JOM 23738

Half-sandwich aminocarbyne complexes of chromium

Alexander C. Filippou, Klaus Wanninger and Christian Mehnert

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, W-8046 Garching (Germany)

(Received March 8, 1993)

Abstract

Efficient methods are described for the synthesis of half-sandwich chromium aminocarbyne complexes starting from *trans*-$X(CO)_4Cr{\equiv}CN^iPr_2$ (**1a**: X = Cl; **1b**: X = Br). Complexes **1a** and **1b** are obtained from $Cr(CO)_6$ in two steps. The first step involves a nucleophilic addition of LiN^iPr_2 to $Cr(CO)_6$ to give the carboxamido complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$, followed by reaction with the Lewis acids ClC(O)C(O)Cl and BrC(O)C(O)Br, respectively. Thermal decarbonylation of **1a** or **1b** with γ-picoline (4-methylpyridine) results in the quantitative formation of $X(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (**2a**: X = Cl; **2b**: X = Br). Complex **2b** reacts with NaCp and KTp' (Tp' = hydridotris(3,5-dimethylpyrazol-1-yl)borate) to afford $Cp(CO)_2Cr{\equiv}CN^iPr_2$ (**3**) and $Tp'(CO)_2Cr{\equiv}CN^iPr_2$ (**4**), respectively. Similarly, when **2b** is treated with KCp* (Cp* = C_5Me_5), the half-sandwich aminocarbyne complex $Cp^*(CO)_2Cr{\equiv}CN^iPr_2$ (**5**) is obtained. Thermal decarbonylation of **1b** with ^{t}BuNC in refluxing CH_2Cl_2 leads exclusively to the cationic aminocarbyne complex $[(^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (**6**). Treatment of **6** with NaCp and KTp' results in the formation of $Cp(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$ (**7**) and $Tp'(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$ (**8**), respectively. In both reactions a minor product, $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$, is formed by a carbonyl substitution reaction of **6** with the released ^{t}BuNC. Complex **6** reacts with KCp* to give a mixture of the half-sandwich aminocarbyne complex $Cp^*(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$ (**9**) and the Cr^0 isocyanide isomers *cis*- and *trans*-$Cr(CO)(CN^iPr)(CN^tBu)_4$ (**10a,b**), the latter probably originating from an electron-transfer or a proton-abstraction reaction of **6** with KCp*. Formation of **10a/b** is avoided when a more electron-rich (less acidic) aminocarbyne complex, such as $Br(CO)(^tBuNC)_3Cr{\equiv}CN^iPr_2$ (**11**), is treated with KCp*.

1. Introduction

Efficient methods for the synthesis of half-sandwich molybdenum and tungsten aminocarbyne complexes, $(\eta^5\text{-}C_5R_5)(CO)_n(L)_{2-n}M{\equiv}CNEt_2$ (R = H, Me; n = 0–2; L = 2e-donor ligand) have recently been developed [1–3], allowing extensive studies of the reactivity of these compounds. These studies have shown that the aminocarbyne complexes $(\eta^5\text{-}C_5R_5)(CO)_n(L)_{2-n}M{\equiv}CNEt_2$ undergo a variety of reactions, such as oxidative decarbonylations, protonations, and cycloadditions [1,2a,2b,3c,4]. Representative examples of this versatile reactivity are the successive chlorination of $Cp^*(CO)_2W{\equiv}CNEt_2$ with $PhICl_2$ to afford $Cp^*(Cl)_2(CO)W{\equiv}CNEt_2$ and $Cp^*(Cl)_4WCNEt_2$ [4b], the protonation of $Cp^*(CO)(L)W{\equiv}CNEt_2$ and $Cp^*(PMe_3)_2W{\equiv}CNEt_2$ with HBr to give the aminocarbene and hydrido(aminocarbyne) complexes $Cp^*(Br)(CO)(L)W{=}C(H)NEt_2$ (L = EtNC, ^{t}BuNC, PMe_3) and $[Cp^*(H)(PMe_3)_2W{\equiv}CNEt_2]$-Br, respectively [3c], and the 2 + 2 cycloaddition of $Cp^*(CO)_2W{\equiv}CNEt_2$ with nitrilium salts $[RC{\equiv}NR']BF_4$ to give the 1-wolfram-2-aza-cyclobutadiene complexes $Cp^*(CO)_2W[\eta^3\text{-}C(NEt_2)C(R)NR']BF_4$ (R, R' = alkyl) [4b]. In contrast, no analogous complexes of chromium have yet been reported, probably due to the lack of a satisfactory synthetic approach to this class of compounds. We therefore decided to seek efficient methods for the synthesis of half-sandwich aminocarbyne complexes of chromium starting from *trans*-$X(CO)_4Cr{\equiv}CN^iPr_2$ (**1a**: X = Cl; **1b**: X = Br).

2. Results and discussion

Two possible methods have recently been reported for the preparation of half-sandwich aminocarbyne complexes of molybdenum and tungsten of the type $(\eta^5\text{-}C_5R_5)(CO)_2M{\equiv}CN(R')R''$ (R = H, Me; R', R'' = alkyl) [1,2]. The first involves alkylation of the isocyanide metallates $Na[(\eta^5\text{-}C_5R_5)M(CO)_2(CNR')]$ (R = H, Me; R' = Et, ^{t}Bu) with Meerwein's salts [2], and is based on the well known activation of isocyanides for

Correspondence to: Dr. A.C. Filippou

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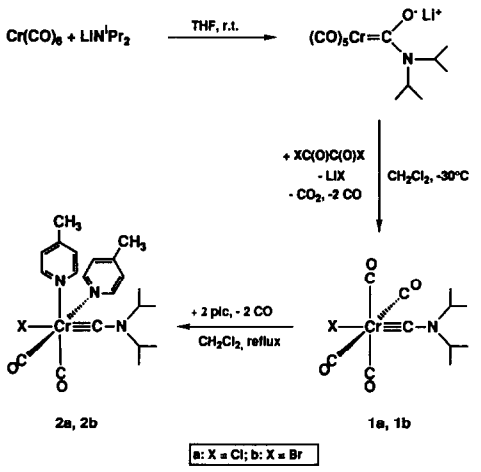


Scheme 1. Synthesis of **2a, 2b** from $Cr(CO)_6$.

an electrophilic attack at the nitrogen atom when these are ligated to an electron-rich metal centre [5]. The second method involves ligand substitution reactions of suitable aminocarbyne precursors, such as $I(CO)_2(py)_2W{\equiv}CNEt_2$, with C_5R_5 transfer reagents [1a].

Application of the first method for the preparation of chromium half-sandwich aminocarbyne complexes was precluded by the non-availability of any isocyanide metallates, $Na[(\eta^5\text{-}C_5R_5)Cr(CO)_2(CNR')]$. We therefore decided to follow the second route and set out to prepare chromium aminocarbyne complexes, which (a) are obtained from $Cr(CO)_6$ by high-yield, large-scale reactions and (b) react with C_5R_5 transfer reagents to give selectively the desired half-sandwich aminocarbyne complexes $(\eta^5\text{-}C_5R_5)(CO)_2Cr{\equiv}CN(R')R''$.

The bis-(γ-picoline)-substituted derivatives $X(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ **(2a,b)** were found to meet both these requirements. Scheme 1 depicts the three-step synthesis of these compounds starting from $Cr(CO)_6$. The synthetic procedure followed is based in large part on methods developed by Fischer *et al.* and Mayr *et al.* for the preparation of analogous alkyl- and arylcarbyne complexes of Group VI transition metals [6]. It begins with the nucleophilic addition of LiN^iPr_2 to one of the carbonyl-carbons of $Cr(CO)_6$ to give the carboxamido complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$. This is followed by the direct conversion of $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ into the chromium aminocarbyne complexes *trans*-$X(CO)_4Cr{\equiv}CN^iPr_2$ **(1a,b)** by treatment with the carbon-based Lewis-acids oxalyl chloride and oxalyl bromide. In the last step thermal decarbonylation of the tetracarbonyl complexes **1a** and **1b** in the presence of γ-picoline gives the desired bis-(γ-picoline) derivatives **2a** and **2b** in an overall yield of 60–75% (Scheme 1).

In the first step LiN^iPr_2 was used as a nucleophile in THF to ensure complete and fast conversion of $Cr(CO)_6$ into the carboxamido complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ [7]. Water must be rigorously excluded in this reaction because the carboxamido complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ is immediately hydrolyzed to give $Cr(CO)_6$ and HN^iPr_2. Evidence of the clean formation of $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ was provided by the IR spectrum of the red reaction solution, which revealed that the ν(CO) absorption of $Cr(CO)_6$ at 1980 cm^{-1} had been replaced by four new absorptions at 2034, 1940, 1905 and 1873 cm^{-1}, assigned respectively to the $A_1^{(2)}$, B_1, E and $A_1^{(1)}$ CO stretching modes of the product $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ [8]. After evaporation of the solvent the Li-metallate was isolated as a yellow solid in quantitative yield. Reaction of the carboxamido complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ with oxalyl chloride or bromide was carried out in CH_2Cl_2 between −30 and −40°C and was accompanied by evolution of gas (CO_2, CO) and a fast change in the colour of the solution from red to brown-yellow. Again IR-monitoring of the reaction revealed a clean conversion of the starting material into the carbyne complexes **1a** and **1b**. This transformation corresponds formally to an abstraction of an oxygen atom from an acyl ligand [6] and is closely related to a large family of reactions of organic carbonyl functionalities with acid halides [9].

Complexes **1a** and **1b** were isolated after purification by column chromatography on silica at −20°C as bright-orange, microcrystalline solids in 60 and 75% yield, respectively. * They are soluble in CH_2Cl_2 and toluene, moderately soluble in Et_2O, but insoluble in n-pentane. The crystalline complex **1a** shows remarkable thermal stability for a tetracarbonyl(carbyne) complex, decomposing when heated in a sealed capillary only at 112°C. Both compounds however decompose in solution at room temperature with evolution of CO. When this thermal decarbonylation is carried out in refluxing CH_2Cl_2 in the presence of an excess of 4-methylpyridine (γ-picoline), clean formation of the substitution products $X(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ **(2a,b)** is observed. This ligand exchange reaction proceeds via an intermediate, which on the basis of its IR spectrum in CH_2Cl_2[ν(CO): 2044w, 1944s; $\nu(C_{carbyne}\cdots N)$: 1534m] is suggested to be the mono-(γ-picoline) substitution product *mer*-$Br(CO)_3(pic)Cr{\equiv}CN^iPr_2$. After removal of the solvent, the excess of the ligand was washed away with Et_2O/n-pentane and the complexes **2a** and **2b** isolated in essentially quantitative yield as

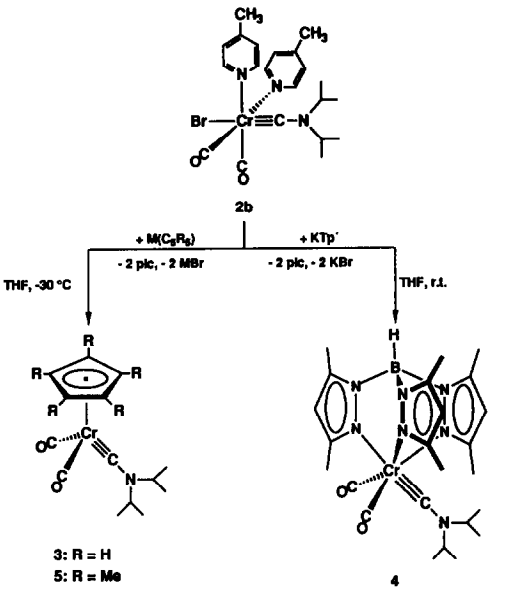
* Complex **1a** has been prepared previously from $[Cr(CO)_5{\equiv}CN^iPr_2]SbCl_6$ and $[(PPh_3)_2N]Cl$, and structurally characterized (H. Fischer, A. Motsch, R. Märkl and K. Ackermann, *Organometallics, 4* (1985) 726.

orange-red, very air-sensitive solids, which are soluble in CH_2Cl_2, but insoluble in Et_2O and n-pentane. Both compounds are thermally stable solids, decomposing when heated in a sealed capillary at 119 and 126°C, respectively. Despite the thermal stability of **2a** and **2b**, which facilitates handling of these compounds (*e.g.* solutions of **2a** and **2b** in CH_2Cl_2 are stable at room temperature if air is rigorously excluded), long-term storage of **2a** and **2b** should preferably be at −30°C.

Complexes **2a** and **2b** are, like their tetracarbonyl precursors **1a** and **1b**, reactive compounds, owing to the presence of two coordinatively labile γ-picoline ligands. Evidence for the coordinative lability of the γ-picoline ligands is provided by (a) the fast ligand exchange reactions of **2b** with isocyanides to give, depending on the reaction conditions, neutral or cationic aminocarbyne complexes of the type $Br(CO)_2(RNC)_2Cr{\equiv}CN^iPr_2$ and $[(RNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (R = Et, ^{t}Bu), respectively [10], and (b) the solution IR spectrum of an analytically pure sample of **2b** in THF prepared with rigorous exclusion of air and water, which reveals, besides the two ν(CO) absorptions of the parent compound at 1960 and 1872 cm^{-1}, the characteristic $\nu(C{\cdots}N)_{ring}$ absorption of uncoordinated γ-picoline at 1604 cm^{-1} and two ν(CO) absorptions at 1947 and 1852 cm^{-1}, tentatively assigned to the A_1 and B_1 stretching modes of the solvolysis product $Br(CO)_2(pic)(THF)Cr{\equiv}CN^iPr_2$.

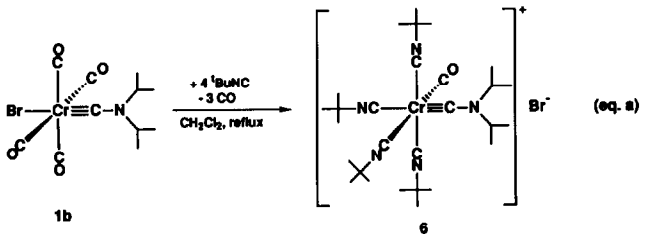
The presence of the γ-picoline ligands in **2a** and **2b** results in a higher electron density at the metal centre, so preventing undesirable redox reactions of **2a** and **2b** with nucleophiles that might act as reducing agents. This property proved to be very useful for the synthesis of cyclopentadienyl-substituted aminocarbyne complexes of chromium, outlined in Scheme 2. Thus, when **2b** was treated with NaCp in THF at −30°C a fast substitution reaction occurred to give selectively the half-sandwich aminocarbyne complex **3** (Scheme 2). This was isolated after purification by column chromatography on silica as a bright-yellow, air-sensitive solid in 84% yield. Similarly, reaction of **2b** with KTp′ resulted in the clean formation of $Tp'(CO)_2Cr{\equiv}CN^iPr_2$ (**4**), which was obtained as a red, slightly air-sensitive solid in 93% yield (Scheme 2). Likewise, reaction of **2b** with KCp* in THF gave $Cp^*(CO)_2Cr{\equiv}CN^iPr_2$ (**5**) (Scheme 2) but this was accompanied by the formation of brown by-products, probably resulting from an electron transfer side reaction of the reactants. However, complex **5** was easily separated from these by-products by column chromatography on silica at −20°C and was isolated as an intensely yellow coloured, air-sensitive solid in 49% yield.

The half-sandwich aminocarbyne complexes **3** and **5** melt without decomposition at 91 and 118°C, respectively, and are soluble in all common organic solvents. The Tp′ complex **4** decomposes upon heating at 208°C and is soluble in CH_2Cl_2 and Et_2O, but sparingly soluble in n-pentane.



Scheme 2. Synthesis of half-sandwich chromium aminocarbyne complexes from **2b**.

The isocyanide-substituted half-sandwich aminocarbyne complexes could also be obtained starting from *trans*-$Br(CO)_4Cr{\equiv}CN^iPr_2$ (**1b**). Complex **1b** was first treated with an excess of ^{t}BuNC in refluxing CH_2Cl_2 to give the cationic aminocarbyne complex $[(^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (**6**) in 96% yield (eqn. a). This was isolated as a red, moderately air-sensitive solid, which is soluble in CH_2Cl_2, sparingly soluble in THF and decomposes at 140°C.



Treatment of **6** with NaCp in THF at 50°C afforded the half-sandwich aminocarbyne complex $Cp(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$ (**7**) in 61% yield (Scheme 3). Complex **7** was purified by column chromatography on alumina at −20°C, and isolated as an intense-yellow, very air-sensitive solid that melts below room temperature and decomposes in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$ (oxidative degradation by the solvent).

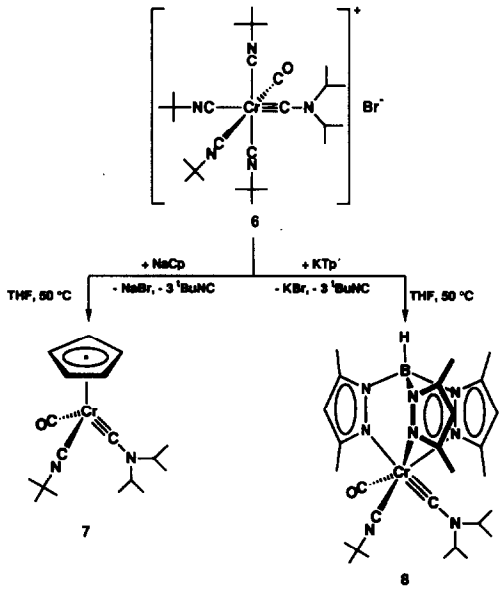
Similarly, reaction of **6** with KTp′ in THF at 50°C gave the Tp′ complex **8**, which was isolated as a red, air-sensitive solid in 58% yield (Scheme 3). Complex **8**

is soluble in all common organic solvents and decomposes at 155°C.

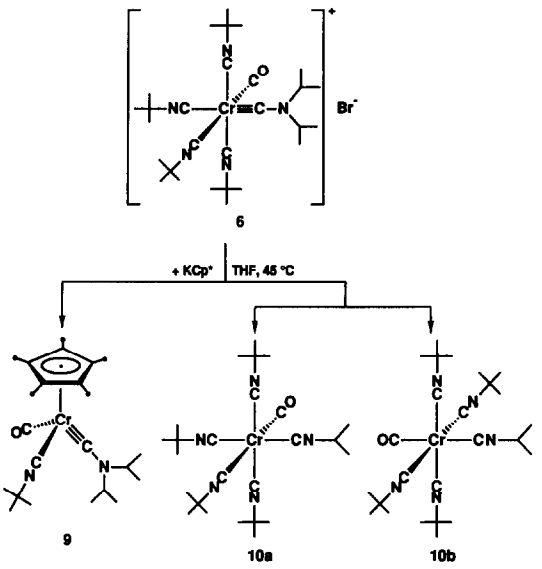
Reactions of **6** with NaCp and KTp', to give **7** and **8** respectively, were accompanied by the formation of a minor, purple-brown product, which was readily separated from **7** and **8** owing to its insolubility in Et_2O and n-pentane, and shown on the basis of its spectroscopic properties to be the cationic aminocarbyne complex $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ [10]. This compound is formed by a competitive carbonyl substitution reaction of **6** with ^{t}BuNC, the latter being evolved in the formation of **7** or **8**. Evidence for this was provided by the independent synthesis of $[(^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$ from **6** and ^{t}BuNC in refluxing THF [10].

In comparison, treatment of **6** with KCp* in THF at 45°C resulted in the formation of two products, the desired half-sandwich aminocarbyne complex $Cp^*(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$ (**9**) and an isomeric mixture of the Cr^0 isopropyl isocyanide complexes *cis*- and *trans*-$Cr(CO)(CN^iPr)(CN^tBu)_4$ (Scheme 4).

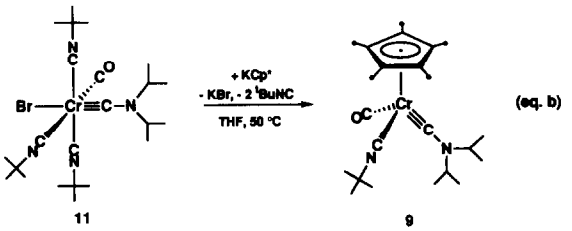
The two products were separated by column chromatography on alumina at −20°C, and isolated as intense-yellow, very air-sensitive, low-melting solids (**9**: m.p. < 20°C; **10a/10b** (3.8/1): m.p. = 57°C) in 25 and 40% yield, respectively. They are soluble in all common organic solvents, but decompose rapidly in CH_2Cl_2 and $CHCl_3$ (oxidative degradation by the solvent). Two possible pathways may be envisaged for the formation of **10a/10b**. The first involves a proton abstraction from one of the methyl groups of the aminocarbyne ligand in **6** by KCp* to afford a zwitterionic intermediate followed by elimination of propene to give **10a**. Complex **10a** then isomerizes to **10b** (this reaction sequence may be compared with the well-known Hofmann elimination of quaternary ammonium salts in organic chemistry [11]). The second pathway involves a one-electron reduction of **6** by KCp* to afford a 19e-aminocarbyne intermediate followed by elimination of an isopropyl radical to give **10a/10b**. Both pathways are fully consistent with the observation that reaction of the less acidic (less easily reduced) aminocarbyne complex $Br(CO)(^tBuNC)_3Cr{\equiv}CN^iPr_2$ (**11**) with KCp* in THF leads exclusively to the half-sandwich aminocarbyne complex **9** (eqn. b). Evidence for the selective transformation of **11** to **9** was provided by the IR spectrum of the reaction solution, which showed that the ν(CO) absorption of the starting material at 1902 cm^{-1} had been replaced at the end of the reaction by the ν(CO) absorption of **9** at 1844 cm^{-1}. Complex **9** was isolated in 76% yield after purification by column chromatography on alumina at −20°C.



Scheme 3. Synthesis of half-sandwich chromium aminocarbyne complexes from **6**.



Scheme 4. Reaction of **6** with KCp*.



A transformation analogous to that of **6** to **10a/10b** (Scheme 4) was previously observed in the reaction of the cationic aminocarbyne complex $[(CO)_5Cr{\equiv}CN^iPr_2]$-$BCl_4$ with Group V nucleophiles, *e.g.* $[(CO)_5CrEPh_2]^-$

(E = As, Sb), to give the isopropyl isocyanide complex $(CO)_5CrCN^iPr$, rather than the desired aminocarbene complexes $(CO)_5Cr[C(N^iPr_2)E(Ph)_2Cr(CO)_5]$ [12].

3. Spectroscopic investigations

3.1. IR spectra

The solution IR spectra of the complexes **1a–10b** exhibit in the region 2200–1480 cm^{-1} characteristic $\nu(C{\equiv}N^tBu)$, $\nu(CO)$ and $\nu(C{\cdots}N)$ absorptions of the coordinated tert-butyl isocyanide, carbonyl, and aminocarbyne ligands, respectively (Table 1).

The number and relative intensities of the $\nu(C{\equiv}NR)$ and $\nu(CO)$ absorptions indicate the relative positions of the isocyanide and carbonyl ligands in the octahedral complexes **1a–10b**. Thus, three $\nu(CO)$ absorptions are observed in the IR spectra of the tetracarbonyl complexes **1a** and **1b**, suggesting a *trans*-orientation of the halo and the aminocarbyne ligand [8a,13,14]. In comparison, complex **6** exhibits four $\nu(C{\equiv}N^tBu)$ absorptions, as expected on the basis of group theory for a *cis*-arrangement of four isocyanide ligands in an octahedral complex (Table 1) [14]. Similarly, two $\nu(CO)$ absorptions of almost equal intensity are observed in the IR spectra of the dicarbonyl complexes **2a–5**, indicating a *cis*-arrangement of the two carbonyl ligands. The higher frequency absorption is assigned to the symmetric A_1 mode and the lower frequency absorption to the antisymmetric B_1 mode [14]. In contrast, the half-sandwich aminocarbyne complexes **7** and **9** show only one $\nu(C{\equiv}N^tBu)$ and one $\nu(CO)$ absorption, which appear at considerably lower frequency than those for free tert-butyl isocyanide [$\nu(C{\equiv}N^tBu)$ in CH_2Cl_2: 2140 cm^{-1}] and carbon monoxide [$\nu(CO)$: 2155 cm^{-1}], respectively, indicating extensive metal-ligand back donation in these electron-rich compounds.

The position of the $\nu(CO)$ bands depends strongly on the polarity of the solvent. This is demonstrated by the IR spectra of **3** and **9** in CH_2Cl_2, Et_2O and n-pentane, which reveal a shift of the $\nu(CO)$ absorptions to lower frequency as the polarity is increased (Table 1).

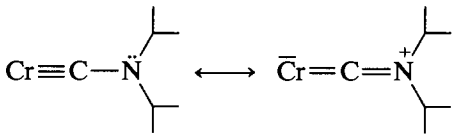
The bis-picoline derivatives **2a** and **2b** exhibit a characteristic absorption at 1619 cm^{-1} that is assigned to the $\nu(C{\cdots}N)$ vibration of the γ-picoline ligands. This absorption appears at higher frequency than that of uncoordinated γ-picoline [$\nu(C{\cdots}N)$ in CH_2Cl_2: 1606 cm^{-1}]. Similarly, the Tp′ complexes **4** and **8** exhibit two weak absorptions at ~2550 and ~2530 cm^{-1} and one absorption of medium intensity at ~1545 cm^{-1}, resulting from the B–H and the pyrazol-1-yl ring stretching vibration, respectively (Table 1).

All the aminocarbyne complexes **1a–9** show an absorption in the range 1570–1500 cm^{-1}, which is assigned to the $\nu(C_{carbyne}{\cdots}N)$ vibration [1,2,8b,13b]. The fairly high frequency of this absorption reveals a strong

TABLE 1. $\nu(BH)$, $\nu(C{\equiv}N^tBu)$, $\nu(CO)$ and $\nu(C{\cdots}N)$ absorptions of **1a–10b** in cm^{-1}; solvents: CH_2Cl_2 (a), Et_2O (b), n-pentane (c).

Complex		$\nu(BH)$	$\nu(C{\equiv}N^tBu)$	$\nu(CO)$	$\nu(C{\cdots}N)_{ring}$	$\nu(C_{carbyne}{\cdots}N)$	solvent
trans-$Cl(CO)_4Cr{\equiv}CN^iPr_2$	**(1a)**	–	–	2098w, 2026s, 1988vs	–	1566s	a
trans-$Br(CO)_4Cr{\equiv}CN^iPr_2$	**(1b)**	–	–	2094w, 2026s, 1989vs	–	1567s	a
$Cl(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$	**(2a)**	–	–	1958vs, 1865vs	1619m	1502m	a
$Br(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$	**(2b)**	–	–	1958vs, 1866vs	1619m	1503m	a
$Cp(CO)_2Cr{\equiv}CN^iPr_2$	**(3)**	–	–	1944vs, 1862vs	–	1552m	a
		–	–	1954vs, 1880vs	–	1545m	b
		–	–	1962vs, 1890vs	–	1540m	c
$Tp'(CO)_2Cr{\equiv}CN^iPr_2$	**(4)**	2551sh, 2527w	–	1953vs, 1856vs	1544m	1504m	a
		2551sh, 2527w	–	1956vs, 1863vs	1545m	1499m	b
$Cp^*(CO)_2Cr{\equiv}CN^iPr_2$	**(5)**	–	–	1929vs, 1847vs	–	1539m, 1527m	a
		–	–	1945vs, 1875vs	–	1530m, 1515m	c
$[(^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$	**(6)**	–	2177s, 2154m, 2123vs, 2063w	1910vs	–	1549m	a
$Cp(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$	**(7)**	–	1962m	1871vs	–	1519m	c
$Tp'(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$	**(8)**	2550sh, 2525w	2093s, 2062m	1826vs	1545m	1486m	a
		2550sh, 2523w	2094s, 2062m	1842vs	1547m	1488m	b
$Cp^*(CO)(^tBuNC)Cr{\equiv}CN^iPr_2$	**(9)**	–	1918m	1826vs	–	1510m	a
		–	1926m	1851vs	–	1509m	b
		–	1930m	1858vs	–	1507m	c
cis/trans-$Cr(CO)(CN^iPr)(CN^tBu)_4$	**(10a/10b)**		2094w, 1959s,br,	1866vs	–	–	c

interaction of the nitrogen lone pair with the metal–carbon triple bond in these compounds, which is represented in valence bond terms by the canonical form **B**:



A **B**

The $\nu(C_{carbyne} \equiv N)$ absorption is shifted to lower frequency as the electron density at the metal centre is increased (stronger metal–carbyne back bonding) (Table 1) [1b,2a–c]. Moreover, the $\nu(C_{carbyne} \equiv N)$ absorption for the chromium aminocarbyne complexes **1a–9** is found at lower frequency than that for analogous molybdenum or tungsten compounds {*e.g.*, $\nu(C \equiv N)$ of $Cp(CO)_2M{\equiv}CNEt_2$ in CH_2Cl_2: 1558 cm^{-1} (M = Mo), 1568 cm^{-1} (M = W) [2b]; $\nu(C \equiv N)$ of $Cp^*(CO)_2M{\equiv}CNEt_2$ in CH_2Cl_2: 1547 cm^{-1} (M = Mo), 1556 cm^{-1} (M = W) [2e]; $\nu(C \equiv N)$ of $Tp'(CO)_2W{\equiv}CNEt_2$ in CH_2Cl_2: 1528 cm^{-1} [15]}.

3.2. ^1H NMR spectra

Further support for the structures assigned to **1a–10b** is provided by the ^1H NMR spectra (Table 2). Thus, one doublet resonance for the methyl protons and one septet resonance for the methine protons of the aminocarbyne ligand are observed in the ^1H NMR

TABLE 2. ^1H NMR data for the complexes **1–10b**; relative intensities and multiplicities in parentheses, coupling constants in Hz.

Complex	$N(CHMe_2)_2$; Me_2HCNC	Me_3CNC	C_5Me_5	Tp′-C*Me* NC_5H_4Me	$N(CHMe_2)_2$; Me_2HCNC	C_5H_5	Tp′-C*H*; NC_5H_4Me	solvent; T (°C)
1a	1.38 (12, d) ^3J(HH) = 6.8	–	–	–	3.24 (2, sept) ^3J(HH) = 6.8	–	–	CD_2Cl_2; −10°C
1b	1.38 (12, d) ^3J(HH) = 6.7	–	–	–	3.24 (2, sept) ^3J(HH) = 6.7	–	–	CD_2Cl_2; −10°C
2a	1.30 (12, d) ^3J(HH) = 6.9	–	–	2.32 (6, s)	3.49 (2, sept) ^3J(HH) = 6.6	–	7.01 (4, d) ^3J(HH) = 5.1; 8.53 (4, d) ^3J(HH) = 5.1	CD_2Cl_2; −10°C
2b	1.28 (12, d) ^3J(HH) = 6.6	–	–	2.32 (6, s)	3.48 (2, sept) ^3J(HH) = 6.6	–	7.02 (4, d) ^3J(HH) = 5.0; 8.54 (4, d) ^3J(HH) = 5.0	CD_2Cl_2; −20°C
3	1.02 (12, d) ^3J(HH) = 6.7	–	–	–	2.55 (2, sept) ^3J(HH) = 6.7	4.68 (5, s)	–	C_6D_6; +20°C
4	1.14 (12, d) ^3J(HH) = 6.9	–	–	2.18 (6, s); 2.20 (3, s); 2.59 (3, s); 2.74 (6, s)	3.07 (2, sept) ^3J(HH) = 6.9	–	5.55 (1, s); 5.70 (2, s)	C_6D_6; +20°C
5	1.08 (12, d) ^3J(HH) = 6.5	–	1.84 (15, s)	–	2.68 (2, sept) ^3J(HH) = 6.5	–	–	CD_2Cl_2; +20°C
6	1.39 (12, d) ^3J(HH) = 6.7	1.44 (9, s); 1.48 (18, s); 1.51 (9, s) [a]	–	–	3.19 (2, sept) ^3J(HH) = 6.7	–	–	CD_2Cl_2; +20°C
7	1.17 (6, d) ^3J(HH) = 6.5; 1.23 (6, d) ^3J(HH) = 6.5;	1.17 (9, s)	–	–	2.73 (2, sept) ^3J(HH) = 6.5	4.88 (5, s)	–	C_6D_6; +20°C
8	1.23 (6, d) ^3J(HH) = 6.7; 1.33 (6, d) ^3J(HH) = 6.7;	0.98 (9, s)	–	2.20 (3, s); 2.23 (3, s); 2.27 (3, s); 2.72 (3, s); 2.83 (3, s); 2.91 (3, s)	3.33 (2, sept) ^3J(HH) = 6.7	–	5.72 (1, s); 5.76 (1, s); 5.86 (1, s)	C_6D_6; +20°C
9	1.17 (6, d) ^3J(HH) = 6.7; 1.22 (6, d) ^3J(HH) = 6.7;	1.24 (9, s)	1.97 (15, s)	–	2.81 (2, sept) ^3J(HH) = 6.7	–	–	C_6D_6; +20°C
10a	1.04 (6, d) ^3J(HH) = 6.5	1.15 (9, s) [b]; 1.27 (9, s); 1.28 (18, s)	–	–	3.45 (1, sept) ^3J(HH) = 6.5	–	–	C_6D_6; +20°C
10b	0.89 (6, d) ^3J(HH) = 6.7	1.27 (36, s)	–	–	3.25 (1, sept) ^3J(HH) = 6.5	–	–	C_6D_6; +20°C

[a] Signal from the tert-butyl isocyanide ligand *trans* to the aminocarbyne ligand.
[b] Signal from the tert-butyl isocyanide ligand *trans* to the carbonyl ligand.

spectra of the complexes **2a–6**, indicating C_s molecular symmetry and rapid rotation of the diisopropylamino group about the $C_{carbyne}$–N bond on the NMR time scale. In contrast, the ^{1}H NMR spectra of the aminocarbyne complexes **7–9** show two doublet resonances in a ratio 1/1 for the diastereotopic methyl protons of the isopropyl groups, indicating the presence of a chiral metal centre in these compounds (C_1 molecular symmetry) (Table 2).

At room temperature the ^{1}H NMR spectra of the Tp′ complexes **4** and **8** display a 2/1 and 1/1/1 pattern for the protons of the pyrazol-1-yl groups, revealing that these compounds are not fluxional. In contrast, the ^{1}H NMR spectra of the analogous tungsten complexes $Tp(CO)_2W{\equiv}CNR_2$ (Tp = hydridotris(pyrazol-1-yl)borato; R = Me, Et) have previously been reported to be temperature dependent owing to ligand fluxionality [16].

Three singlet resonances in a ratio 1/2/1 are observed for the tert-butyl protons of the isocyanide ligands in **6** suggesting, in accordance with the IR data, a *cis*-structure for this compound. The lower field

TABLE 3. ^{13}C-NMR data for the complexes **1–10b**

Complex	C_5Me_5; Tp′*CMe*; NC_5H_4Me	$N(CHMe_2)_2$	Me_3CNC; Me_2HCNC	$N(CHMe_2)_2$	Me_3CNC; Me_2HCNC	C_5H_5; C_5Me_5	Tp′*C*H	Tp′*C*Me; NC_5H_4Me	Me_3CNC	*C*O	Cr≡*C*	solvent; T (°C)
1a	–	22.7	–	55.8	–	–	–	–	–	212.6	266.3	CD_2Cl_2; −10°C
1b	–	22.6	–	55.5	–	–	–	–	–	211.8	266.3	CD_2Cl_2; −10°C
2a	20.8	23.1	–	52.0	–	–	–	124.8 (C_m); 149.0 (C_p); 152.8 (C_o)	–	236.2	257.1	CD_2Cl_2; −10°C
2b	20.8	23.0	–	51.8	–	–	–	124.7 (C_m); 149.0 (C_p); 153.2 (C_o)	–	235.6	259.7	CD_2Cl_2; −20°C
3	–	22.7	–	54.7	–	87.9	–	–	–	245.7	281.7	C_6D_6; +20°C
4	12.6 [a]; 13.5; 14.9; 16.2 [a]	22.5	–	52.3	–	–	106.3 [a]; 106.8	143.4 [a]; 143.6; 151.0; 151.2 [a]	–	239.2	256.4	C_6D_6; +20°C
5	11.3	23.0	–	54.8	–	100.4	–	–	–	247.5	279.4	CD_2Cl_2; +20°C
6	–	23.0	30.6 [b]; 30.9 [c] 31.1	55.8	56.7; 57.6 [c]; 57.8 [b]	–	–	–	157.7 [b]; 166.4; 170.3 [c]	224.5	271.6	CD_2Cl_2; +20°C
7	–	23.0; 23.3	31.4	54.3	57.3	87.6	–	–	212.4	249.2	276.6	C_6D_6; +20°C
8	12.6; 12.7; 12.8; 15.5; 16.4; 16.6	22.7; 23.3	30.7	51.4	55.7	–	105.8; 106.0; 106.2	142.7; 143.1 [d]; 150.6; 151.0; 151.3	191.8	242.8	254.6	C_6D_6; +20°C
9	11.6	23.1; 23.4	32.0	54.1	57.3	99.3	–	–	222.8	250.7	275.2	C_6D_6; +20°C
10a	–	–	24.8 [e]; 31.4 [f]; 31.9 [g];	–	47.7 [e]; 54.9 [f]; 55.5 [g];	–	–	–	187.1 [f]; 195.0 [e]; 198.8 [h]; 199.0 [c]	230.1	–	C_6D_6; +20°C
10b	–	–	24.2 [e]; 32.0 [g]	–	47.0 [e]; 55.4 [g]	–	–	–	184.6 [e]; 198.9 [h]	229.8	–	C_6D_6; +20°C

[a] Carbon resonance of the two equivalent pyrazol-1-yl groups; [b] resonance of the tert-butyl isocyanide ligand, which is oriented *trans* to the aminocarbyne-ligand; [c] resonance of the two mutually *trans*-oriented tert-butyl isocyanide ligands; [d] resonances of two pyrazol-1-yl ring-carbons are by accident coincident; [e] resonance of the isopropyl isocyanide ligand; [f] signal of the tert-butyl isocyanide ligand, which is oriented *trans* to the carbonyl ligand; [g] an unequivocal assignment of these resonances is not possible; [h] resonance of either the tert-butyl isocyanide ligands of isomer **10b** or the tert-butyl isocyanide ligand of **10a**, which is oriented *trans* to the isopropyl isocyanide ligand.

resonance (δ 1.51) is assigned to the tert-butyl isocyanide ligand that is *trans* to the aminocarbyne ligand (Table 2). This assignment is based on a comparison with the ^{1}H NMR spectrum of $[(^t\text{BuNC})_5\text{Cr}{\equiv}\text{CN}^i\text{Pr}_2]\text{Br}$ (CD_2Cl_2, 20°C), which reveals that the tert-butyl protons of the *trans*-oriented isocyanide ligand are more deshielded (δ 1.49) than those of the four equivalent *cis*-oriented isocyanide ligands (δ 1.42) [10].

The ^{1}H NMR spectrum of the mixture of isomers **10a** and **10b** displays two well separate doublet and septet resonances for the methyl and methine protons, respectively of the isopropyl isocyanide ligand. The ratio **10a/10b** was calculated from the relative intensity of these signals to be 3.8/1. In comparison, the tert-butyl isocyanide ligands of **10a/10b** give rise to only three instead of the four expected singlet resonances at δ 1.15, 1.27 and 1.28. However, an unequivocal assignment of these resonances becomes possible on the basis of the relative signal intensity, the ratio **10a/10b**, and the chemical shift of the tert-butyl protons compared with that of the Cr^0 isocyanide complexes *fac*-$Cr(CO)_3(CN^t\text{Bu})_3$ (δ_{Me} 0.99; C_6D_6, 20°C) and $Cr(CN^t\text{Bu})_6$ (δ_{Me} 1.36; C_6D_6, 20°C) [10].

3.3. $^{13}C\{^1H\}$ NMR spectra

The ^{13}C NMR spectra also support the structures proposed for **1a–10b** (Table 3). Thus, only one resonance is observed for the four equivalent carbonyl ligands of **1a** and **1b**, indicating a *trans*-geometry for these complexes. Similarly, one resonance is found for the two equivalent *cis*-oriented carbonyl ligands in **2a–5** (Table 3). A considerable downfield shift of these carbonyl resonances is observed on going from the tetracarbonyl complexes **1a** and **1b** to the more electron-rich dicarbonyl derivatives **2a–5**. This trend is consistent with previous NMR studies on carbonyl complexes of Group VI transition metals, which have shown that a stronger metal–carbonyl back bonding causes a deshielding of the carbonyl carbon [17]. The same trend is observed for the isocyanide carbon resonances, as demonstrated by the ^{13}C NMR spectra of **7** and **9**, and allows an unequivocal assignment of the three isocyanide carbon resonances of **6** at δ 157.7, 166.4 and 170.3 (*i.e.* the metal-bound carbon of the isocyanide ligand, which is *trans*-oriented to the weakest π-acceptor, is the most deshielded one) (Table 3) [18]. It also helps, in combination with the signal intensity, to assign the six isocyanide carbon resonances observed in the ^{13}C NMR spectrum of the isomeric mixture **10a/10b** at δ 184.6–199.0.

All the aminocarbyne complexes show a distinctive low-field resonance for the carbyne-carbon at δ 254.6–279.4. This resonance appears at a lower field than that for analogous molybdenum or tungsten compounds, which is consistent with the ^{13}C shielding trend observed for the Group VI metal triad [2,17,19].

4. Summary

A high yield synthetic route to half-sandwich chromium aminocarbyne complexes of the type (η^5-C_5R_5)(CO)(L)Cr≡$CN^i\text{Pr}_2$ (R = H, Me; L = CO, ^{t}BuNC) has been developed starting from $Cr(CO)_6$. It is characterized by a sequence of clean, large scale reactions involving the readily accessible and well characterized compounds *trans*-$X(CO)_4\text{Cr}{\equiv}CN^i\text{Pr}_2$, *trans*-$X(CO)_2(\text{pic})_2\text{Cr}{\equiv}CN^i\text{Pr}_2$ (X = Cl, Br) and $[(^t\text{BuNC})_4(CO)\text{Cr}{\equiv}CN^i\text{Pr}_2]\text{Br}$. The availability of the complexes (η^5-C_5R_5)(CO)(L)Cr≡$CN^i\text{Pr}_2$ allows extensive studies of their reactions. These studies are aimed at determining the effect of chromium on several electrophile promoted CC-coupling reactions observed for electron-rich carbyne complexes of the heavier Group VI metals [20].

5. Experimental details

Standard Schlenk procedures were used for all syntheses and sample manipulations. The solvents were dried by standard methods (n-pentane, Et_2O and THF 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. All column chromatography was performed on a silica or neutral alumina (Merck, activity I, 0063–0.2 mm, dried *in vacuo* and stored under nitrogen) in a thermostated column of 45 cm length and 2.0 cm diameter.

Elemental analyses were performed by the Microanalytical Laboratory of this department. IR spectra were recorded on a Nicolet 5DX and a Perkin Elmer 1650 FT spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded in dry deoxygenated methylene-d_2 chloride or benzene-d_6 on a JEOL-JMX-GX 400 instrument. Chemical shifts were referred to residual solvent signals (CD_2Cl_2, δ_H 5.32 and δ_C 53.8 ppm; C_6D_6, δ_H 7.15 and δ_C 128.0 ppm). Mass spectra were obtained with a Varian MAT 311A and MAT 90A spectrometer; *m/z* values refer to the ^{52}Cr and ^{11}B isotopes. Complex **11** was prepared as described previously [10b].

5.1. *trans*-$Cl(CO)_4\text{Cr}{\equiv}CN^i\text{Pr}_2$ (**1a**)

To a suspension of 7.92 g (36.0 mmol) of $Cr(CO)_6$ in 70 ml of THF was added dropwise at −30°C a solution of 3.91 g (36.50 mmol) of $LiN^i\text{Pr}_2$ in 50 ml of THF. The mixture was allowed to warm to room temperature and was stirred for 1 h. Completion of the reaction was revealed by IR spectroscopy (replacement of the ν(CO)

absorption of the starting material at 1980 cm^{-1} by the ν(CO) absorptions of $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ at 2034, 1940, 1905 and 1873 cm^{-1}). The resulting red solution was evaporated to dryness and the oily residue washed once with cold n-pentane (−30°C) to remove traces of $Cr(CO)_6$, frozen in liquid nitrogen, pulverized, and then dried *in vacuo* at −20°C. The resulting yellow powder of the metallate $Li[(CO)_5Cr[C(O)N^iPr_2]]$ was suspended in 100 ml of CH_2Cl_2 and treated at −40°C with a solution of 3.09 ml (36.03 mmol) of ClC(O)C(O)Cl in 20 ml of CH_2Cl_2. The mixture was then stirred for 3 h at −30°C and the resulting brown-yellow suspension evaporated to dryness at −20°C. The residue was purified by column chromatography on silica at −20°C. Elution with CH_2Cl_2 gave an orange fraction, from which complex **1a** was obtained as a bright-orange, microcrystalline solid after removal of the solvent *in vacuo* at −20°C. M.p.: 112°C (dec.). Yield: 6.73 g (60%). Found: C, 42.15; H, 4.71; Cl, 11.96; Cr, 16.69; N, 4.53; O, 20.52. $C_{11}H_{14}ClCrNO_4$ (311.69) calc.: C, 42.39; H, 4.53; Cl, 11.37; Cr, 16.68; N, 4.49; O, 20.53%.

5.2. trans-$Br(CO)_4Cr{\equiv}CN^iPr_2$ (1b)

To a suspension of 6.15 g (27.95 mmol) of $Cr(CO)_6$ in 70 ml of THF was added dropwise at −10°C a solution of 3.00 g (28.00 mmol) of LiN^iPr_2 in 60 ml of THF. The mixture was allowed to warm to room temperature and was stirred for 1 h until the reaction was complete (IR monitoring). The acyl complex $Li[(CO)_5Cr\{C(O)N^iPr_2\}]$ was isolated as described above (synthesis of **1a**), suspended in 60 ml of CH_2Cl_2, and treated at −40°C with a solution of 3.98 ml (27.98 mmol) of BrC(O)C(O)Br in 20 ml of CH_2Cl_2. The mixture was stirred for 3 h at −40°C and the resulting brown-yellow suspension worked up as described for the preparation of **1a** to give complex **1b** as a bright-orange, microcrystalline solid. Yield: 7.46 g (75%). Found: C, 37.14; H, 3.96; Br, 22.26; Cr, 14.75; N, 3.96. $C_{11}H_{14}BrCrNO_4$ (356.13) calc.: C, 37.10; H, 3.96; Br, 22.44; Cr, 14.60; N, 3.93%.

5.3. $Cl(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (2a)

Complex **1a** (2.50 g, 8.02 mmol) was dissolved at −40°C in 70 ml of cold CH_2Cl_2 and the orange solution treated with 2.04 ml (20.81 mmol) of γ-picoline. The mixture was allowed to warm to room temperature and refluxed for 5 h. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 2098, 2026 and 1988 cm^{-1} by the two ν(CO) absorptions of the product at 1958 and 1865 cm^{-1}). The resulting dark-red solution was reduced in volume, cooled to −40°C, and a mixture of cold Et_2O/pentane (1/5) was added until precipitation of complex **2a** was complete. The supernatant pale-yellow solution was decanted off and the residue washed with pentane and dried *in vacuo* at −20°C. Orange-red solid. M.p.: 119°C (dec.). Yield: 3.36 g (95%). Found: C, 55.93; H, 6.32; Cl, 8.93; Cr, 11.47; N, 9.46; O, 7.58. $C_{21}H_{28}ClCrN_3O_2$ (441.92) calc.: C, 57.08; H, 6.39; Cl, 8.02; Cr, 11.77; N, 9.51; O, 7.24%.

5.4. $Br(CO)_2(pic)_2Cr{\equiv}CN^iPr_2$ (2b)

Complex **1b** (1.22 g, 3.43 mmol) of **1b** was dissolved at −40°C in 60 ml of cold CH_2Cl_2 and the orange solution treated with 1.00 ml (10.20 mmol) of γ-picoline. The mixture was allowed to warm to room temperature and refluxed for 3 h until reaction was complete (IR monitoring). The resulting dark-red solution was worked up as described above for the synthesis of **2a** to give complex **2b** as an orange-red solid. M.p.: 126°C (dec.). Yield: 1.65 g (99%). Found: C, 51.08; H, 5.84; Br, 16.20; Cr, 9.87; N, 8.41; O, 7.00. $C_{21}H_{28}BrCrN_3O_2$ (486.37) calc.: C, 51.86; H, 5.80; Br, 16.43; Cr, 10.69; N, 8.64; O, 6.58%.

5.5. $Cp(CO)_2Cr{\equiv}CN^iPr_2$ (3)

A mixture of 590 mg (1.21 mmol) of **2b** and 140 mg (1.59 mmol) of NaCp was suspended in 50 ml of cold THF (−60°C) and stirred for 0.5 h at −30°C. Completion of the reaction was revealed by IR-spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1960 and 1872 cm^{-1} by the two ν(CO) absorptions of the product at 1948 and 1871 cm^{-1}; presence of the $\nu(C_{carbyne}{\equiv}N)$ absorption of the product at 1550 cm^{-1} and the $\nu(C{\equiv}N)_{ring}$-absorption of uncoordinated γ-picoline at 1604 cm^{-1}). The resulting yellow-brown slurry was then evaporated to dryness and the residue purified by column chromatography on silica at −20°C. Traces of γ-picoline were first removed with n-pentane. Further elution with Et_2O/pentane (1/5) afforded a yellow fraction, from which complex **3** was obtained as an intense-yellow, microcrystalline solid by removal of the solvent *in vacuo*. M.p.: 91°C. Yield: 290 mg (84%). Found: C, 58.91; H, 6.74; Cr, 18.23; N, 4.90; O, 11.40. $C_{14}H_{19}CrNO_2$ (285.31) calc.: C, 58.94; H, 6.71; Cr, 18.22; N, 4.91; O, 11.22%. CI-MS: *m/z* 285 (M^+) (base peak), 257 ($[M - CO]^+$), 229 ($[M - 2CO]^+$), 186 ($[M - 2CO - {}^iPr]^+$).

5.6. $Tp'(CO)_2Cr{\equiv}CN^iPr_2$ (4)

A solution of 360 mg (1.07 mmol) of KTp' in 30 ml of THF was added to a solution of 500 mg (1.03 mmol) of **2b** in 40 ml of cold THF (−30°C). The mixture was allowed to warm to room temperature then stirred for 2 h during which the colour changed from orange to red and precipitation of KBr was observed. Completion

of the reaction was revealed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 1960 and 1872 cm^{-1} by the two ν(CO) absorptions of the product at 1952 and 1857 cm^{-1}; presence of the $\nu(C_{carbyne} \equiv N)$ absorption of the product at 1500 cm^{-1} and the $\nu(C \equiv N)_{ring}$-absorption of uncoordinated γ-picoline at 1604 cm^{-1}). The solvent was then stripped off and the residue extracted with Et_2O. The red extract was filtered through a filter canula and concentrated *in vacuo*, and n-pentane was added slowly to bring about precipitation of complex **4**. The supernatant yellow solution was decanted and the residue dried *in vacuo*. Red, microcrystalline solid. M.p.: 208°C (dec.). Yield: 495 mg (93%). Found: C, 56.54; H, 7.09; Cr, 9.39; N, 19.16; O, 6.29. $C_{24}H_{36}BCrN_7O_2$ (517.40) calc.: C, 55.71; H, 7.01; Cr, 10.05; N, 18.95; O, 6.18%. EI-MS (70 eV): *m/z* 461 ($[M - 2CO]^+$), 418 ($[M - 2CO - {}^iPr]^+$), 349 ($[M - 2CO - {}^iPr - {}^iPrNC]^+$) (base peak), 253 ($[M - 2CO - {}^iPr - {}^iPrNC - 3,5\text{-dimethylpyrazole}]^+$).

5.7. $Cp^*(CO)_2Cr{\equiv}CN^iPr_2$ (5)

A solution of 390 mg (0.80 mmol) of **2b** in 50 ml of cold THF (−40°C) was transferred via a canula into a suspension of 180 mg (1.03 mmol) of KCp^* in 20 ml of THF and the mixture stirred for 2 h at −30°C. After all **2b** had been consumed (monitoring by IR as in the syntheses of **3** and **4**) the resulting brown suspension was warmed to room temperature and evaporated to dryness, and the residue was purified by column chromatography on silica at 0°C. Traces of γ-picoline were first removed with n-pentane. Further elution with Et_2O/n-pentane (1/5) gave a yellow fraction, from which complex **5** was isolated as an intense-yellow, microcrystalline solid by evaporation of the solvent. M.p.: 118°C. Yield: 140 mg (49%). Found: C, 64.11; H, 8.33; N, 3.86. $C_{19}H_{29}CrNO_2$ (355.44) calc.: C, 64.20; H, 8.22; N, 3.94%. CI-MS: *m/z* 355 (M^+) (base peak), 256 ($[M - 2CO - {}^iPr]^+$).

5.8. $[({}^tBuNC)_4(CO)Cr{\equiv}CN^iPr_2]Br$ (6)

A solution of 680 mg (1.91 mmol) of **1b** in 50 ml of cold CH_2Cl_2 (−40°C) was treated with 1.0 ml (8.84 mmol) of ^tBuNC and the mixture warmed to room temperature and then refluxed for 6 h, during which evolution of gas was observed and the initially orange solution turned red. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorptions of the starting material at 2098, 2026 and 1988 cm^{-1} by the ν(CO) absorption of the product at 1910 cm^{-1}). The solution was concentrated *in vacuo* and treated with a cold Et_2O/pentane mixture (1/1), (−80°C). The supernatant, slightly yellow, solution was decanted, and the oily residue washed once with a THF/pentane mixture (1/1) to give complex **6** as a rose coloured solid. Yield: 1.10 g (96%). M.p.: 140°C (dec.). Found: C, 56.13; H, 8.43; Br, 12.78; Cr, 8.72; N, 11.76; O, 3.02. $C_{28}H_{50}BrCrN_5O$ (604.64) calc.: C, 55.62; H, 8.33; Br, 13.22; Cr, 8.60; N, 11.58; O, 2.65%. FD-MS: *m/z* 524 (M^+).

5.9. $Cp(CO)({}^tBuNC)Cr{\equiv}CN^iPr_2$ (7)

A wine-red suspension of a mixture of 1.17 g (1.94 mmol) of **6** and 220 mg (2.50 mmol) of NaCp in 50 ml of THF was stirred for 20 h at 50°C. Completion of the reaction was confirmed by IR spectroscopy (disappearance of the ν(CO) absorption of the starting material at 1910 cm^{-1}). The resulting brown suspension was evaporated to dryness and the residue extracted twice with 25 ml of n-pentane. The extract was filtered to leave an insoluble purple-brown solid, which was shown by IR-spectroscopy to contain the complex $[({}^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$, and the filtrate was evaporated to dryness. The resulting oily residue was purified by column chromatography on alumina at −20°C. Elution with Et_2O/n-pentane (1/5) gave a yellow fraction, from which the solvent was removed *in vacuo*. The resulting oil solidified to an intense-yellow, microcrystalline solid after being dried for 24 h at −78°C and stored for several days on dry ice. M.p.: < 20°C. Yield: 400 mg (61%). Found: C, 63.79; H, 8.58; N, 7.67. $C_{18}H_{28}CrN_2O$ (340.43) calc.: C, 63.51; H, 8.29; N, 8.23%.

5.10. $Tp'(CO)({}^tBuNC)Cr{\equiv}CN^iPr_2$ (8)

The wine-red suspension of a mixture of 270 mg (0.45 mmol) of **6** and 220 mg (0.65 mmol) of KTp' in 50 ml of THF was stirred for 7 days at 50°C until reaction was complete (IR monitoring, see synthesis of complex **7**). The suspension was then evaporated to dryness and the residue extracted with a mixture of Et_2O/n-pentane (1/5). The red extract was filtered (to leave an insoluble purple-brown residue containing $[({}^tBuNC)_5Cr{\equiv}CN^iPr_2]Br$) and the filtrate evaporated to dryness. The residue was crystallized from Et_2O/n-pentane to give complex **8** as a red, microcrystalline solid. M.p.: 155°C (dec.). Yield: 150 mg (58%). Found: C, 58.05; H, 7.93; Cr, 8.61; N, 19.07. $C_{28}H_{45}BCrN_8O$ (572.52) calc.: C, 58.74; H, 7.92; Cr, 9.08; N, 19.57%. EI-MS (70 eV): *m/z* 544 ($[M - CO]^+$), 501 ($[M - CO - {}^iPr]^+$), 461 ($[M - CO - {}^tBuNC]^+$), 444 ($[M - CO - {}^iPr - {}^tBu]^+$), 432 ($[M - CO - {}^iPr - {}^iPrNC]^+$), 418 ($[M - CO - {}^tBuNC - {}^iPr]^+$), 349 ($[M - CO - {}^tBuNC - {}^iPr - {}^iPrNC]^+$) (base peak).

5.11. $Cp^*(CO)({}^tBuNC)Cr{\equiv}CN^iPr_2$ (9) and cis/trans-$Cr(CO)(CN^iPr)(CN^tBu)_4$ (10a/10b) from 6 and KCp^*

The wine-red suspension of a mixture of 1.74 g (2.88 mmol) of **6** and 810 mg (4.65 mmol) of KCp^* in 50 ml

of THF was heated for 1 h at 45°C. After all **6** had been consumed (monitoring by IR as in the synthesis of **7** and **8**), the resulting brown suspension was evaporated to dryness and the residue extracted twice with 25 ml of n-pentane. The extract was evaporated to dryness and the resulting oily residue purified by column chromatography on alumina at −20°C. Complex **9** was eluted with Et_2O/n-pentane (2/25) and the yellow eluate evaporated to dryness at −20°C. The resulting oil solidified after storage for several days on dry ice to give an intense-yellow microcrystalline solid, which melted below room temperature. Yield: 300 mg (25%). $C_{23}H_{38}CrN_2O$ (410.56). CI-MS: *m/z* 410 (M^+) (base peak), 382 ($[M - CO]^+$), 339 ($[M - CO - {}^iPr]^+$), 283 ($[M - CO - {}^iPr - Me_2C{=}CH_2]^+$), 256 ($[M - CO - {}^iPr - {}^tBuNC]^+$). Further elution with Et_2O/n-pentane (1/5) afforded another yellow fraction, from which the isomeric mixture **10a/10b** (3.8/1) was isolated as an intense-yellow solid by evaporation of the solvent at −20°C. M.p.: 57°C. Yield: 550 mg (40%). Found: C, 63.05; H, 9.12; Cr, 9.94; N, 14.03; O, 3.75. $C_{25}H_{43}CrN_5O$ (481.64) calc.: C, 62.34; H, 9.00; Cr, 10.80; N, 14.54; O, 3.32%. EI-MS (70 eV): *m/z* 481 (M^+), 301 ($[M - CO - {}^tBuNC - {}^iPrNC]^+$), 287 ($[M - CO - 2{}^tBuNC]^+$), 218 ($[M - CO - 2{}^tBuNC - {}^iPrNC]^+$) (base peak), 204 ($[M - CO - 3{}^tBuNC]^+$), 162 ($[M - CO - 3{}^tBuNC\text{-}Me_2C{=}CH_2]^+$).

5.12. *Cp*(CO)(tBuNC)Cr≡CNiPr2 (9) from 11 and KCp**

A solution of 250 mg (0.48 mmol) of **11** in 25 ml of THF was added to a suspension of 115 mg (0.66 mmol) of KCp^* in 25 ml THF and the mixture heated for 2 h at 50°C. Completion of the reaction was confirmed by IR spectroscopy (replacement of the ν(CO) absorption of the starting material at 1910 cm^{-1} by the ν(CO) absorption of the product at 1844 cm^{-1}). The resulting yellow-brown suspension was evaporated to dryness and the residue purified by column chromatography on alumina at −20°C. Elution with Et_2O/n-pentane (1/5) gave a yellow band, from which complex **9** was isolated as an intense-yellow oil and characterized by comparing its IR, ^1H and ^{13}C-NMR spectra with those of a pure sample of **9** obtained as described above. Yield: 150 mg (76%).

Acknowledgments

We thank Professor W.A. Herrmann for providing institute facilities, the Volkswagen Stiftung, the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, M. Barth, I. Liss and A. Fuß for elemental analyses and R. Dumitrescu and I. Werner for recording the mass spectra.

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