a bis-carbyne intermediate, which gives by coupling of the two carbyne ligands the aminoalkyne complex [3b,3c,6]. These and related studies on coupling reactions of terminal two-faced π-acceptor ligands [3,5–7] have prompted us to isolate first mononuclear tungsten bis-aminocarbyne complexes of the type [Cp*(RNC)W(≡CN(R)Et)(≡CNEt$_2$)]BF$_4$ (R = Et or ^{t}Bu) and to demonstrate carbyne–carbyne coupling in these compounds by the addition of nucleophiles or oxidants (Scheme 1) [8]. The experimental work was recently supported by extended Hückel calculations illustrating the effect of a π-donor substituent at the carbyne carbon on the stability of the bis-carbyne complexes relative to the alkyne coupling products [9].

Given the well-known differences between the chemistry of complexes of a first-row transition metal compared with those of a second- or third-row transition metal, we were interested to examine whether we would be able to extend this C$_1$ + C$_1$-ligand coupling chemistry of molybdenum and tungsten to the lighter congener chromium. We therefore set out to prepare suitable precursors for such coupling reactions and report here efficient methods for the synthesis of chromium aminocarbyne complexes containing isocyanide ligands [10].

2. Results and discussion

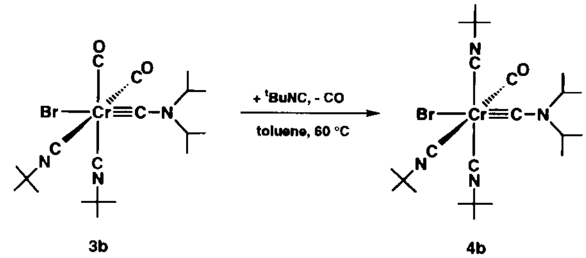
We have earlier reported that tungsten aminocarbyne complexes of the type I(CO)$_n$(^{t}BuNC)$_{4-n}$W≡CNEt$_2$ (n = 0–2) and [(^{t}BuNC)$_{5-n}$(CO)$_n$W≡CNEt$_2$]I (n = 0, 1) can be prepared with a high yield starting from W(CO)$_6$ [11]. The synthetic procedure involved a stepwise transformation of W(CO)$_6$ to the aminocarbyne complex I(CO)$_2$(py)$_2$W≡CNEt$_2$ (py = pyridine) followed by ligand substitution reactions of the latter with tert-butyl isocyanide. Application of the same methodology to the preparation of related chromium complexes looked promising, since analogous chromium aminocarbyne complexes of the type X(CO)$_2$(pic)$_2$Cr≡CN^{i}Pr$_2$ (X = Cl or Br; pic = γ-picoline) have been recently obtained from Cr(CO)$_6$ with a high yield and have been shown to be quite reactive owing to the presence of two coordinatively labile γ-picoline ligands [12].

Indeed, when a solution of Br(CO)$_2$(pic)$_2$Cr≡CN^{i}Pr$_2$ (**2**) in CH$_2$Cl$_2$ was treated at −30°C with two equivalents of ethyl or tert-butyl isocyanide, a rapid ligand exchange reaction occurred, accompanied by a colour change from red to orange, to give Br(CO)$_2$(RNC)$_2$Cr≡CN^{i}Pr$_2$ (R = Et (**3a**); R = ^{t}Bu (**3b**)):

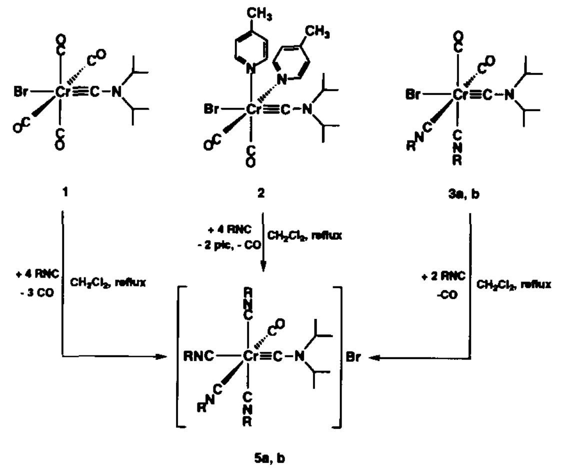


2 **3a, b** (2)

Evidence for the clean conversion of **2** to **3a** and **3b** was given by the IR spectra of the reaction solutions, which revealed (a) that the two ν(CO) absorptions of the starting material at 1958 and 1866 cm^{-1} had been replaced at the end of the reaction by those of the products at 1990 and 1923 cm^{-1} (**3a**) and 1988 and 1922 cm^{-1} (**3b**) and (b) the presence of two new ν(C≡NR) absorptions at 2179 and 2158 cm^{-1} (**3a**) and 2166 and 2143 cm^{-1} (**3b**). After filtration of the solutions over a short layer of silica, **3a** and **3b** were isolated as orange–yellow, slightly air-sensitive microcrystalline solids with 97 and 90% yields respectively. They are soluble in CH$_2$Cl$_2$, tetrahydrofuran (THF) and toluene, moderate soluble in Et$_2$O, but insoluble in n-pentane; they melt, when heated in a sealed capillary under nitrogen, at 76°C (**3a**) and 94°C (**3b**) without decomposition. Complex **3b** shows remarkable thermal stability as evidenced by a thermogravimetry (TG)–mass spectroscopy (MS) analysis, which indicates decomposition at 140°C (extrapolated onset). However, both compounds decompose slowly in solution at room temperature to give a mixture of products. If this thermal decomposition is carried out in the presence of isocyanide, then selective formation of neutral or ionic CO substitution products is observed depending on the reaction conditions. Thus treatment of **3b** with slightly more than one equivalent of tert-butyl isocyanide in toluene at 60°C afforded the neutral aminocarbyne complex Br(CO)(^{t}BuNC)$_3$Cr≡CN^{i}Pr$_2$ (**4b**):



3b **4b** (3)



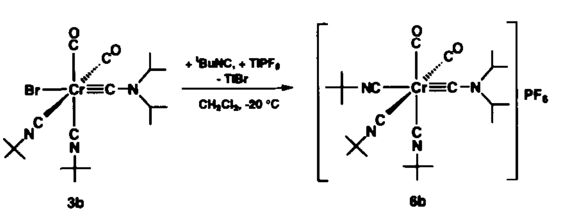
Scheme 2.

Compound **4b** was isolated as a yellow air-sensitive solid with a 71% yield. It is soluble in THF, toluene and Et_2O but sparingly soluble in n-pentane and decomposes at 127°C, when heated in a sealed capillary under nitrogen. The reaction of **3b** with ^tBuNC to give **4b** was accompanied by the formation of a minor amount of a red solid, which was readily separated from **4b** owing to its insolubility in Et_2O and shown on the basis of its IR and ^1H NMR spectral data to be a mixture of the cationic aminocarbyne complexes $[(^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (**5b**) and $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ (**7b**).

The reaction of **3a** and **3b** with slightly more than two equivalents of RNC in refluxing CH_2Cl_2 afforded selectively the cationic aminocarbyne complexes $[(RNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (R = Et (**5a**); R = ^{t}Bu (**5b**)) (Scheme 2). Alternatively, **5a** and **5b** could be obtained with an essentially quantitative yield, when $Br(CO)_4Cr{\equiv}CN^iPr_2$ (**1**) or $Br(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (**2**) were reacted with four equivalents of RNC in refluxing CH_2Cl_2 (Scheme 2).

Compounds **5a** and **5b** were isolated as rose-coloured, moderately air-sensitive solids, that are soluble in CH_2Cl_2 but insoluble in THF and toluene. They decompose, when heated in a sealed capillary under nitrogen, at 95 and 140°C respectively.

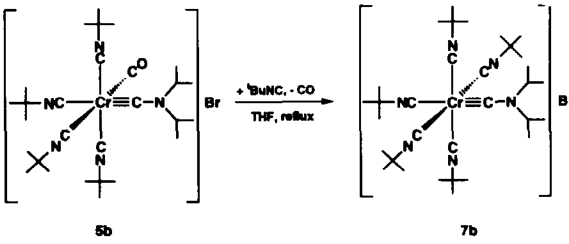
The reaction of **3b** with ^tBuNC to afford **5b** proceeds in two steps. In the first step the bromo ligand in **3b** is replaced by the isocyanide to give the ionic dicarbonyl complex $[(^tBuNC)_3(CO)_2Cr{\equiv}CN^iPr_2]Br$ (**6b′**). This is followed by a carbonyl–isocyanide exchange reaction of **6b′** to afford **5b**. Evidence for this pathway was given by the IR spectra of the reaction solutions, which showed increases in two new $\nu(CO)$ absorptions at 1998 and 1937 cm^{-1}, well separated in position from those of the starting material **3b** and the product **5b**. These absorptions are assigned to the *cis*-oriented carbonyl ligands of **6b′** on the basis of the IR spectral data of the analogous PF_6 salt $[(^tBuNC)_3(CO)_2Cr{\equiv}CN^iPr_2]PF_6$ (**6b**). The latter was selectively formed, when **3b** was treated with slightly more than one equivalent of $TlPF_6$ and ^tBuNC in CH_2Cl_2 at −20°C and isolated as an orange, slightly air-sensitive solid with a 85% yield:



(4)

Complex **6b** is soluble in CH_2Cl_2, THF and 1,2-dimethoxyethane (DME) and decomposes, when heated in a sealed capillary under nitrogen, at 138°C.

Complexes **5b** and **6b** are convenient starting materials for the synthesis of carbonyl-free substitution products. Thus treatment of **5b** with ^tBuNC in refluxing THF afforded selectively the aminocarbyne complex $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ (**7b**), which was isolated as a purple–brown, slightly air-sensitive solid with a 81% yield:



(5)

Complex **7b** is soluble in CH_2Cl_2, sparingly soluble in DME and THF and decomposes according to a TG–MS analysis at 128°C (extrapolated onset) under evolution of isobutene and HCN (Fig. 1).

Similarly, reaction of **6b** with more than two equiva-

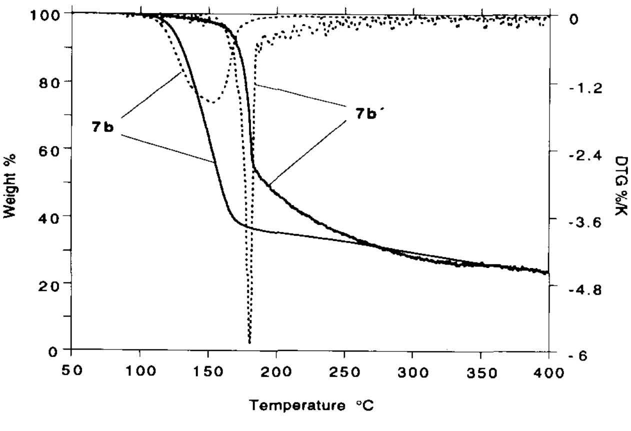
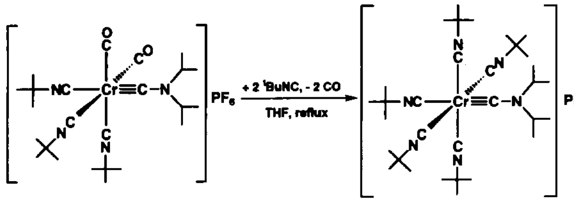


Fig. 1. TG and differential TG curves of **7b** and **7b′**.

lents of ^{t}BuNC resulted in the formation of the analogous PF_6 salt [(^{t}BuNC)$_5$Cr≡CN^{i}Pr$_2$]PF_6 (**7b′**):



6b **7b′** (6)

Again IR monitoring of this reaction revealed a clean conversion of **6b** to **7b′**, which was isolated as a purple-brown solid, soluble in CH_2Cl_2, THF and DME. Complex **7b′** is thermally more stable than **7b** as evidenced by a TG–MS analysis, which indicates decomposition at 175°C (extrapolated onset) under evolution of isobutene and HCN (Fig. 1).

3. Spectroscopic investigations

3.1. IR, ^{1}H NMR and ^{13}C NMR spectra

The solution IR spectra of **3a**–**7b′** reveal in the region 2200–1500 cm^{-1} characteristic ν(C≡NR), ν(CO) and $\nu(C_{carbyne} \overset{..}{-} N)$ absorptions of the coordinated isocyanide, carbonyl and aminocarbyne ligands respectively (Table 1). The number and relative intensities of the ν(C≡NR) and ν(CO) absorptions indicate the relative positions of the isocyanide and carbonyl ligands in the octahedral complexes. Thus two ν(C≡NR) and two ν(CO) absorptions of almost equal intensity are observed in the IR spectra of **3a** and **3b**, suggesting a *cis* arrangement of the two isocyanide and carbonyl ligands respectively. Similarly, the *cis*-oriented carbonyl ligands in **6b** give rise to two strong ν(CO) absorptions in CH_2Cl_2 at 2000 and 1940 cm^{-1}. In comparison, **5a** and **5b** exhibit four ν(C≡NR) absorptions as expected on the basis of group theory for an $M(CNR)_4$ fragment of local C_{2v} symmetry [13]. A comparison of the IR data of **3a** and **3b** with those of **4b** and of **5a** and **5b** with those of **7b** shows a decrease in the ν(C≡NR) and ν(CO) frequencies upon replacement of the carbonyl ligands by the weaker π-acceptor ligands EtNC and ^{t}BuNC. This decrease is a consequence of the higher electron density at the metal centre, which results in a stronger metal–isocyanide and metal–carbonyl back bonding (Table 1) [14].

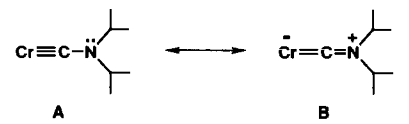


Fig. 2. Resonance forms for the metal–amine–carbyne bond in **3a**–**7b′**.

The aminocarbyne complexes **3a**–**7b′** are distinguished by an absorption in the range 1570–1505 cm^{-1}, which is assigned to the $\nu(C_{carbyne} \overset{..}{-} N)$ vibration [8a,9–11]. The fairly high frequency of this absorption reveals extensive π donation by the nitrogen lone pair into one of the two carbyne-carbon p orbitals, which is represented in valence bond terms by the canonical form B (Fig. 2).

A comparison of the aminocarbyne complexes **3a** and **3b** with **4b** or **6b** with **5b** and **7b** reveals that the $\nu(C_{carbyne} \overset{..}{-} N)$ absorption is shifted to lower wavenumbers as the electron density at the metal centre is increased [9,11,12]. Moreover the $\nu(C_{carbyne} \overset{..}{-} N)$ absorption of the chromium complexes **3a**–**7b′** is observed at a lower frequency than that of analogous tungsten compounds (e.g. $\nu(C_{carbyne} \overset{..}{-} N)$ of Br(CO)$_2$(^{t}BuNC)$_2$-W≡CN^{i}Pr$_2$ in CH_2Cl_2, 1539 cm^{-1}; $\nu(C_{carbyne} \overset{..}{-} N)$ of Cl(CO)(^{t}BuNC)$_3$W≡CN^{i}Pr$_2$ in Et_2O, 1527 cm^{-1}) [15].

Further support for the structures assigned to **3a**–**7b** is given by the ^{1}H NMR spectra (Table 2). Thus one doublet resonance and one septet resonance are observed for the methyl and the methine protons of the aminocarbyne ligand, indicating rapid rotation of the

Table 1
ν(C≡NR), ν(CO) and $\nu(C_{carbyne}-N)$ absorptions of **3a**–**7b′**.

Complex	ν(C≡NR) (cm^{-1})	ν(CO) (cm^{-1})	$\nu(C_{carbyne}-N)$ (cm^{-1})	Solvent
Br(CO)$_2$(EtNC)$_2$Cr≡CN^{i}Pr$_2$ (**3a**)	2197 w, sh, 2179 s, 2158 s	1990 vs, 1923 vs	1535 m, 1527 m	CH_2Cl_2
Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CN^{i}Pr$_2$ (**3b**)	2166 s, 2143 s	1988 vs, 1922 vs	1536 m, 1525 m	CH_2Cl_2
	2160 s, 2134 s	1989 vs, 1929 vs	1522 s	Toluene
Br(CO)(^{t}BuNC)$_3$Cr≡CN^{i}Pr$_2$ (**4b**)	2141 sh, 2110 s, 2076 m	1904 vs	1506 m	Toluene
	2136 sh, 2109 s, 2074 m	1911 vs	1506 m	Et_2O
[(EtNC)$_4$(CO)Cr≡CN^{i}Pr$_2$]Br (**5a**)	2200 m, 2186 m, 2145 vs, 2105 w	1910 s	1550 m	CH_2Cl_2
[(^{t}BuNC)$_4$(CO)Cr≡CN^{i}Pr$_2$]Br (**5b**)	2177 s, 2154 w, 2123 vs, 2063 w	1910 vs	1549 m	CH_2Cl_2
	2174 m, 2156 w, 2121 vs, 2062 w	1909 vs	1551 m	DME
[(^{t}BuNC)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$]PF_6 (**6b**)	2186 s, 2170 m, 2149 m	2000 vs, 1940 vs	1566 m	CH_2Cl_2
	2185 s, 2169 m, 2153 m	1992 vs, 1934 vs	1569 m	THF
[(^{t}BuNC)$_5$Cr≡CN^{i}Pr$_2$]Br (**7b**)	2164 s, 2131 w,sh, 2093 vs, 2042 vs	–	1522 m	CH_2Cl_2
[(^{t}BuNC)$_5$Cr≡CN^{i}Pr$_2$]PF_6 (**7b′**)	2163 s, 2032 w,sh, 2093 vs, 2040 vs	–	1522 m	THF

Table 2
^{1}H NMR data for **3a**–**7b** (relative intensities, multiplicities and coupling constants in parentheses)

Complex	(ppm)					
	N(CHMe_2)$_2$	Me_3CNC; CH_3CH$_2$NC	N(CHMe$_2$)$_2$	CH$_3$CH_2NC	Solvent	T (°C)
3a	1.33 (12, d, ^3J(HH) = 6.4 Hz)	1.39 (6, t, ^3J(HH) = 7.0 Hz)	3.10 (2, sept, ^3J(HH) = 6.4 Hz)	3.69 (4, q, ^3J(HH) = 7.0 Hz)	CD$_2$Cl$_2$	20
3b	1.35 (12, d, ^3J(HH) = 6.4 Hz)	1.49 (18, s)	3.10 (2, sept, ^3J(HH) = 6.4 Hz)	–	CD$_2$Cl$_2$	20
4b	1.25 (12, d, ^3J(HH) = 6.6 Hz)	1.10 (9, s); 1.16 (18, s)	2.60 (2, sept, ^3J(HH) = 6.6 Hz)	–	C$_7$D$_8$	20
5a	1.37 (12, d, ^3J(HH) = 6.7 Hz)	1.39 (9, t, ^3J(HH) = 7.0 Hz) [a], 1.42 (3, t, ^3J(HH) = 7.0 Hz) [b]	3.21 (2, sept, ^3J(HH) = 6.7 Hz)	3.62 (2, q, ^3J(HH) = 7.0 Hz), 3.72 (6, q, ^3J(HH) = 7.0 Hz) [a]	CD$_2$Cl$_2$	20
5b	1.39 (12, d, ^3J(HH) = 6.7 Hz)	1.44 (9, s); 1.48 (18, s); 1.51 (9, s) [b]	3.19 (2, sept, ^3J(HH) = 6.7 Hz)	–	CD$_2$Cl$_2$	20
6b	1.41 (12, d, ^3J(HH) = 6.7 Hz)	1.49 (18, s); 1.52 (9, s)	3.31 (2, sept, ^3J(HH) = 6.7 Hz)	–	CD$_2$Cl$_2$	0
7b	1.35 (12, d, ^3J(HH) = 6.7 Hz)	1.42 (36, s); 1.49 (9, s)	3.10 (2, sept, ^3J(HH) = 6.7 Hz)	–	CD$_2$Cl$_2$	20

[a] Signals of the ethyl isocyanide ligands, which are oriented *cis* relative to the aminocarbyne ligand, are by accident coincident.

[b] Signal of the isocyanide ligand, which is oriented *trans* relative to the aminocarbyne ligand.

diisopropylamino group about the $C_{carbyne}$–N bond on the NMR time scale. In addition, the ^{1}H NMR spectra of **3a** and **3b** reveal equivalent isocyanide ligands, as evidenced by the one triplet resonance and one quartet resonance observed for the methyl and methylene protons of the ethyl isocyanide ligands in **3a** or the one singlet resonance found for the tert-butyl isocyanide ligands in **3b**. They show, in connection with the IR and ^{13}C NMR data of **3a** and **3b**, unequivocally a *trans* orientation of the bromo and the aminocarbyne ligand in these compounds. In comparison, the ^{1}H NMR spectrum of **5b** displays three singlet resonances for the tert-butyl isocyanide ligands in the ratios 1:2:1, suggesting in accordance with the IR data, a *cis* orientation of the carbonyl and the aminocarbyne ligand in this compound. The lower field resonance ($\delta = 1.51$ ppm) is assigned to the tert-butyl isocyanide ligand, which is located *trans* relative to the aminocarbyne ligand. This assignment is supported by the ^{1}H NMR spectra of **6b** and **7b**, which reveal that the tert-butyl protons of the *trans*-oriented isocyanide ligand (relative to the aminocarbyne ligand) are more deshielded (**6b**, $\delta = 1.52$ ppm; **7b**, $\delta = 1.49$ ppm) than those of the two or four equivalent *cis*-oriented isocyanide ligands (**6b**, $\delta = 1.49$ ppm; **7b**, $\delta = 1.42$ ppm). By analogy, the lower field triplet resonance of **5a** at $\delta = 1.42$ ppm is assigned to the methyl protons of the *trans*-oriented ethyl isocyanide ligand (relative to the aminocarbyne ligand) (Table 2).

The ^{13}C NMR spectra also support the structures proposed for **3a–7b** (Table 3). Thus only one resonance is observed for the two carbonyl ligands of **6b**. This shows, in combination with the IR data, unequivocally a facial arrangement of the three tert-butyl isocyanide ligands in this compound. A small downfield shift of the carbonyl resonance is observed on going from the dicarbonyl complexes **3a** and **3b** to the more electron-rich monocarbonyl derivative **4b**, or the dicarbonyl complex **6b** to the monocarbonyl derivatives **5a** and **5b**. This trend is consistent with previous NMR studies on carbonyl complexes of Group 6 transition metals, which have shown that a stronger metal–carbonyl back bonding causes a deshielding of the carbonyl-carbon [16]. The same trend is observed for the metal-bound isocyanide–carbon resonances [9,17] and allows, in combination with the signal intensity, an unequivocal assignment of the three isocyanide–carbon resonances of **5a** and **5b** at $\delta = 157.8$, 166.4, 170.2 and 157.7, 166.4 and 170.3 ppm respectively (i.e. the metal-bound carbon of the isocyanide ligand, which is located *trans* to the strongest π-acceptor ligand, is the most shielded) (Table 3). The primary and tertiary carbon atoms of the isocyanide ligands of **5b** can also be unequivocally assigned on the basis of the relative signal intensity and the chemical shifts compared with those of **6b** and **7b**.

All the aminocarbyne complexes are distinguished by a low field resonance for the carbyne carbon at $\delta = 259.3$–272.4 ppm. A comparison of **3a** and **3b** with **4b** and of **6b** with **5b** and **7b** reveals that this resonance is shifted to a lower field, as successive substitution of carbonyl by isocyanide ligands occurs (Table 3). In addition, the carbyne carbon resonance of **3a–7b** appears at a lower field than that of analogous tungsten complexes (e.g. $Br(CO)_2(^tBuNC)_2W{\equiv}CN^iPr_2$, $\delta = 235.0$ ppm (CD_2Cl_2, 20°C); $Cl(CO)(^tBuNC)_3W{\equiv}CN^iPr_2$, $\delta = 235.5$ ppm (CD_2Cl_2, 20°C); $[(^tBuNC)_4(CO)W{\equiv}CNEt_2]I$, $\delta = 250.1$ ppm (CD_2Cl_2, −5°C); $[(^tBuNC)_5W{\equiv}CNEt_2]I$,

Table 3

^{13}C-NMR data for the complexes **3a–7b**; coupling constants in Hz

Complex	$\mathit{C}\mathrm{H_3CH_2NC}$	$\mathrm{N(CH}\mathit{Me}_2)_2$	$\mathit{Me}_3\mathrm{CNC}$	$\mathrm{CH_3}\mathit{C}\mathrm{H_2NC}$	$\mathrm{N(}\mathit{C}\mathrm{HMe_2)_2}$	$\mathrm{Me_3}\mathit{C}\mathrm{NC}$	RN*C*	*C*O	Cr≡*C*	solvent; t(°C)
3a	15.3	22.7	–	39.3	54.1	–	163.5	224.4	263.7	CD_2Cl_2; 20°C
3b	–	23.0	30.7	–	54.2	56.7	163.1	224.8	263.6	CD_2Cl_2; 20°C
4b	–	23.1	30.7 [a]; 30.9	–	54.1	55.1; 56.0 [a]	178.3 [a,b]	225.9	259.3	C_7D_8; +20°C
5a	15.1 [c]; 15.5 [a]; 15.8	22.7	–	39.4; 40.0 [d]	55.3	–	157.8 [c]; 166.4; 170.2 [a]	224.7	270.6	CD_2Cl_2; 20°C
5b	–	23.0	30.6 [c]; 30.9 [a]; 31.1	–	55.8	56.7; 57.6 [a]; 57.8 [c]	157.7 [c]; 166.4; 170.3 [a]	224.5	271.6	CD_2Cl_2; 20°C
6b	–	22.8	30.2 [c]; 30.5	–	56.2	57.9; 58.6 [c]	152.3 [c] $^1J(CN) = 15.3$; 159.1 $^1J(CN) = 15.9$	223.6	272.4	CD_2Cl_2; 0°C
7b	–	23.2	30.7 [c]; 31.3	–	54.7	56.4; 56.9 [c]	162.7 [c]; 180.2	–	264.4	CD_2Cl_2; +20°C

[a] Resonance of the two mutually *trans*-oriented isocyanide ligands; [b] The resonance of the isocyanide ligand, which is oriented *trans* relative to the carbonyl ligand, was not observed; [c] Resonance of the isocyanide ligand, which is oriented *trans* relative to the aminocarbyne-ligand; [d] This resonance corresponds to three methylene carbons.

$\delta = 244.1$ ppm (CD_2Cl_2, -10°C)] [11b,11c,15]. This is a consequence of the Group 6 transition metal triad ^{13}C shielding trend [16].

4. Conclusion

Convenient syntheses of neutral and cationic chromium aminocarbyne complexes of the type $Br(CO)_n(RNC)_{4-n}Cr{\equiv}CN^iPr_2$ ($n = 1, 2$; R = Et or ^tBu) and $[(RNC)_{5-n}(CO)_nCr{\equiv}CN^iPr_2]Br$ ($n = 0$–2; R = Et or ^tBu) have been developed, which are based on selective ligand exchange reactions of the easily accessible complexes $Br(CO)_4Cr{\equiv}CN^iPr_2$ and $Br(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ with alkyl isocyanides. The availability of these complexes facilitates exploration of their reactions, particularly those with electrophiles. These studies, which are currently in progress, are aimed at determining the effect of chromium on several electrophile-promoted C–C coupling reactions observed so far only for carbyne complexes of the heavier Group 6 metals.

5. Experimental details

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (*n*-pentane over CaH_2; Et_2O, toluene, THF and DME over Na-benzophenone; CH_2Cl_2 over P_2O_5 and Na–Pb alloy), distilled under nitrogen and stored over 4 Å molecular sieves prior to use. The silica used for filtration (Merck; activity I; 0063–0.2 mm) was degassed, dried at room temperature in vacuo and then saturated with nitrogen. Elemental analyses were performed in the Microanalytical Laboratory of the Inorganic Chemistry Department of Technische Universität München. IR spectra were recorded on a Nicolet 5DX Fourier transform IR and a Perkin–Elmer 1650 Fourier transform IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in dry deoxygenated methylene-d_2-chloride or toluene-d_8 on a JEOL-GX 400 instrument. Chemical shifts were referenced to residual solvent signals (CD_2Cl_2, $\delta_H = 5.32$ ppm and δ_C 53.8 ppm; C_7D_8, $\delta_H = 2.03$ ppm, and $\delta_C = 20.4$ ppm). Mass spectra were obtained with a Varian MAT 311A spectrometer; m/z values are relative to the ^{52}Cr isotope. TG–MS analyses of **3b**, **7b** and **7b′** were performed by virtue of a TGA 7 thermobalance (Perkin–Elmer) and a QMG 420 mass spectrometer (Balzers), which were coupled by a capillary system heated to 280°C. Samples of 1–4 mg mass were heated in a dynamic He atmosphere (purity, 5.0; flow, 45 standard cm^3 min^{-1}). A temperature programme was used between 50 and 400°C with a heating rate of 10 K min^{-1}.

Complexes **1** and **2** were prepared as described previously [12]. EtNC and ^tBuNC were prepared according to published procedures [18] and stored under nitrogen.

5.1. *$Br(CO)_2(EtNC)_2Cr{\equiv}CN^iPr_2$ (**3a**)*

Complex **2** (730 mg, 1.50 mmol) was dissolved in 40 ml of cold CH_2Cl_2 (-30°C) and the red solution treated with 0.23 ml (3.09 mmol) of EtNC. The mixture was then stirred for 3 h at -30°C. Completion of the reaction was revealed by IR spectroscopy (replacement of the two ν(CO) absorptions of the starting material at 1958 and 1866 cm^{-1} by those of the product at 1990 and 1923 cm^{-1}). The resulting orange solution was evaporated to dryness, the residue dissolved in a cold CH_2Cl_2–Et_2O mixture (1 : 1) (-30°C) and the solution filtered through silica (2 × 3 cm) at -30°C. The orange filtrate was concentrated in vacuo at -30°C and treated with a cold Et_2O–*n*-pentane mixture (1 : 9) (-78°C) to precipitate **3a**. The supernatant pale-yellow solution was decanted off and the orange–yellow microcrystalline solid washed once with *n*-pentane and dried in vacuo (melting point (m.p.), 76°C; yield, 600 mg (97%)). Anal. Found: C, 43.75; H, 5.96; Br, 20.00; Cr, 12.25; N, 10.23; O, 8.08. $C_{15}H_{24}BrCrN_3O_2$ (410.28) Calc.: C, 43.91; H, 5.90; Br, 19.48; Cr, 12.67; N, 10.24; O, 7.80%.

5.2. *$Br(CO)_2(^tBuNC)_2Cr{\equiv}CN^iPr_2$ (**3b**)*

A solution of 430 mg (0.88 mmol) of **2** in 40 ml of CH_2Cl_2 was treated at -30°C with 0.20 ml (1.77 mmol) of ^tBuNC and stirred for 3 h. The resulting orange solution was worked up as described above for the synthesis of **3a** to give **3b** as an orange–yellow microcrystalline solid (m.p., 94°C; yield, 370 mg (90%)). Anal. Found: C, 49.05; H, 6.86; Br, 17.42; Cr, 11.19; N, 8.92; O, 7.23. $C_{19}H_{32}BrCrN_3O_2$ (466.39) Calc.: C, 48.93; H, 6.92; Br, 17.13; Cr, 11.15; N, 9.01; O, 6.86%.

5.3. *$Br(CO)(^tBuNC)_3Cr{\equiv}CN^iPr_2$ (**4b**)*

A solution of 850 mg (1.82 mmol) of **3b** in 60 ml of toluene was treated with 0.21 ml (1.86 mmol) of ^tBuNC and the mixture heated for 5 h at 60°C. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1989 and 1929 cm^{-1} by the ν(CO) absorption of the product at 1904 cm^{-1}). The solution was evaporated to dryness and the residue extracted with Et_2O. The yellow extract was filtered to leave an insoluble red residue consisting of a mixture of **5b** and **7b**. The filtrate was evaporated to dryness to afford **4b** as a yellow microcrystalline solid (m.p., 127°C (decomposition); yield, 670 mg (71%)). Anal. Found: C, 52.70; H, 7.76; Br, 15.49; Cr, 9.90; N, 10.69; O, 3.51.

$C_{23}H_{41}BrCrN_4O$ (521.51) Calc.: C, 52.97; H, 7.92; Br, 15.32; Cr, 9.97; N, 10.74; O, 3.07%.

5.4. $[(EtNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (**5a**) from **3a** and EtNC

A solution of 210 mg (0.51 mmol) of **3a** in 25 ml of CH_2Cl_2 was treated with 0.10 ml (1.35 mmol) of EtNC and refluxed for 7 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1990 and 1923 cm^{-1} by the ν(CO) absorption of the product at 1910 cm^{-1}). The resulting red solution was concentrated in vacuo and treated with a cold Et_2O–*n*-pentane mixture (1 : 1) (−78°C). The supernatant, slightly yellow solution was decanted and the oily residue washed once with a THF–*n*-pentane mixture (1 : 2) to afford **5a** as a rose-coloured solid (m.p., 95°C (decomposition); yield, 220 mg (87%)). Anal. Found: C, 48.36; H, 6.87; Br, 16.24; Cr, 10.88; N, 14.29; O, 4.09. $C_{20}H_{34}BrCrN_5O$ (492.43) Calc.: C, 48.78; H, 6.96; Br, 16.23; Cr, 10.56; N, 14.22; O, 3.25%. FD MS: m/z 412 (M^+).

5.5. $[(^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (**5b**) from **3b** and ^tBuNC

A solution of 380 mg (0.81 mmol) of **3b** in 50 ml of CH_2Cl_2 was treated with 0.21 ml (1.86 mmol) of ^tBuNC and refluxed for 7 h. The resulting red solution was worked up as described above for the synthesis of **5a** to afford **5b** as a rose-coloured microcrystalline solid (m.p., 140°C (decomposition); yield, 400 mg (81%)). Anal. Found: C, 55.99; H, 8.31; N, 11.71. $C_{28}H_{50}BrCrN_5O$ (604.64) Calc.: C, 55.62; H, 8.33; N, 11.58%. FD MS: m/z 524 (M^+).

5.6. $[(^tBuNC)_3(CO)_2Cr{\equiv}CN^iPr_2]PF_6$ (**6b**)

A solution of 750 mg (1.61 mmol) of **3b** in 25 ml of cold CH_2Cl_2 (−78°C) was treated with 0.20 ml (1.80 mmol) of ^tBuNC and 590 mg (1.69 mmol) of $TlPF_6$ and the mixture stirred for 2 h at −20°C until reaction was complete (IR monitoring). The resulting suspension was treated with 25 ml of Et_2O, the white precipitate of TlBr allowed to settle and the supernatant orange–red solution filtered at −20°C through a filter canula. The filtrate was concentrated in vacuo at −20°C and a cold Et_2O–*n*-pentane mixture (1 : 2) (−78°C) was added to bring about precipitation of **6b** as an orange microcrystalline solid (m.p., 138°C (decomposition); yield, 840 mg (85%)). Anal. Found: C, 46.70; H, 6.73; Cr, 8.23; F, 18.24; N, 9.22; P, 4.96. $C_{24}H_{41}CrF_6N_4O_2P$ (614.57) Calc.: C, 46.90; H, 6.72; Cr, 8.46; F, 18.55; N, 9.12; P, 5.04%. FD MS: m/z 469 (M^+).

5.7. $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ (**7b**)

A suspension of 270 mg (0.45 mmol) of **5b** in 30 ml of THF was treated with 0.10 ml (0.88 mmol) of ^tBuNC and the mixture refluxed for 8h. Completion of the reaction was confirmed by IR spectroscopy (disappearance of the ν(CO) absorption of the starting material at 1904 cm^{-1}). The suspension was allowed to cool to room temperature and Et_2O was added. The supernatant almost colourless solution was decanted and the residue washed once with Et_2O and dried in vacuo to give a purple–brown microcrystalline solid (yield, 240 mg (81%)). Anal. Found: C, 57.41; H, 8.81; N, 12.28. $C_{32}H_{59}BrCrN_6$ (659.77) Calc: C, 58.26; H, 9.01; N, 12.74%. FD MS: m/z 579 (M^+).

5.8. $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]PF_6$ (**7b′**)

A solution of 480 mg (0.78 mmol) of **6b** in 50 ml of THF was treated with 0.26 ml (2.30 mmol) of ^tBuNC and then refluxed for 5 h, during which evolution of gas was observed and the initially orange solution turned purple. Completion of the reaction was confirmed by IR spectroscopy (disappearance of the ν(CO) absorptions of the starting material at 1992 and 1934 cm^{-1}). The solution was evaporated to dryness and the residue dissolved in the minimum amount of CH_2Cl_2. The solution was cooled to −78°C and a cold Et_2O–*n*-pentane mixture (1 : 2) (−78°C) was added to bring about complete precipitation of **7b′** as a purple–brown, microcrystalline solid (yield, 530 mg (94%)). Anal. Found: C, 52.62; H, 8.00; Cr, 7.19; F, 16.29; N, 11.33; P, 4.39. $C_{32}H_{59}CrF_6N_6P$ (724.82) Calc.: C, 53.03; H, 8.20; Cr, 7.17; F, 15.73; N, 11.59; P, 4.27%.

Acknowledgements

We thank Professor W.A. Hermann for providing institute facilities, the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support, Mr. M. Barth for elemental analyses and Professor F.R. Kreiβl and Ms. R. Dumitrescu for recording the mass spectra.

References

[1] (a) E.O. Fischer, W. Schambeck and F.R. Kreiβl, *J. Organomet. Chem.*, 169 (1979) C27; (b) E.O. Fischer and W. Schambeck, *J. Organomet. Chem.*, *201* (1980) 311.

[2] (a) D.S. Gill, P.K. Baker, M. Green, K.E. Paddick, M. Murray and A.J. Welch, J. *Chem. Soc., Chem. Commun.*, (1981) 986; (b) P.K. Baker, G.K. Barker, D.S. Gill, M. Green, A.G. Orpen, I.D. Williams and A.J. Welch, *J. Chem. Soc., Dalton Trans.*, (1989) 1321.

[3] (a) A.C. Filippou and W. Grünleitner, *Z. Naturforsch. 44b*

(1989) 1023; (b) A.C. Filippou, *Polyhedron, 9* (1990) 727; (c) A.C. Filippou and W. Grünleitner, *J. Organomet. Chem.*, 393 (1990) C10; (d) A.C. Filippou and W. Grünleitner, *Z. Naturforsch., 46b* (1991) 216.

[4] (a) A.C. Filippou, C. Völkl, W. Grünleitner and P. Kiprof, *Angew. Chem., 102* (1990) 224; *Angew. Chem., Int. Edn. Engl., 29* (1990) 207; (b) A.C. Filippou, C. Völkl, W. Grünleitner and P. Kiprof, *Z. Naturforsch, 45b* (1990) 351.

[5] (a) F.R. Kreiβl, A. Frank, U. Schubert, T.L. Lindner and G. Huttner, *Angew. Chem., 88* (1976) 649; *Angew. Chem. Int. Edn. Engl., 15* (1976) 632; (b) F.R. Kreiβl, K. Eberl and W. Uedelhoven, *Chem. Ber., 110* (1977) 3782; (c) H. Fischer, P. Hofmann, F.R. Kreiβl, R.R. Schrock, U. Schubert and K. Weiss, *Carbyne Complexes,* VCH, Weinheim, 1988; (d) G.L. Geoffroy and S.L. Bassner, *Adv. Organomet. Chem., 28* (1988) 1; (e) A. Mayr and C.M. Bastos, *Prog. Inorg. Chem.*, 40 (1992) 1.

[6] A. Mayr and C.M. Bastos, *J. Am. Chem. Soc., 112* (1990) 7797.

[7] (a) C.T. Lam, P.W.R. Corfield and S.J. Lippard, *J. Am. Chem. Soc., 99* (1977) 617; (b) C.M. Giandomenico, C.T. Lam and S.J. Lippard, *J. Am. Chem. Soc., 104* (1982) 1263; (c) P.A. Bianconi, R.N. Vrtis, Ch. P. Rao, I.D. Williams, M.P. Engeler and S.J. Lippard, *Organometallics, 6* (1987) 1968; (d) G.A. McDermott and A. Mayr, *J. Am. Chem. Soc., 109* (1987) 580; (e) A. Mayr, *Comments Inorg. Chem., 10* (1990) 227; (f) R.N. Vrtis and S.J. Lippard, *Isr. J. Chem., 30* (1990) 331; (g) R.N. Vrtis, S. Liu, Ch. P. Rao, S.G. Bott and S.J. Lippard, *Organometallics, 10* (1991) 275; (h) E.M. Carnahan and S.J. Lippard, *J. Chem. Soc., Dalton Trans.*, (1991) 699; (i) A. Mayr, C.M. Bastos, N. Daubenspeck and G.A. McDermott, *Chem. Ber., 125* (1992) 1583.

[8] (a) A.C. Filippou, W. Grünleitner, C. Völkl and P. Kiprof, *Angew. Chem., 103* (1991) 1188; *Angew. Chem., Int. Edn. Engl., 30* (1991) 1167; (b) A.C. Filippou, C. Völkl, W. Grünleitner and P. Kiprof, *J. Organomet. Chem., 434* (1992) 201; (c) J.J.R.F. da Silva, M.A. Pellinghelli, A.J.L. Pombeiro, R.L. Richards, A. Tiripicchio and Y. Wang, *J. Organomet. Chem.*, 454 (1993) C8.

[9] A.C. Filippou, P. Hofmann, P. Kiprof, H.R. Schmidt and C. Wagner, *J. Organomet. Chem., 459* (1993) 233.

[10] C. Mehnert, *Diplomarbeit*, Technische Universität München, 1992.

[11] (a) A.C. Filippou, E.O. Fischer and R. Paciello, *J. Organomet. Chem., 347* (1988) 127; (b) A.C. Filippou and E.O. Fischer, *J. Organomet. Chem., 352* (1988) 141; (c) A.C. Filippou and E.O. Fischer, *J. Organomet. Chem., 365* (1989) 317.

[12] A.C. Filippou, K. Wanninger and C. Mehnert, *J. Organomet. Chem., 461* (1993) 99.

[13] (a) F.A. Cotton and C.S. Kraihanzel, *J. Am. Chem. Soc., 84* (1962) 4432; (b) D.M. Adams, *Metal-Ligand and Related Vibrations*, Edward Arnold, London, 1967.

[14] (a) F.A. Cotton and F. Zingales, *J. Am. Chem. Soc., 83* (1961) 351; (b) J.A. Connor, E.M. Jones, G.K. McEwen, M.K. Lloyd and J.A. McCleverty, *J. Chem. Soc., Dalton Trans.*, (1972) 1246.

[15] A.C. Filippou and B. Lungwitz, to be published.

[16] L.J. Todd and J.R. Wilkinson, *J. Organomet. Chem., 77* (1974) 1.

[17] (a) D.L. Cronin, J.R. Wilkinson and L.J. Todd, *J. Magn. Reson., 17* (1975) 353; (b) A.C. Filippou and E.O. Fischer, *J. Organomet. Chem., 383* (1990) 179; (c) A.M. Martins, M.J. Calhorda, C.C. Romao, C. Völkl, P. Kiprof and A.C. Filippou, *J. Organomet. Chem., 423* (1992) 367.

[18] (a) J. Casanova (Jr.), R.E. Schuster and N.D. Werner, *J. Chem. Soc.*, (1963) 4280; (b) R.E. Schuster, J.E. Scott and J. Casanova, Jr., *Org. Synth., 46* (1966) 75.