Metal–carbon multiple bonds: synthesis, structure, and electrochemistry of chromium aminocarbyne and phenylcarbyne complexes bearing phosphine or alkyl isonitrile ligands [1]

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Abstract

The synthesis, structure and cyclic voltammetry studies of neutral and cationic chromium carbyne complexes bearing phosphine or alkyl isonitrile ligands are reported. Treatment of cis-X(CO)$_2$(pic)$_2$Cr≡CN^{i}Pr$_2$ (pic: 4-methylpyridine) (**1a**: X = Cl; **1b**: X = Br) with two equivalents of PMe$_3$ and PMe$_2$Ph, or one equivalent of 1,2-bis(diphenylphosphino)ethane (dppe) affords the aminocarbyne complexes cis-Cl(CO)$_2$(PMe$_3$)$_2$Cr≡CN^{i}Pr$_2$ (**2a**), cis-Cl(CO)$_2$(dppe)Cr≡CN^{i}Pr$_2$ (**2b**) and cis-Br(CO)$_2$(PMe$_2$Ph)$_2$Cr≡CN^{i}Pr$_2$ (**2c**) respectively. In comparison, reaction of **1a** with two equivalents of P(OMe)$_3$ gives selectively the trans-isomer Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr≡CN^{i}Pr$_2$ (**3**). Complex **2c** is converted with TlPF$_6$ and PMe$_2$Ph to the cationic aminocarbyne complex [fac-(PMe$_2$Ph)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$][PF$_6$] (**4**). Similarly, the cationic phenylcarbyne complex [fac-(^{t}BuNC)$_3$(CO)$_2$Cr≡CPh][PF$_6$] (**6a**) is obtained from cis-Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CPh (**5a**), TlPF$_6$ and ^{t}BuNC. Treatment of **1a** with four equivalents of isopropyl isonitrile affords the cationic aminocarbyne complex [cis-(^{i}PrNC)$_3$(CO)Cr≡CN^{i}Pr$_2$]Cl (**9a**), which is converted with TlPF$_6$ to [cis-(^{i}PrNC)$_3$(CO)Cr≡CN^{i}Pr$_2$][PF$_6$] (**9b**). Comparative cyclic voltammetry studies of the aminocarbyne complexes **2a**, **2c**, **4**, cis-Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CN^{i}Pr$_2$ (**5b**), [fac-(^{t}BuNC)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$][PF$_6$] (**6b**), mer-Br(^{t}BuNC)$_3$(CO)Cr≡CN^{i}Pr$_2$ (**7**), [cis-(^{t}BuNC)$_4$(CO)Cr≡CN^{i}Pr$_2$][PF$_6$] (**8b**), [(^{t}BuNC)$_5$Cr≡CN^{i}Pr$_2$][PF$_6$] (**10**) and the phenylcarbyne complexes **5a** and **6a** are reported. The crystal structures of the aminocarbyne complexes **2a** and **2c** are described.

Keywords: Chromium; Carbyne complexes; Isonitrile complexes; Cyclic voltammetry; Multiple bonds

1. Introduction

Mononuclear aminocarbyne complexes were first prepared by Fischer et al. in 1974 [1]. Since then, extensive studies have been carried out on the synthesis, structure and reactivity of these compounds [2,3]. Of specific interest are those reactions of aminocarbyne complexes where the electronic difference between an aminocarbyne ligand and an alkyl- or arylcarbyne ligand is manifested. Examples for this are: (a) the nucleophile-induced carbyne–carbonyl coupling reaction of Fischer-type carbyne complexes to give ketenyl complexes [4,5], which is hindered by the presence of an

amino group at the carbyne-carbon [6,7]; (b) the synthesis and stabilisation of mononuclear bis(aminocarbyne) complexes [8], which are important intermediates in the electrophile-assisted carbyne–isonitrile coupling reaction of Fischer-type carbyne complexes [4,9,10] and the reductive isonitrile–isonitrile coupling reaction of the Mo^{II} and W^{II} complexes [M(CNR)$_6$X]$^+$ (R = alkyl; X = halide) [11]; (c) the oxidation of Fischer-type carbyne complexes, which affords carbonyl-containing Schrock-type carbyne complexes, when the carbyne-carbon atom bears an amino-substituent [12-14]. In comparison, electrochemical studies on carbyne complexes are rare [15]. Accordingly, we have prepared several Fischer-type chromium carbyne complexes bearing phosphine or alkyl isonitrile ligands and describe herein the structure and the redox properties of these compounds studied by cyclic voltammetry.

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[1] Dedicated to Professor Dr. Walter Siebert on the occasion of his 60th birthday on the 7th January 1997.

2. Results and discussion

We have recently reported a highly efficient method for the synthesis of the chromium aminocarbyne complexes cis-X(CO)$_2$(pic)$_2$Cr≡CN^{i}Pr$_2$ (**1a**: X = Cl; **1b**: X = Br; pic: 4-methylpyridine) [16] and have shown that these compounds are like other pyridine-substituted carbyne complexes [7,9,13,14,17,18] useful starting materials for the preparation of various substitution products owing to the presence of the coordinatively labile 4-methylpyridine ligands [16,19]. This property also proved to be useful for the synthesis of the compounds outlined in Scheme 1.

Thus, when a solution of **1a** in CH$_2$Cl$_2$ was treated with two equivalents of PMe$_3$ or one equivalent of 1,2-bis(diphenylphosphino)ethane (dppe) at ambient temperature, a rapid ligand exchange reaction occurred to give the complexes **2a** and **2b** respectively (Scheme 1). Evidence for the clean conversion of **1a** to **2a** and **2b** was given by the IR spectra of the reaction solutions, which showed that the two ν(CO) absorptions of the starting material at 1958 and 1965 cm^{-1} had been replaced at the end of the reaction by those of the products at 1970 and 1887 cm^{-1} (**2a**) and 1972 and 1892 cm^{-1} (**2b**). Similarly, treatment of the bromo complex **1b** with two equivalents of PMe$_2$Ph afforded the complex **2c** (Scheme 1).

Complexes **2a–2c** were purified by column chromatography on silica and isolated in high yields as orange, slightly air-sensitive solids, which were soluble in CH$_2$Cl$_2$ and THF but insoluble in Et$_2$O; they melted without decomposition at 144 °C, 177 °C and 149 °C

Scheme 1.
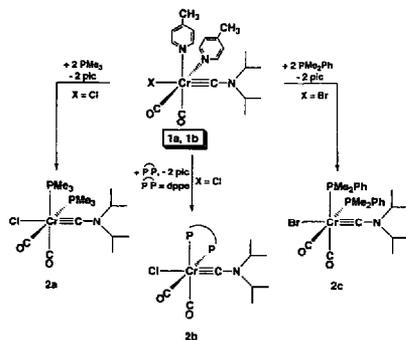
respectively. Their thermal stability was considerably higher than that of mer-Br(CO)$_3$(PPh$_3$)Cr≡CNEt$_2$, the only other known phosphine-substituted neutral chromium aminocarbyne complex, which decomposes upon heating at 109 °C [20]. The presence of two ν(CO) absorptions of almost equal intensity in the IR spectra of **2a–2c** (Table 1), of a singlet resonance in the ^{31}P{^{1}H} NMR spectra (Table 2) and of a triplet resonance for the carbyne-carbon nucleus in the ^{13}C{^{1}H} NMR spectra (Table 2) shows unequivocally the cis arrangement of the carbonyl ligands and the trans orientation of the halo and the carbyne ligand in these compounds.

Table 1
Selected IR data of the complexes **2a–10**

Complex	ν(C ≡ NR) (cm^{-1})	ν(CO) (cm^{-1})	ν(C$_{carbyne}$–N) (cm^{-1})	Solvent
cis-Cl(CO)$_2$(PMe$_3$)$_2$Cr≡CN^{i}Pr$_2$ (**2a**)	—	1970 vs, 1887 vs	1505 m	CH$_2$Cl$_2$
cis-Cl(CO)$_2$(dppe)Cr≡CN^{i}Pr$_2$ (**2b**)	—	1972 vs, 1892 vs	1508 m	CH$_2$Cl$_2$
cis-Br(CO)$_2$(PMe$_2$Ph)$_2$Cr≡CN^{i}Pr$_2$ (**2c**)	—	1970 vs, 1886 vs	1506 m	CH$_2$Cl$_2$
trans-Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr≡CN^{i}Pr$_2$ (**3**)	—	1896 vs	1533 m	CH$_2$Cl$_2$
[fac-(PMe$_2$Ph)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$]PF$_6$ (**4**)	—	1963 s, 1894 vs	1524 m	CH$_2$Cl$_2$
cis-Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CPh (**5a**) [21]	2182 s, 2171 s	2025 vs, 1976 vs	—	CH$_2$Cl$_2$
cis-Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CN^{i}Pr$_2$ (**5b**) [19]	2166 s, 2143 s	1988 vs, 1922 vs	1536 m, 1525 m	CH$_2$Cl$_2$
[fac-(^{t}BuNC)$_3$(CO)$_2$Cr≡CPh]PF$_6$ (**6a**)	2205 s, 2189 s, 2178 s	2037 vs, 1987 vs	—	CH$_2$Cl$_2$
[fac-(^{t}BuNC)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$]PF$_6$(**6b**) [19]	2186 s, 2170 m, 2149 m	2000 vs, 1940 vs	1566 m	CH$_2$Cl$_2$
mer-Br(CO)(^{t}BuNC)$_3$Cr≡CN^{i}Pr$_2$ (**7**) [19]	2136 sh, 2109 s, 2074 m	1911 vs	1506 m	Et$_2$O
[cis-(^{t}BuNC)$_4$(CO)Cr≡CN^{i}Pr$_2$]Br (**8a**) [19]	2177 s, 2154 w, 2123 vs, 2063 w	1910 vs	1549 m	CH$_2$Cl$_2$
[cis-(^{i}PrNC)$_4$(CO)Cr≡CN^{i}Pr$_2$]Cl (**9a**)	2185 s, 2163 w, 2136 vs, 2122 s,sh	1908 s	1549 m	CH$_2$Cl$_2$
[(^{t}BuNC)$_5$Cr≡CN^{i}Pr$_2$]PF$_6$] (**10**) [19]	2164 s, 2133 w, 2093 vs, 2042 vs	—	1520 m	CH$_2$Cl$_2$

Table 2
Selected ^{13}C and ^{31}P NMR data of the complexes 2a–4, 6a and 9a; chemical shifts are given in parts per million, multiplicities of the signals are in parentheses, and coupling constants in hertz

Compound	Cr≡C	CO	CNR	^{31}P	Solvent; T (°C)
cis-Cl(CO)₂(PMe₃)₂Cr≡CN¹Pr₂ (2a)	256.0 (t) ^2J(CP) = 25.4	231.0	—	1.6	CD₂Cl₂; −10
cis-Cl(CO)₂(dppe)Cr≡CN¹Pr₂ (2b)	257.1 (t) ^2J(CP) = 22.2	233.9	—	62.1	CD₂Cl₂; +20
cis-Br(CO)₂(PMe₂Ph)Cr≡CN¹Pr₂ (2c)	258.2 (t) ^3J(CP) = 23.2	229.9	—	7.1	CDCl₃; +20
trans-Cl(CO)₂[P(OMe)₃]₂Cr≡CN¹Pr₂ (3)	261.2 (t) ^3J(CP) = 36.2	220.3 (t) ^2J(CP) = 25.6	—	181.6	C₆D₆; +20
[fac-(PMe₂Ph)₃(CO)₂Cr≡CN¹Pr₂][PF₆] (4)	272.3 (m)	230.8 (m)	—	−2.4 (t) ^2J(PP) = 39.0; 8.1 (d) ^2J(PP) = 39.0	CDCl₃; +20
[fac-(¹BuNC)₃(CO)₂Cr≡CPh][PF₆] (6a)	323.7	218.6	142.8 [a]; 152.5	—	CD₂Cl₂; −20
[cis-(¹PrNC)₄(CO)Cr≡CN¹Pr₂]Cl (9a)	271.0	224.5	157.5 [a]; 166.2 [b]; 170.0	—	CD₂Cl₂; +20

[a] Resonance of the isonitrile ligand, which is in trans position relative to the carbyne ligand. [b] Resonance of the isonitrile ligand, which is in trans position relative to the carbonyl ligand.

In addition, the aminocarbyne complexes 2a–2c are distinguished by an absorption in the solution IR spectra at ca. 1510 cm⁻¹, which can be assigned to the ν(C$_{carbyne}$–N) vibration. The fairly high frequency of this vibration reveals the strong π conjugation of the amino group with the metal–carbon triple bond in these compounds [2,3,16,19].

The stereochemistry of the compounds 2a and 2c was also confirmed by single crystal X-ray diffraction studies. The structures of 2a and of one of the two molecules of 2c in the asymmetric unit are shown in Figs. 1 and 2 respectively. Selected bond lengths and angles of 2a and 2c are summarized in Tables 3 and 4 respectively. The bond lengths and angles of the two molecules of 2c in the asymmetric unit are very similar.
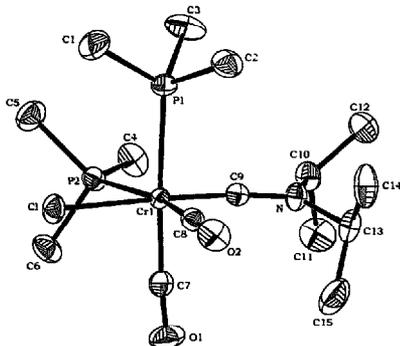
Therefore the discussion is based on the data obtained for one of the two molecules of 2c, shown in Fig. 2.

Both complexes are distorted octahedral and show the expected [22] trans orientation of the halo ligand to the carbyne ligand with the phosphine ligands occupying two cis coordination sites. The plane of the aminocarbyne ligand defined by the atoms N, C(10) and C(13) (2a) and N(1), C(4) and C(7) (2c) is eclipsed to one phosphine and one carbonyl ligand (P(2) and C(8) in 2a and P(1) and C(1) in 2c). These ligands are bent out of the equatorial plane towards the halo ligand as shown for 2a by the angles Cl–Cr(1)–P(2) (82.11°) and
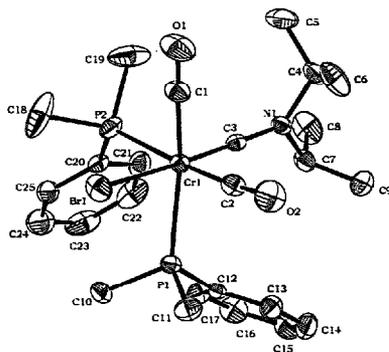

Fig. 1. ORTEP plot of the structure of 2a.

Fig. 2. ORTEP plot of the structure of one of the two molecules of 2c in the crystallographic asymmetric unit showing the atom labeling scheme. The second molecule contains the atoms Cr2, Br2, P3, P4, N2, O3, O4, and C26 to C50.

Cl–Cr(1)–C(8) (84.85°) (Table 3) and for **2c** by the angles Br(1)–Cr(1)–P(1) (82.27°) and Br(1)–Cr(1)–C(1) (84.1°) (Table 4). By contrast, the other phosphine and carbonyl ligand is slightly bent out of the equatorial plane towards the aminocarbyne ligand as shown for **2a** by the angles Cl–Cr(1)–P(1) (91.28°) and Cl–Cr(1)–C(7) (92.87°) (Table 3) and for **2c** by the angles Br(1)–Cr(1)–P(2) (90.50°) and Br(1)–Cr(1)–C(2) (90.9°) (Table 4). The Cr–C$_{carbyne}$–N linkages in both complexes are almost linear (**2a**: 175.2°; **2c**: 173.8°). The Cr–C$_{carbyne}$ bond lengths of 174.0(2) pm (**2a**) and 173.3(4) pm (**2c**) are similar to those reported for other Fischer-type aminocarbyne complexes, which contain a π-donor ligand in trans-position to the carbyne ligand, such as trans-Cl(CO)$_4$Cr≡CN^{i}Pr$_2$ (Cr–C$_{carbyne}$ = 174.7(5) pm) [23] and Cp(CO)$_2$Cr≡CN^{i}Pr$_2$ (Cr–C$_{carbyne}$ = 172.8(8) pm) [24]. In comparison, the Cr–halogen bonds of **2a** and **2c** (**2a**: Cr–Cl = 246.67(10) pm; **2c**: Cr–Br = 261.54(10) pm) are longer than those of the related tetracarbonyl complexes trans-Cl(CO)$_4$Cr≡CN^{i}Pr$_2$ (Cr–Cl = 241.2(1) pm) [23] and trans-Br(CO)$_4$Cr≡CNEt$_2$ (Cr–Br = 256.4(2) pm) [25], which shows, that π-donation of the halogen ligand to the metal center is reduced when the electron density at the metal center is enhanced. This also offers an explanation for the observed increase in reactivity of the complexes **2a** and **2c** towards halide abstraction reagents such as TlPF$_6$ (see Eq. (2)). The C$_{carbyne}$–N bonds of (**2a**) (131.2(3) pm) and of (**2c**) (131.2(5) pm) are intermediate in length between that expected for a C(sp)–N(sp^2) single and double bond; this is in full agreement with the IR spectra, and indicates a high degree of π-bonding between the carbyne-carbon atom and the amino-nitrogen atom in these compounds [3]. Further evidence for this π-bonding is given by the planarity of the aminocarbyne ligand. No isomerization of the cis-dicarbonyl complexes **2a** and **2c** to the trans-dicarbonyl complexes is observed in solution, whereas the analogous tungsten aminocarbyne complex cis-I(CO)$_2$(PMe$_3$)$_2$W≡CNEt$_2$, when heated in the solid state or stirred in Et$_2$O at ambient temperature, to trans-I(CO)$_2$(PMe$_3$)$_2$W≡CNEt$_2$ [18]. In comparison, the analogous phenylcarbyne complexes of

molybdenum and tungsten cis-X(CO)$_2$(PR$_3$)$_2$M≡CPh (X = Cl, Br; R = Me, Ph) have previously been shown to undergo a photoinduced isomerization to the trans isomers, whereas the related chromium phenylcarbyne complex cis-Br(CO)$_2$(PMe$_3$)$_2$Cr≡CPh loses carbon monoxide upon irradiation with visible light [26].

Treatment of **1a** with slightly more than two equivalents of P(OMe)$_3$ in CH$_2$Cl$_2$ at ambient temperature resulted in the formation of trans-Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr≡CN^{i}Pr$_2$ (3) (Eq. (1)).

$$(1)$$
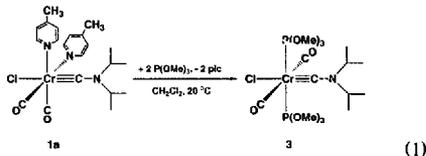
Complex **3** was purified by column chromatography on silica at 0°C and isolated as a yellow microcrystalline solid which was soluble in CH$_2$Cl$_2$, THF, benzene and Et$_2$O, but scarcely soluble in pentane; it melted without decomposition at 158°C. The IR spectrum of **3** exhibits one strong ν(CO) absorption at 1896 cm^{-1} (Table 1), the ^{31}P spectrum one singlet resonance at δ 181.6, and the ^{13}C NMR spectrum one triplet resonance for the equivalent CO ligands at δ 220.3 ppm (^2J(CP) = 25.6 Hz) and one triplet resonance for the carbyne-carbon nucleus at δ 261.2 (^2J(CP) = 36.2 Hz) (Table 2); all these data indicate a trans disposition of both the carbonyl and the phosphite ligands in **3**. IR monitoring of the reaction of **1a** with

Table 4
Selected bond lengths (pm) and bond angles (deg) with estimated standard deviations for the two molecules of **2c** in the crystallographic asymmetric unit

Bond lengths			
Cr(1)–C(1)	186.9(6)	Cr(2)–C(26)	187.0(6)
Cr(1)–C(2)	183.5(5)	Cr(2)–C(27)	183.3(5)
Cr(1)–C(3)	173.3(4)	Cr(2)–C(28)	174.3(4)
Cr(1)–P(1)	242.9(2)	Cr(2)–P(3)	243.0(2)
Cr(1)–P(2)	240.68(14)	Cr(2)–P(4)	240.7(2)
Cr(1)–Br(1)	261.54(10)	Cr(2)–Br(2)	261.65(10)
C(3)–N(1)	131.2(5)	C(28)–N(2)	130.7(5)
C(4)–N(1)	150.3(6)	C(29)–N(2)	148.6(5)
C(7)–N(1)	148.7(5)	C(32)–N(2)	148.9(6)
Bond lengths			
Br(1)–Cr(1)–P(1)	82.27(4)	Br(2)–Cr(2)–P(3)	82.48(4)
Br(1)–Cr(1)–P(2)	90.50(4)	Br(2)–Cr(2)–P(4)	90.46(4)
Br(1)–Cr(1)–C(1)	84.1(2)	Br(2)–Cr(2)–C(26)	83.7(2)
Br(1)–Cr(1)–C(2)	90.9(2)	Br(2)–Cr(2)–C(27)	90.7(2)
Br(1)–Cr(1)–C(3)	174.58(13)	Br(2)Cr(2)–C(28)	174.67(13)
Cr(1)–C(3)–N(1)	173.8(3)	Cr(2)–C(28)–N(2)	173.3(3)
C(3)–N(1)–C(4)	122.5(4)	C(28)–N(2)–C(29)	119.3(4)
C(3)–N(1)–C(7)	119.3(4)	C(28)–N(2)–C(32)	122.4(4)
C(4)–N(1)–C(7)	117.8(4)	C(29)–N(2)–C(32)	118.1(4)

Table 3
Selected bond lengths (pm) and bond angles (deg) with estimated standard deviations for **2a**

Cr(1)–C(7)	184.9(2)	Cl–Cr(1)–P(1)	91.28(3)
Cr(1)–C(8)	188.8(2)	Cl–Cr(1)–P(2)	82.11(4)
Cr(1)–C(9)	174.0(2)	Cl–Cr(1)–C(7)	92.87(7)
Cr(1)–P(1)	238.87(9)	Cl–Cr(1)–C(8)	84.85(7)
Cr(1)–P(2)	241.24(10)	Cl–Cr(1)–C(9)	175.38(7)
Cr(1)–Cl	246.67(10)	Cr(1)–C(9)–N	175.2(2)
C(9)–N	131.2(3)	C(9)–N–C(10)	118.6(2)
C(10)–N	149.2(3)	C(9)–N–C(13)	122.1(2)
C(13)–N	149.3(3)	C(10)–N–C(13)	118.7(2)

P(OMe)$_3$ revealed the intermediate formation of another complex with a ν(CO) absorption at 1993 cm^{-1} which was well separated from the ν(CO) absorption of 3. Upon comparison with the IR spectrum of *cis*-I(CO)$_2$[P(OMe)$_3$]$_2$W≡CNEt$_2$ (ν(CO) in CH$_2$Cl$_2$: 1992 and 1918 cm^{-1}) [27], the absorption at 1993 cm^{-1} may be assigned to the symmetric A$_1$ CO stretching vibration of *cis*-Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr≡CN^{i}Pr$_2$, the antisymmetric B$_1$ CO stretching vibration giving rise to an absorption that is probably obscured by the ν(CO) absorption of the trans isomer 3. We therefore suggest a two-step reaction of **1a** with P(OMe)$_3$ to give in the first step the γ-picoline ligands of **1a** are replaced by the phosphite to give *cis*-Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr≡CN^{i}Pr$_2$, which subsequently isomerizes to the trans complex 3. Formation of a *trans*-dicarbonyl complex has also previously been observed in the reaction of the phenylcarbyne complex *trans*-Cl(CO)$_4$Cr≡CPh with triphenylphosphite to afford *trans*-Cl(CO)$_2$[P(OPh)$_3$]$_2$Cr≡CPh and has been explained by a combination of steric and electronic factors [21]. In the present case we assume that the steric constraint resulting from the facial disposition of the bulky aminocarbyne and the two trimethylphosphite ligands outweighs the electronic advantage of three donor ligands being coordinated trans to three π-acceptor ligands and, therefore, the initial formation of the cis complex is followed by an isomerization to the trans-complex 3. In comparison, the reaction of the analogous tungsten aminocarbyne complex *cis*-I(CO)$_2$py$_2$W≡CNEt$_2$ with P(OMe)$_3$ has previously been shown to give a mixture of the isolable cis and trans isomers of I(CO)$_2$[P(OMe)$_3$]$_2$W≡CNEt$_2$; these equilibrate in solution at ambient temperature, with the trans isomer being the thermodynamically more stable complex [27].

Attempts to prepare more 'electron-rich' aminocarbyne complexes, by replacing one or both carbonyl ligands in **2c** by PMe$_2$Ph, have so far proven unsuccessful. Thus, the complex **2c** was recovered, when a solution of **2c** in toluene was heated at 90 °C for 10 h in the presence of excess PMe$_2$Ph.

However, introduction of a third phosphine ligand can be achieved, if the halo ligand is abstracted from the metal center in the presence of phosphine. Thus, treatment of **2c** with slightly more than one equivalent of TlPF$_6$ and PMe$_2$Ph in CH$_2$Cl$_2$ at -20 °C affords the cationic aminocarbyne complex [*fac*-(PhMe$_2$P)O(CO)$_2$Cr≡CN^{i}Pr$_2$]PF$_6$] (**4**), which was isolated as a yellow-orange solid in 59% yield. It is soluble in CH$_2$Cl$_2$ and THF and melts at 134 °C (Eq. (2)).

$$ \text{(2)} $$
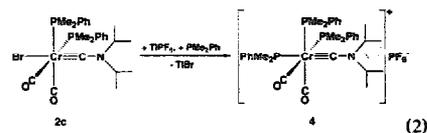
Similarly, reaction of the related phenylcarbyne complex *cis*-Br(CO)$_2$(^{t}BuNC)$_2$Cr≡CPh (**5a**) with slightly more than one equivalent of TlPF$_6$ and ^{t}BuNC in CH$_2$Cl$_2$ at -10 °C resulted in the formation of the cationic phenylcarbyne complex [(^{t}BuNC)$_3$(CO)$_2$Cr≡CPh]PF$_6$] (**6a**) (Eq. (3)). This was isolated in 91% yield as a red-brown solid which was soluble in CH$_2$Cl$_2$ and THF; this decomposed slowly in

Table 5
Voltammetric data for the complexes **2a**, **2c**, **5a–7**, **8b** and **10** [a]

Complex	E_{pa} (V)	E_{pc} (V)	I_a/I_c	$(E_{pa} - E_{pc})$ (mV)	$E_{1/2}$ (V)
2a	−0.11	—	—	—	—
	0.88	—	—	—	—
2c	0.03	—	—	—	—
	0.95	—	—	—	—
4	0.53	—	—	—	—
	1.10	—	—	—	—
5a	0.46	—	—	—	—
5b	0.03	—	—	—	—
6a	0.85	0.73	2.25	120	—
6b	0.57	—	—	—	—
7	−0.41	—	—	—	—
	1.03	—	—	—	—
8b	0.03	−0.05	1.00	78	−0.01
	1.01	—	—	—	—
10 [b]	−0.58	−0.66	1.01	78	−0.62
	0.72	0.61	1.35	110	—

[a] All measurements in CH$_2$Cl$_2$–TBAPF$_6$ at 25 °C at a scan rate of 0.1 V s^{-1}; potentials are in volts vs. the ferrocene/ferrocenium redox couple.
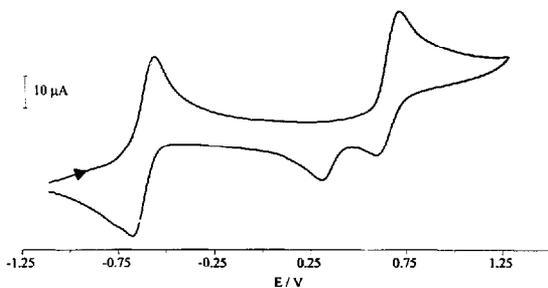[b] An additional cathodic peak is observed at 0.32 V.

solution at ambient temperature and in the solid state at 81 °C. Complex **6a** is thus considerably less stable than the analogous aminocarbyne complex [('BuNC)$_3$(CO)$_2$Cr≡CN^{i}Pr$_2$][PF$_6$] (**6b**), which decomposes in the solid state at 138 °C [19].

$$(3)$$

The presence of two $\nu(CO)$ absorptions of almost equal intensity in the IR spectra of **4** and **6a** (Table 1) and of one resonance for the carbonyl-carbon nuclei in the ^{13}C{^{1}H} NMR spectra (Table 2) show unequivocally the facial arrangement of the three phosphine and *tert*-butyl isonitrile ligands in **4** and **6a** respectively. The $\nu(CO)$ absorptions of the phenylcarbyne complex **6a** appear at higher wavenumbers than those of the analogous aminocarbyne complex, indicating the stronger π acceptor ability of the phenylcarbyne ligand. This is also reflected in the redox properties of these compounds, the phenylcarbyne complex **6a** being less easily oxidized than **6b** (Table 5).

Reaction of **1a** with four equivalents of isopropyl isonitrile in refluxing CH$_2$Cl$_2$ affords the cationic aminocarbyne complex [(^{i}PrNC)$_4$(CO)Cr≡CN^{i}Pr$_2$]Cl (**9a**), which was isolated as a red solid in 85% yield (Eq. (4)). Complex **9a** is soluble in CH$_2$Cl$_2$, scarcely soluble in THF and insoluble in Et$_2$O; it decomposes upon heating in the solid state at 108 °C. It can be easily converted with TlPF$_6$ to the PF$_6$ salt **9b**.

$$(4)$$

The IR spectrum of **9a** shows four $\nu(C≡N^i Pr)$ absorptions, as expected on the basis of group theory for an M(CNR)$_4$ fragment of local C_{2v} symmetry [28], and one $\nu(CO)$ absorption at 1908 cm^{-1}. In the ^{13}C NMR spectrum of **9a**, one low-field resonance is observed for the carbyne-carbon and the carbonyl-carbon nucleus at 271.0 ppm and 224.5 ppm respectively, and three resonances of relative intensity 1:1:2 are observed for the metal-bound isonitrile carbons at 157.5, 166.2 and 170.0 ppm.

Cyclic voltammetry studies of some of the chromium carbyne complexes prepared were conducted in CH$_2$Cl$_2$ at 25 °C in order to determine the influence of the ligand sphere on the electrochemical properties of this class of compounds. All the complexes studied were electrochemically active and the data are summarized in Table 5.

The voltammograms of the neutral carbyne complexes **2a**, **2c**, **5a** and **5b** display one irreversible anodic peak at $E_p = -0.11$ (**2a**), 0.03 (**2c**), 0.03 (**5b**) and 0.46 V (**5a**) at a scan rate v of 100 mV s^{-1}: this presumably originates from the formation and subsequent decomposition of a monocationic 17 e$^-$ Cr^I carbyne complex (the carbyne moiety is considered here as a monocationic two-electron ligand with a doubly occupied orbital of σ-symmetry and a pair of empty, orthogonal acceptor orbitals of π-symmetry). The phosphine complexes **2a** and **2c** display an additional anodic signal at $E_p = 0.88$ V and 0.95 V respectively. In all cases, no cathodic peaks were observed in the potential range -0.5 to 1.3 V vs. ferrocene. The anodic peak potential of the phenylcarbyne complex **5a** is 430 mV more positive than that of the aminocarbyne complex **5b**, which can be explained by the stronger π-acceptor ability of the phenylcarbyne ligand than the aminocarbyne ligand.

The voltammetric behavior of the cationic carbyne complexes **4** and **6b** is similar regarding the oxidation to a dicationic 17 e$^-$ Cr^I carbyne complex. The voltammogram of **4** shown in Fig. 3 displays two irreversible oxidation steps at $E_p = 0.53$ and 1.10 V vs. ferrocene at $v = 250$ mV s^{-1}. The first step probably corresponds to the formation of a dicationic 17 e$^-$ Cr^I carbyne complex. No cathodic processes were observed in the range -0.5 to 1.3 V and at scan rates up to 1000 mV s^{-1}.

In comparison, the electrochemical behavior of [('BuNC)$_3$(CO)$_2$C≡CPh][PF$_6$] (**6a**) is different from that of the analogous aminocarbyne complex **6b**. There is only one peak on the anodic wave at 0.85 V with a corresponding cathodic peak at 0.73 V ($v =$

Fig. 3. Cyclic voltammogram of **4** in CH$_2$Cl$_2$–TBAPF$_6$ at 25 °C. Fc/Fc$^+$ = 0.0 V; scan rate: 0.1 V s^{-1}.

Fig. 4. Cyclic voltammogram of **10** in CH_2Cl_2–TBAPF$_6$ at 25 °C. Fc/Fc$^+$ = 0.0 V; scan rate: 0.25 V s^{-1}.

100 mV s^{-1}). The anodic to cathodic current ratio I_{pa}/I_{pc} was 2.25 and decreased with an increase in scan rate to 1.74 ($v = 1000$ mV s^{-1}).

The anodic sweep of the 'electron-rich' aminocarbyne complexes **8b** and **10** displays one reversible and one irreversible response at $E_p = 0.03$ and 1.01 V (**8b**) and at $E_p = -0.58$ and 0.72 V (**10**) respectively. The cathodic wave for complex **10** shows two additional responses at 0.61 and 0.32 V ($v = 10$ mV s^{-1}) which were not studied further (Fig. 4).

For both compounds, the anodic to cathodic current ratio of the first couple was 1.00 ± 0.05, and the difference of the anodic and cathodic peak potentials (78 mV) was virtually identical with that of ferrocene measured under the same conditions (80 mV). The response was therefore characteristic for a reversible one-electron couple [29], indicating that oxidation of **8b** or **10** might provide a synthetic route to 17 e$^-$ chromium aminocarbyne complexes. In fact, preliminary studies show that oxidation of **10** with one equivalent of [Cp$_2$Fe][PF$_6$] affords the carbyne complex [(^{t}BuNC)$_5$Cr≡N^{t}Pr$_2$][PF$_6$]$_2$ [30]. Finally, a comparison of the voltammograms of the cationic aminocarbyne complexes **6b**, **8b** and **10** reveals a decrease of the anodic peak potential by ca. 1 V, indicating a large increase in the electron density at the chromium center, when carbon monoxide, which is a good π-acceptor ligand, is successively replaced by *tert*-butyl isonitrile, which is a modest π-acceptor ligand.

3. Experimental section

3.1. General procedures

Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents were dried by standard methods (*n*-pentane over CaH$_2$; Et$_2$O, THF and toluene over Na–benzophenone;

CH$_2$Cl$_2$ over P$_2$O$_5$ and Na–Pb alloy), distilled under nitrogen and stored over 4 Å molecular sieves prior to use. All column chromatography was carried out in a thermostated column of 20 cm length and 2.0 cm diameter. The stationary phase was silica (Merck, activity I, 0.063–0.2 mm), which was degassed, dried in vacuo at room temperature and saturated with nitrogen. Elemental analyses were obtained from the Zentrale Analytische Gruppe des Instituts für Chemie der Humboldt Universität zu Berlin. IR spectra were recorded using a Bruker IFS-55 spectrometer. ^{1}H, ^{13}C{^{1}H} and ^{31}P NMR spectra were recorded on a Bruker AM-300 spectrometer. The ^{1}H and ^{13}C{^{1}H} spectra were calibrated against the solvent signals (methylene-d_2-chloride: δ_H 5.32 and δ_C 53.8 ppm; benzene-d_6: δ_H 7.15 and δ_C 128.0 ppm; chloroform-d_1: δ_H 7.24 and δ_C 77.0 ppm) and the ^{31}P spectra against an external 85% H$_3$PO$_4$ solution in water. The ^3J(H,H) coupling constants in the isopropyl groups are 6.6 Hz. Melting points were determined using a Buchi 530 melting point apparatus and are not corrected. The samples were sealed in capillary tubes under argon.

Cyclic voltammetry was carried out under nitrogen in 15 ml of CH$_2$Cl$_2$ containing the substrate (0.1 mmol l^{-1}) and tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (0.1 mol l^{-1}). A 5 mm Pt wire (0.1 mm) was used as the working electrode and a Ag/AgCl//CH$_3$CN/[NBu$_4$]Cl electrode, which was separated from the solution by a double fritted cartridge system (Metrohm), was used as a reference. Ferrocene (0.1 mmol l^{-1}) was used as external standard (E_{pa} = 0.74 V; E_{pc} = 0.67 V). The solution resistance was not compensated. All measurements were carried out using an Autolab PGSTAT 20 potentiostat (Metrohm) and a commercially available electrochemical cell. The cell was purged with nitrogen prior to use and then charged with the freshly prepared solution of the sample and the supporting electrolyte. The scan rate was 0.1 V s^{-1} unless otherwise stated.

Compounds **1a**, **1b**, **5a**, **5b**, **6b**, **7** and **10** were prepared as previously described [16,19,21]. Complex **8b** was obtained from [('BuNC)$_4$(CO)Cr$\equiv$CN^{i}Pr$_2$]Br (**8a**) [19] and TlPF$_6$ in CH$_2$Cl$_2$, at room temperature. Isopropyl isonitrile and *tert*-butyl isonitrile were prepared following published procedures [31].

3.2. Preparations

3.2.1. cis-Cl(CO)$_3$(PMe$_3$)$_2$Cr$\equiv$CN^{i}Pr$_2$ (2a)

A solution of 410 mg (0.93 mmol) of **1a** in 25 ml of CH$_2$C$_2$ was treated with 0.19 ml (1.87 mmol) of PMe$_3$ and stirred at ambient temperature. Completion of the reaction after 1 h was confirmed by IR spectroscopy. The solvent was removed in vacuo, then the residue was dissolved in a minimum amount of CH$_2$Cl$_2$ and purified by column chromatography on silica at 0 °C. An orange fraction was eluted with CH$_2$Cl$_2$–Et$_2$O (1:1) and concentrated in vacuo to a few milliliters. Cold pentane was added to precipitate complex **2a** as an orange microcrystalline solid. M.p.: 144 °C. Yield: 350 mg (92%). Anal. Found: C, 44.26; H, 7.91; Cl. 8.91; N. 3.46. C$_{15}$H$_{33}$ClCrNO$_2$P$_2$ (407.81). Calc.: C. 44.18; H, 7.91; Cl. 8.69; N, 3.43%. ^{1}H NMR (CD$_2$Cl$_2$, −10 °C): δ 1.22 (d, 12H, 2 × CH *Me*$_2$), 1.35 (m, 18H. PMe$_3$), 3.34 (h, 2H, 2 × C*H*Me$_2$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, −10 °C): δ 18.1 (virtual triplet, 11.2 Hz, 2 × P*Me*$_3$), 22.4 (CH *Me*$_2$), 50.5 (*C*HMe$_2$), 231.0 (*C*O), 256.0 (t, ^{2}J(CP) = 25.4 Hz, Cr$\equiv$C). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 1.62 (*P*Me$_3$).

3.2.2. cis-Cl(CO)$_3$(dppe)Cr$\equiv$CN^{i}Pr$_2$ (2b)

Following the procedure described above for **2a**, complex **2b** was obtained as an orange microcrystalline solid after treatment of 330 mg (0.75 mmol) of **1a** with 280 mg (0.76 mmol) of dppe. M.p.: 177 °C. Yield: 420 mg (92%). Anal. Found: C, 64.90; H, 6.10; Cl. 5.24; N, 2.15. C$_{35}$H$_{38}$ClCrNO$_2$P$_2$ (654.09). Calc.: C. 64.27; H. 5.86; Cl, 5.42; N, 2.14%. ^{1}H NMR (CD$_2$Cl$_2$): δ 0.82 (d, 12H, 2 × CH *Me*$_2$), 2.60 (h, 2H, 2 × C*H*Me$_2$), 2.60 and 2.80 (m, 4H, PC*H$_2$C H$_2$*P), 7.35–7.72 (m, 20H, C$_6$H$_5$). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): δ 22.2 (CH *Me*$_2$), 24.8 (virtual triplet, 18.6 Hz, P*C$_2$H$_4$*P), 53.1 (*C*HMe$_2$), 128.3, 129.0, 129.7, 129.8, 131.8, 133.4, 135.2, 139.6 (C$_6$H$_5$), 233.9 (CO), 257.1 (t, ^{2}J(CP) = 22.2 Hz, Cr$\equiv$C). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ 62.1.

3.2.3. cis-Br(CO)$_3$(PMe$_2$Ph)$_2$Cr$\equiv$CN^{i}Pr$_2$ (2c)

Following the procedure described above for **2a**, complex **2c** was obtained as an orange microcrystalline solid after treatment of 600 mg (1.23 mmol) of **1b** with 0.36 ml (2.52 mmol) of PMe$_2$Ph. M.p.: 149 °C. Yield: 380 mg (53%). Anal. Found: C, 51.47; H, 6.47; N. 2.42%. C$_{25}$H$_{36}$BrCrNO$_2$P$_2$ (576.40). Calc.: C. 52.09; H, 6.29; N, 2.43%. ^{1}H NMR (CDCl$_3$): δ 1.05 (d, 12H, 2 × CH *Me*$_2$), 1.53 (virtual triplet, 6H, 3.4 Hz, 2 ×

PMe$_A$Me$_B$Ph), 1.70 (virtual triplet, 6H, 3.4 Hz, 2 × PMe$_A$*Me$_B$*Ph), 2.91 (h, 2H, 2 × C*H*Me$_2$), 7.28–7.40 (m, 10H, 2 × C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 15.6 (virtual triplet, 11.6 Hz, P*Me$_A$*Me$_B$Ph), 18.6 (virtual triplet, 11.6 Hz, PMe$_A$*Me$_B$*Ph), 22.2 (CH *Me*$_2$), 49.9 (N*C*HMe$_2$), 128.1, 128.4, 129.7, 142.2 (C$_6$H$_5$), 229.9 (*C*O), 258.2 (t, ^{2}J(CP) = 23.2 Hz, Cr$\equiv$C). ^{31}P{^{1}H} (CDCl$_3$): δ 7.11.

3.2.4. trans-Cl(CO)$_2$[P(OMe)$_3$]$_2$Cr$\equiv$CN^{i}Pr$_2$ (3)

A solution of 500 mg (1.13 mmol) of **1a** in 20 ml of CH$_2$Cl$_2$, was treated with 0.30 ml (2.51 mmol) of P(OMe)$_3$ and stirred for 1 h at ambient temperature. Completion of the reaction was confirmed by IR spectroscopy. The solvent was then removed in vacuo and the residue dissolved in a minimum amount of CH$_2$Cl$_2$ and chromatographed on silica at 0 °C. Elution with ether–pentane (2:1) gave a yellow eluate, which was evaporated to dryness to afford the complex as a yellow microcrystalline solid. M.p.: 158 °C. Yield: 510 mg (89%). Anal. Found: C, 36.08; H. 6.55; Cl. 7.12; N, 2.79. C$_{15}$H$_{33}$ClCrNO$_8$P$_2$ (503.81). Calc.: C, 35.76; H, 6.40; Cl. 7.04; N, 2.78%. ^{1}H NMR (C$_6$D$_6$): δ 1.08 (d, 12H, 2 × CH *Me*$_2$), 3.28 (h, 2H, 2 × C*H*Me$_2$), 3.75 (virtual triplet, 18H, 5.3 Hz, 2 × P(O*Me*)$_3$). ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 21.7 (CH *Me*$_2$), 51.3 (virtual triplet, 6.4 Hz, P(O*Me*)$_3$), 52.1 (*C*HMe$_2$), 220.3 (t, ^{2}J(CP) = 25.6 Hz, *C*O), 261.2 (t, ^{2}J(CP) = 36.2 Hz, Cr$\equiv$C). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 181.6.

3.2.5. [fac-(PMe$_2$Ph)$_3$(CO)$_2$Cr$\equiv$CN^{i}Pr$_2$][PF$_6$] (4)

156 mg (0.27 mmol) of **2c** were dissolved in 30 ml of cold (−20 °C) CH$_2$Cl$_2$ and treated with 0.05 ml (0.35 mmol) of PMe$_2$Ph and 100 mg (0.29 mmol) of TlPF$_6$. The mixture was then stirred at −20 °C for 2.5 h. Completion of the reaction was confirmed by IR spectroscopy. The suspension was treated with 10 ml of Et$_2$O, the white precipitate of TlBr was allowed to settle and the supernatant orange-red solution was filtered. The filtrate was concentrated in vacuo to a few milliliters at −20 °C and a cold (−78 °C) Et$_2$O–pentane mixture (1:2) was added to precipitate complex **4**. Yellow-orange powder. M.p.: 134 °C. Yield: 125 mg (59%). Anal. Found: C, 49.48; H, 5.95; N, 1.80. C$_{33}$H$_{47}$CrF$_6$NO$_2$P$_4$ (779.62). Calc.: C, 50.84; H, 6.08; N, 1.80%. ^{1}H NMR (CDCl$_3$): δ 1.33 (d, 12H, 2 × CH *Me*$_2$), 1.37 (d, 6H, ^{2}J(HP) = 6.6 Hz, 1 × P*Me$_2$*Ph), 1.60 (virtual triplet, 6H, 3.3 Hz, 2 × PMe$_A$Me$_B$Ph), 1.64 (virtual triplet, 3.3 Hz, 2 × PMe$_A$*Me$_B$*Ph), 3.55 (h, 2H, 2 × C*H*Me$_2$), 7.08–7.39 (m, 15H, 3 × C$_6$H$_5$). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 16.6 (d, 1 × PMe$_2$Ph, ^{1}J(CP) = 22.5 Hz), 19.9 (virtual triplet, 12.2 Hz, 2 × P*Me$_A$*Me$_B$Ph), 20.1 (virtual triplet, 12.2 Hz, 2 × P(Me$_A$*Me$_B$*Ph), 22.4 (CH *Me*$_2$), 53.1 (*C*HMe$_2$), 128.9–140.0 (C$_6$H$_5$), 230.8 (m, CO), 272.3 (m, Cr$\equiv$C). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): δ −143.5 (h, ^{1}J(PF) = 711 Hz, *P*F$_6$) −2.4 (t, 1 × P*Me$_2$*Ph, ^{2}J(PP) = 39.0 Hz), 8.1 (d, ^{2}J(PP) = 39.0 Hz, 2 × *P*Me$_2$Ph).

3.2.6. [fac-('BuNC)₃(CO)₂Cr≡CPh][PF₆] (6a)

A solution of 230 mg (0.52 mmol) of cis-Br(CO)₂('BuNC)₂Cr≡CPh (5a) in 15 ml of cold (−10°C) CH₂Cl₂ was treated with 0.07 ml (0.62 mmol) of 'BuNC and 195 mg (0.56 mmol) of TlPF₆ and the mixture was stirred at −10°C. Completion of the reaction after 3 h was confirmed by IR spectroscopy. The suspension was treated with 5 ml of Et₂O, the white precipitate of TlBr was allowed to settle and the supernatant red solution was filtered. The filtrate was concentrated in vacuo to a few milliliters and a cold (−78°C) Et₂O–pentane (1:2) mixture was added to precipitate complex 6a as a red-brown solid. M.p.: 81°C (dec.). Yield: 280 mg (91%). C₂₄H₃₂CrF₆N₃O₂P (591.49). ¹H NMR (CD₂Cl₂, −20°C): δ 1.54 (s, 27H, 3 × CNCMe₃), 7.32–7.51 (m, 5H, C₆H₅). ¹³C{¹H} NMR (CD₂Cl₂, −20°C): δ 29.6 (1 × CMe₃), 30.0 (2 × CMe₃), 58.5 (2 × CMe₃), 59.0 (1 × CMe₃), 128.4,

Table 6
Summary of crystallographic data for the complexes 2a and 2c

	2a	2c
Empirical formula	C₁₅H₃₂ClCrNO₂P₂	C₂₅H₃₆BrCrNO₂P₂
Molecular weight	407.81	576.40
Crystal color	orange	red-orange
Crystal size (mm³)	0.3×0.4×0.6	0.76×0.38×0.19
Temperature (K)	190(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	9.552(4)	10.084(2)
b (Å)	13.601(4)	16.340(3)
c (Å)	16.654(6)	17.351(3)
α (deg)		89.89(2)
β (deg)	93.78(3)	89.87(2)
γ (deg)		89.98(2)
V (Å³)	2158.9(14)	2859.0(10)
Z	4	4
ρ_{calcd} (g cm⁻³)	1.255	1.339
μ Mo Kα (mm⁻¹)	0.791	1.918
$F(000)$	864	1192
Radiation (Mo Kα) (Å)	0.71073	0.71073
2Θ min.. max.(deg)	4, 50	4, 49
hkl range	−11, 11/0, 16/0,19	−11, 11/−18, 18/0,19
Total data	3987	20321
Unique data for 2a ($I > 4\sigma I$)	3238	8619 ($R(int) = 0.0644$)
for 2c ($I > 2\sigma I$)		
Min./max. density (e Å⁻³)	0.257/−0.255	0.697/−0.458
No. of parameters refined	199	577
R_1 [a]	0.0289	0.0485
wR_2 [b]	0.0718	0.0938
GOF [c]	1.051	0.969

[a] $R_1 = \Sigma \|F_o| - |F_c\|/\Sigma|F_o|$; [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; [c] GOF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

Table 7
Atomic coordinates (×10⁴) and equivalent isotropic displacement parameters (Å² × 10³) for 2a

Atom	x	y	z	U_{eq} [a]
Cr(1)	216(1)	2355(1)	2611(1)	18(1)
Cl	2021(1)	2791(1)	1680(1)	32(1)
P(1)	1203(1)	754(1)	2815(1)	24(1)
C(1)	2637(3)	363(2)	2220(2)	43(1)
C(2)	1968(3)	531(2)	3834(2)	39(1)
C(3)	5(3)	−289(2)	2722(2)	45(1)
P(2)	−1065(1)	1884(1)	1374(1)	24(1)
C(4)	−2803(2)	1342(2)	1418(2)	39(1)
C(5)	−250(3)	1049(2)	682(1)	41(1)
C(6)	−1438(3)	2938(2)	721(1)	37(1)
C(7)	−658(2)	3565(2)	2495(1)	26(1)
O(1)	−1260(2)	4304(1)	2474(1)	46(1)
C(8)	1497(2)	2869(2)	3416(1)	26(1)
O(2)	2233(2)	3214(1)	3909(1)	41(1)
C(9)	−992(3)	2114(1)	3323(1)	22(1)
N	−1895(2)	2010(1)	3878(1)	26(1)
C(10)	−3252(2)	1502(2)	3660(1)	30(1)
C(11)	−4432(3)	2250(2)	3536(2)	48(1)
C(12)	−3562(3)	712(2)	4268(2)	45(1)
C(13)	−1699(3)	2501(2)	4679(1)	35(1)
C(14)	−472(3)	2044(2)	5175(1)	47(1)
C(15)	−1549(3)	3610(2)	4592(2)	53(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

130.4, 131.8, 145.2 (C₆H₅), 142.8 (1 × CNCMe₃), 152.5 (2 × CNCMe₃), 218.6 (CO), 323.7 (Cr≡C).

3.2.7. [cis-('PrNC)₄(CO)Cr≡CN'Pr₂]Cl (9a)

A solution of 800 mg (1.81 mmol) of 1a in 40 ml of CH₂Cl₂ was first treated at −40°C with 0.66 ml (7.25 mmol) of 'PrNC, then warmed to room temperature and refluxed. Evolution of gas was observed and the initially orange solution turned red. Completion of the reaction after 8 h was confirmed by IR spectroscopy. The resulting red solution was concentrated in vacuo to a few milliliters and treated with cold (−78°C) Et₂O. The supernatant, slightly yellow solution was decanted off and the oily residue was dried in vacuo at ambient temperature. It was then frozen in liquid nitrogen, pulverized and then dried in vacuo at −40°C. This procedure was repeated twice to afford complex 9a as a red solid. M.p.: 108°C (dec.). Yield: 780 mg (85%). Anal. Found: C, 56.73; H, 8.65; Cl, 7.59; N, 13.28. C₂₄H₄₂ClCrN₅O (504.08). Calc.: C, 57.19; H, 8.40; Cl, 7.03; N, 13.89. ¹H NMR (CD₂Cl₂): δ 1.36 (d, 18H, N(CHMe₂)₂ and 1 × CNCHMe₂), 1.39 (d, 12H, 2 × CNCHMe₂), 1.42 (d, 6H, CNCHMe₂), 3.19 (h, 2H, N(CHMe₂)₂), 3.91 (h, 1H, CNCHMe₂), 4.03 (h, 3H, 3 × CNCHMe₂). ¹³C{¹H} NMR (CD₂Cl₂): δ 22.8 (N(CHMe₂)₂), 23.1 (CNCHMe₂), 23.6 (2 × CNCHMe₂), 23.9 (CNCHMe₂), 48.1 (1 × CNCHMe₂), 48.9 (2 × CNCHMe₂), 55.5 (N(CHMe₂)₂), 157.5 (1 × CNCHMe₂, trans to carbyne), 166.2 (1 × CNCHMe₂,

Table 8
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2c**

Atom	x	y	z	U_{eq} [a]
Cr(1)	−267(1)	−891(1)	2416(1)	32(1)
Br(1)	2655(1)	−32(1)	3278(1)	65(1)
C(1)	2920(5)	−1679(3)	2461(3)	51(1)
O(1)	2090(4)	−2156(3)	2453(2)	91(1)
C(2)	3518(5)	−467(3)	1539(3)	49(1)
O(2)	3079(4)	−257(3)	958(2)	94(1)
C(3)	5203(4)	−1494(3)	1801(2)	31(1)
N(1)	5797(4)	−1957(2)	1288(2)	38(1)
C(4)	5090(5)	−2629(3)	865(3)	59(2)
C(5)	4751(6)	−3328(3)	1402(3)	81(2)
C(6)	3893(6)	−2310(4)	442(3)	97(2)
C(7)	7174(5)	−1757(3)	1045(3)	48(1)
C(8)	8110(5)	−2464(4)	1195(3)	80(2)
C(9)	7196(6)	−1498(4)	204(3)	82(2)
P(1)	5561(1)	362(1)	2453(1)	35(1)
C(10)	5975(5)	817(3)	3385(2)	51(1)
C(11)	4694(5)	1226(3)	2007(3)	59(2)
C(12)	7145(4)	361(3)	1944(2)	34(1)
C(13)	7216(5)	522(3)	1157(2)	51(1)
C(14)	8415(6)	487(3)	768(3)	62(2)
C(15)	9550(5)	279(3)	1153(3)	62(2)
C(16)	9497(5)	113(3)	1929(3)	61(2)
C(17)	8315(5)	163(3)	2318(3)	49(1)
P(2)	5188(1)	−1532(1)	3545(1)	48(1)
C(18)	4283(5)	−1413(5)	4442(3)	116(3)
C(19)	5236(7)	−2641(3)	3460(4)	112(3)
C(20)	6896(4)	−1338(3)	3830(2)	37(1)
C(21)	7917(5)	−1616(3)	3378(3)	58(2)
C(22)	9239(6)	−1446(3)	3563(4)	75(2)
C(23)	9502(6)	−990(4)	4205(4)	78(2)
C(24)	8517(7)	−729(4)	4668(3)	72(2)
C(25)	7219(5)	−901(3)	4489(2)	48(1)
Cr(2)	733(1)	5890(1)	7416(1)	33(1)
Br(2)	2346(1)	5032(1)	8277(1)	65(1)
C(26)	2078(5)	6676(3)	7462(3)	52(1)
O(3)	2900(4)	7154(3)	7457(2)	89(1)
C(27)	1487(5)	5467(3)	6541(3)	52(1)
O(4)	1919(4)	5259(3)	5958(2)	92(1)
C(28)	−211(4)	6499(3)	6800(2)	30(1)
N(2)	−797(4)	6958(2)	6285(2)	41(1)
C(29)	−2171(5)	6756(3)	6043(2)	46(1)
C(30)	−3104(5)	7464(4)	6197(3)	77(2)
C(31)	−2197(6)	6491(4)	5207(3)	82(2)
C(32)	−97(5)	7632(3)	5874(3)	60(2)
C(33)	251(6)	8329(3)	6408(3)	78(2)
C(34)	1098(6)	7314(4)	5444(3)	96(2)
P(3)	−562(1)	4637(1)	7453(1)	36(1)
C(35)	308(5)	3775(3)	7005(3)	60(2)
C(36)	−978(5)	4186(3)	8387(2)	54(1)
C(37)	−2146(4)	4635(3)	6943(2)	34(1)
C(38)	−2219(5)	4478(3)	6159(3)	51(1)
C(39)	−3423(6)	4511(4)	5774(3)	66(2)
C(40)	−4556(5)	4726(3)	6154(3)	62(2)
C(41)	−4498(5)	4886(3)	6930(3)	62(2)
C(42)	−3304(5)	4841(3)	7324(3)	48(1)
P(4)	−187(1)	6532(1)	8545(1)	49(1)
C(43)	706(5)	6417(5)	9443(3)	123(3)
C(44)	−236(7)	7641(3)	8462(4)	111(3)
C(45)	−1897(4)	6338(3)	8831(3)	38(1)
C(46)	−2910(5)	6618(3)	8375(3)	58(2)
C(47)	−4234(6)	6442(4)	8556(4)	75(2)

Table 8 (continued)

Atom	x	y	z	U_{eq} [a]
C(48)	−4511(6)	6000(4)	9202(4)	77(2)
C(49)	−3522(6)	5725(4)	9665(3)	70(2)
C(50)	−2218(5)	5897(3)	9489(3)	51(1)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

trans to CO), 170.0 ($2 \times CNCHMe_2$), 224.5 (CO), 271.0 (Cr≡C).

3.2.8. [cis-($^iPrNC)_4(CO)Cr \equiv CN^iPr_2$][$PF_6$] (9b)

A solution of 505 mg (1.00 mmol) of **9a** in 30 ml of CH_2Cl_2 was treated with 350 mg (1.00 mmol) of solid TlPF$_6$ and stirred for 1 h at room temperature. The suspension was treated with 5 ml of Et$_2$O, the white precipitate of TlCl was allowed to settle and the supernatant red solution was filtered. The filtrate was worked up as described above for the isolation of **9a** to give complex **9b** as red solid. Yield: 580 mg (94%). The product was characterized by IR and ^{1}H NMR spectroscopy.

3.2.9. Crystal structure determinations of 2a and 2c

A summary of the crystal data, data collection and refinement for **2a** and **2c** is given in Table 6.

Data collection for **2a** was performed on a STOE STADI4 four circle diffractometer equipped with a low temperature device and for **2c** on a Stoe IPDS image plate. Lattice parameters derived for **2a** from the setting angles of 24 reflections in the range of $28° \leq 2\Theta \leq 30°$ and for **2b** from 2000 reflections after data collection. Data were collected in the ω–2Θ scan mode. The crystal of **2c** was oscillated in 2.3° steps to yield 96 exposures, each of which was irradiated for 3 min. After every 2 h, three standard reflections were monitored for **2a** and the crystal reoriented for deviations between 0.1 and 0.15°. Intensity data for **2a** were corrected for Lorentz and polarization effects. Absorption correction was carried out using the empirical method DIFABS (min: 0.88, max: 1.10) [32]. Intensity data for **2c** were integrated and converted into a SHELX *hkl*-file with the Stoe IPDS software [33]. The input files for the SHELX programs were prepared with the program UTILITY [34]. Structure solution was performed with Patterson methods (SHELXS-86) [35] and subsequent difference-Fourier synthesis (SHELXL-93) [36]. Refinement on F^2 was carried out by full-matrix least squares techniques (SHELXL-93). Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U_{iso} = 0.08 Å^2. Neutral atom scattering factors were taken from Cromer and Mann [37]. Illustrations were performed with ZORTEP [38]. Final positional and equiv-

alent isotropic thermal parameters are given in Table 7 for **2a** and in Table 8 for **2c**.

The crystal of compound **2c** is pseudo orthorhombic. However, the intensity statistics show no higher symmetry then a center of inversion. Each unit cell of **2c** contains two independent molecules.

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-405583 for **2a** and CSD-405584 for **2c**, the names of the authors and the journal citation.

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