

# Metal–carbon multiple bonds: Half-sandwich phenylcarbyne complexes of chromium—synthesis, structure, electrochemistry and reactions with $\text{PMe}_3$ <sup>1</sup>

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## Abstract

The chromium phenylcarbyne complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Cr}\equiv\text{CPh}$  (**2a**: R = H; **2b**: R = Me) have been prepared and their structure, cyclic voltammetry and reactions with  $\text{PMe}_3$  are reported. The compounds **2a** and **2b** are obtained as red and purple thermolabile solids respectively after treatment of *cis*- $\text{Br}(\text{CO})_2(\text{pic})_2\text{Cr}\equiv\text{CPh}$  (pic = 4-methylpyridine) (**1**) with  $\text{NaCp}$  (Cp =  $\text{C}_5\text{H}_5$ ) and  $\text{KCp}^*$  (Cp\* =  $\text{C}_5\text{Me}_5$ ) respectively. Complex **2a** adds  $\text{PMe}_3$  at the carbyne-carbon atom to give the green  $\alpha$ -phosphonocarbene complex  $\text{Cp}(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}$  (**3**), whereas **2b** undergoes with  $\text{PMe}_3$  a carbyne–carbonyl coupling reaction to afford the green  $\eta^2$  ketylenyl complex  $\text{Cp}^*(\text{CO})(\text{PMe}_3)\text{Cr}[\text{C}(\text{Ph})\text{CO}]$  (**4**). Cyclic voltammetry studies show the phenylcarbyne complexes **2a** and **2b** and the carbene complex **3** to undergo a reversible one-electron oxidation in  $\text{CH}_2\text{Cl}_2$  at  $E_{1/2} = 0.39$  V,  $E_{1/2} = 0.20$  V and  $E_{1/2} = -0.52$  V respectively (potentials vs. the ferrocene/ferrocenium redox couple). In comparison, the ketylenyl complex **4** is electrochemically inactive in the potential range of  $-1.5$  to  $1.0$  V. The crystal structures of **2a** and **3** are reported. © 1997 Elsevier Science S.A.

**Keywords:** Chromium; Carbyne complexes; Carbene complexes; Ketylenyl complexes; Cyclic voltammetry

## 1. Introduction

The chemistry of compounds having a metal–carbon triple bond has grown into a major branch of organometallic chemistry since the discovery of the first transition metal carbyne complexes by Fischer and coworkers in 1973 [1]. Several types of carbyne complexes have been prepared in order to study the influence of the ligand sphere and the electron configuration of the metal center on the reactivity of the metal–carbon triple bond [2]. Among them the half-sandwich molybdenum and tungsten carbyne complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{M}\equiv\text{CR}'$  (R = H, Me; R' = alkyl, aryl) have been extensively studied and have been found to be particularly useful building blocks for transition metal clusters [3]. Stimulated by the well-known differences between the chemistry of a first-row transition metal and that of a second- or third-row transition metal, we

thought it would be of interest to study the reactions of analogous chromium compounds [4]. Therefore we recently have prepared the chromium aminocarbyne complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_{2-n}(\text{L})_n\text{Cr}\equiv\text{CN}^i\text{Pr}_2$  (R = H, Me; L = CO, <sup>t</sup>BuNC;  $n = 0, 1$ ) [5] and studied their oxidation and protonation reactions to afford first carbyne and carbene complexes of chromium in a high oxidation-state [6,7]. Continuing this work we report in the present paper on the synthesis, structure and reactions of analogous phenylcarbyne complexes of chromium.

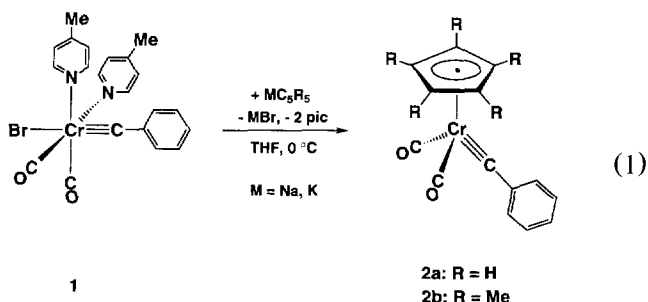
## 2. Results and discussion

Starting material for the chemistry described below was the complex *cis*- $\text{Br}(\text{CO})_2(\text{pic})_2\text{Cr}\equiv\text{CPh}$  (**1**) (pic = 4-methylpyridine). This was obtained by the reaction of *trans*- $\text{Br}(\text{CO})_4\text{Cr}\equiv\text{CPh}$  with slightly more than 2 equiv. of 4-methylpyridine in  $\text{CH}_2\text{Cl}_2$  following the procedure reported by Fischer for the synthesis of the analogous phenylcarbyne complex *cis*- $\text{Br}(\text{CO})_2(\text{py})_2\text{Cr}\equiv\text{CPh}$  [8]. Complex **1** was isolated in 94% yield as a red-brown solid, which is soluble in  $\text{CH}_2\text{Cl}_2$  and THF, but spar-

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<sup>1</sup> Dedicated to Professor Dr. G. Huttner on the occasion of his 60th birthday on the 1st August 1997.

ingly soluble in Et<sub>2</sub>O. It decomposes slowly in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and in the solid state at 114 °C, when heated in a sealed capillary under argon. Complex **1** was found like other pyridine-substituted carbyne complexes [9] to be a useful starting material for the synthesis of half-sandwich carbyne complexes bearing cyclopentadienyl ligands. Thus treatment of **1** with NaCp (Cp = C<sub>5</sub>H<sub>5</sub>) or KCp\* (Cp\* = C<sub>5</sub>Me<sub>5</sub>) in THF at -60 °C and warming of the reaction solutions to 0 °C afforded the phenylcarbyne complexes ( $\eta^5$ -C<sub>5</sub>R<sub>5</sub>)(CO)<sub>2</sub>Cr≡CPh (**2a**: R = H; **2b**: R = Me) (Eq. (1)). Evidence for the clean conversion of **1** to **2a** and **2b** was given by the IR spectra of the THF solutions, which showed that the two  $\nu$ (CO) absorptions of the starting material at 1997 and 1926 cm<sup>-1</sup> had been replaced at the end of the reaction by those of the products at 1990 and 1923 cm<sup>-1</sup> (**2a**) and 1976 and 1908 cm<sup>-1</sup> (**2b**), and that the  $\nu$ (CN) absorption of the 4-methylpyridine ligands of **1** at 1619 cm<sup>-1</sup> had been replaced by that of uncoordinated 4-methylpyridine at 1605 cm<sup>-1</sup>.



Complexes **2a** and **2b** were purified by column chromatography on silica and isolated as red and purple microcrystalline solids in 63% and 50% yields respectively. Both compounds are soluble in hydrocarbons and decompose in solution at room temperature. IR monitoring of the decomposition of **2a** and **2b** in *n*-pentane revealed a gradual decrease in intensity of the  $\nu$ (CO) absorptions of the carbyne complexes without concomitant formation of any carbonyl-containing product. The red pentane solutions of **2a** and **2b** turned thereby to

brown and a green solid precipitated out of the solution. Complex **2a** starts decomposing in the solid state at 35 °C and complex **2b** below room temperature.

Two strong  $\nu$ (CO) absorptions of almost equal intensity are observed in the IR spectra of **1**, **2a** and **2b** indicating the presence of two cis-oriented carbonyl ligands (Table 1). The  $\nu$ (CO) absorptions of **2a** and **2b** appear at higher wavenumbers than those of the analogous aminocarbyne complexes Cp(CO)<sub>2</sub>Cr≡CN<sup>i</sup>Pr<sub>2</sub> ( $\nu$ (CO) in *n*-pentane: 1962 and 1890 cm<sup>-1</sup>) and Cp\*(CO)<sub>2</sub>Cr≡CN<sup>i</sup>Pr<sub>2</sub> ( $\nu$ (CO) in *n*-pentane: 1945 and 1875 cm<sup>-1</sup>) [5], which shows that the phenylcarbyne ligand is a much better  $\pi$ -acceptor ligand than a dialkylaminocarbyne ligand.

The carbyne complexes **1**, **2a** and **2b** show in the <sup>13</sup>C NMR spectra a distinctive low-field resonance for the carbyne-carbon nucleus at  $\delta$  302.4, 325.7 and 323.7 respectively (Table 2).

This resonance appears at lower-field than those of the analogous tungsten complexes *cis*-Br(CO)<sub>2</sub>(pic)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbyne</sub>): 263.1 (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)) [10], Cp(CO)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbyne</sub>): 299.3 (CD<sub>2</sub>Cl<sub>2</sub>, -20 °C)) [11] and Cp\*(CO)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbyne</sub>): 301.3 (CD<sub>2</sub>Cl<sub>2</sub>, 0 °C)) [12], which is consistent with the <sup>13</sup>C shielding trend observed for the Group VI metal triad [13]. For the same reason the carbon nucleus resonance of the equivalent carbonyl ligands of **1**, **2a** and **2b** appears at lower field (Table 2) than that of the analogous tungsten complexes *cis*-Br(CO)<sub>2</sub>(pic)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbonyl</sub>): 221.3 (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C)) [10], Cp(CO)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbonyl</sub>): 221.3 (CD<sub>2</sub>Cl<sub>2</sub>, -20 °C)) [11] and Cp\*(CO)<sub>2</sub>W≡CPh ( $\delta$ (C<sub>carbonyl</sub>): 226.6 (CD<sub>2</sub>Cl<sub>2</sub>, 0 °C)) [12].

The molecular structure of **2a** was determined by a single-crystal X-ray diffraction study. Suitable crystals were obtained, when a saturated *n*-pentane solution of **2a** was cooled slowly to -78 °C. A ZORTEP plot of a single molecule with the atom-labeling scheme adopted is shown in Fig. 1. Selected bond lengths and angles are listed in Table 3.

The coordination geometry of **2a** can be described as pseudo-octahedral, with the cyclopentadienyl ligand oc-

Table 1  
Selected IR data of the complexes 1–4

| Complex   | $\nu$ (CO) (cm <sup>-1</sup> )                           | $\nu$ (C=O) <sub>ketenyl</sub> (cm <sup>-1</sup> ) | $\nu$ (C-N) <sub>pic</sub> (cm <sup>-1</sup> ) | Solvent   |
|---|--|--|--|---|
| Br(CO) <sub>2</sub> (pic) <sub>2</sub> Cr≡CPh ( <b>1</b> )      | 2000 vs, 1924 vs<br>1997 vs, 1926 vs                     | —  | 1622 m<br>1619 m                               | CH <sub>2</sub> Cl <sub>2</sub><br>THF            |
| Cp(CO) <sub>2</sub> Cr≡CPh ( <b>2a</b> )                        | 1991 vs, 1922 vs<br>1990 vs, 1923 vs<br>1999 vs, 1937 vs | —  | —  | CH <sub>2</sub> Cl <sub>2</sub><br>THF<br>pentane |
| Cp*(CO) <sub>2</sub> Cr≡CPh ( <b>2b</b> )                       | 1976 vs, 1908 vs<br>1984 vs, 1921 vs                     | —  | —  | THF<br>pentane                                    |
| Cp(CO) <sub>2</sub> Cr=C(PMe <sub>3</sub> )Ph ( <b>3</b> )      | 1889 vs, 1787 vs<br>1894 vs, 1795 vs                     | —  | —  | CH <sub>2</sub> Cl <sub>2</sub><br>THF            |
| Cp*(CO)(PMe <sub>3</sub> ) <sub>2</sub> CrC(Ph)CO] ( <b>4</b> ) | 1877 s   | 1721 m   | —  | CH <sub>2</sub> Cl <sub>2</sub>                   |

Table 2

Selected  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR data of the complexes **1–4** in  $\text{CD}_2\text{Cl}_2$ ; chemical shifts are given in parts per million, multiplicities of the signals in parentheses and coupling constants in hertz

| Compound  | $^1\text{H}$ NMR                       |  | $^{13}\text{C}$ NMR                 |                                |                                      | $^{31}\text{P}$ NMR                  | $T$ ( $^\circ\text{C}$ ) |                |
|-----------|--|--|-------------------------------------|--------------------------------|--------------------------------------|--------------------------------------|--------------------------|----------------|
|           | $\text{PMe}_3$                         | $\text{C}_5\text{Me}_5$ , $\text{C}_5\text{H}_5$ | $\text{PMe}_3$                      | $\text{C}(\text{Ph})\text{CO}$ | $\text{CO}$                          |                                      |                          | $\text{CrCPh}$ |
| <b>1</b>  | —                                      | —  | —                                   | —                              | 230.2                                | 302.4                                | —                        | –40            |
| <b>2a</b> | —                                      | 5.14 (5, s)                                      | —                                   | —                              | 238.1                                | 325.7                                | —                        | –40            |
| <b>2b</b> | —                                      | 1.96 (15, s)                                     | —                                   | —                              | 241.2                                | 323.7                                | —                        | –40            |
| <b>3</b>  | 1.59 (9, d)<br>$^2J(\text{HP}) = 12.0$ | 4.79 (5, s)                                      | 13.1 (d)<br>$^1J(\text{CP}) = 54.9$ | —                              | 267.5 (d)<br>$^3J(\text{CP}) = 6.4$  | 261.5 (d)<br>$^1J(\text{CP}) = 8.0$  | 7.9                      | –30            |
| <b>4</b>  | 1.12 (9, d)<br>$^2J(\text{HP}) = 8.7$  | 1.74 (15, s)                                     | 18.6 (d)<br>$^1J(\text{CP}) = 26.1$ | 216.1                          | 247.8 (d)<br>$^2J(\text{CP}) = 33.9$ | 253.6 (d)<br>$^2J(\text{CP}) = 20.4$ | 33.7                     | –40            |

cupping three facial coordination sites. This is shown by the bond angles between the carbonyl ligands and the carbyne ligand, which deviate slightly from  $90^\circ$  (Table 3). The  $\text{Cr}-\text{C}_{\text{carbyne}}-\text{C}_{\text{phenyl}}$  linkage is almost linear, as shown by the angle  $\text{Cr}-\text{C}6-\text{C}7$  of  $175.5(2)^\circ$ . The chromium carbonyl groups are also approximately linear, the  $\text{Cr}-\text{C}-\text{O}$  bond angles being  $178.6(2)^\circ$  and  $176.8(2)^\circ$ . The  $\text{Cr}-\text{C}_{\text{carbyne}}$  bond length of  $170.5(2)\text{ pm}$  is almost identical to that of the alkenylcarbyne complex  $[\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CC}(\text{Ph})]_2$  ( $\text{Cr}-\text{C}_{\text{carbyne}} = 170.7(2)\text{ pm}$ ) [14] and corresponds well to the sum of the triple bond radii of a carbon atom ( $r_{\text{C}} = 60.5\text{ pm}$ ) and a chromium atom ( $r_{\text{Cr}} = 110.7\text{ pm}$ ), calculated from the  $\text{C}-\text{C}$  bond length of an alkyne [ $d(\text{C}\equiv\text{C}) = 121\text{ pm}$ ] [15] and the  $\text{Cr}-\text{Cr}$  bond length of  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{Cr}(\text{CO})_2\text{Cp}$  [ $d(\text{Cr}\equiv\text{Cr}) = 220.0(3)$  and  $223.0(3)\text{ pm}$ , two independent molecules] [16]. The  $\text{Cr}-\text{C}_{\text{carbyne}}$  bond of **2a** is, however, slightly shorter than that of the analogous aminocarbyne complex  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CN}^i\text{Pr}_2$  ( $\text{Cr}-\text{C}_{\text{carbyne}} = 172.8(8)\text{ pm}$ ) [12]. This can be attributed to the delocalization of the electron density in the  $\text{Cr}-\text{C}-\text{N}$  unit of the aminocarbyne complex resulting in a slight elongation of the  $\text{Cr}-\text{C}$  triple bond.

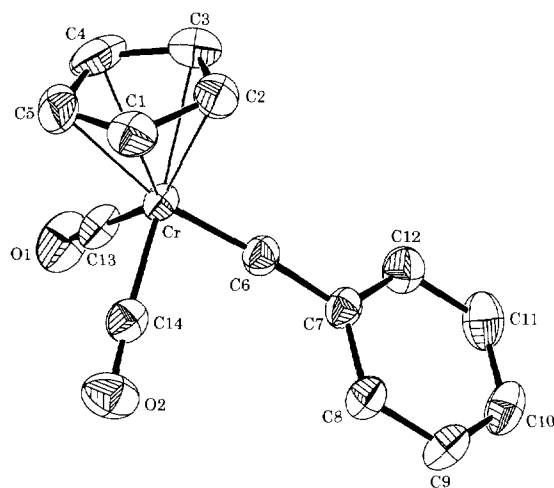


Fig. 1. ORTEP plot of the structure of **2a** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity reasons.

The  $\text{Cr}-\text{Cp}_{\text{centroid}}$  bond length of **2a** is with  $186.0\text{ pm}$  close to that of the electronically related nitrosyl complex  $\text{CpCr}(\text{CO})_2\text{NO}$  ( $\text{Cr}-\text{Cp}_{\text{centroid}} = 184.4\text{ pm}$ ) [17] and the aminocarbyne complex  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CN}^i\text{Pr}_2$  ( $\text{Cr}-\text{Cp}_{\text{centroid}} = 184.7\text{ pm}$ ) [12]. The phenyl ring plane is almost coplanar to one of the carbonyl ligands, as shown by the dihedral angle of  $16.7^\circ$  between the planes defined by the atoms  $\text{C}6$ ,  $\text{Cr}$ ,  $\text{C}14$  and the phenyl-carbon atoms  $\text{C}7-\text{C}12$  respectively. Cyclic voltammetry studies of the phenylcarbyne complexes **2a** and **2b** show that both compounds are electrochemically active, undergoing in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  a reversible one-electron oxidation. For example the voltammogram of **2a** shown in Fig. 2 displays only one peak on the anodic wave at  $0.43\text{ V}$  with a corresponding peak on the cathodic wave at  $0.35\text{ V}$  ( $v = 100\text{ mV s}^{-1}$ ).

The reversibility of the electron transfer was shown by the anodic to cathodic peak current ratio, which was  $0.99 \pm 0.05$ , the difference of the anodic and cathodic peak potentials ( $80\text{ mV}$ ), which was identical with that of ferrocene measured under the same conditions, and the anodic peak current, which was proportional to the square root of the scan rate [18]. The voltammetric behavior of **2b** is similar to that of **2a**, implying that the  $17e^-$  chromium phenylcarbyne complexes  $[(\eta^5-\text{C}_5\text{R}_5)(\text{CO})_2\text{Cr}\equiv\text{CPh}]^+$  are stable species on the cyclic voltammetry time scale. The half-wave potential of **2b** ( $E_{1/2} = 0.20\text{ V}$ ) is by  $190\text{ mV}$  smaller than that of **2a** ( $E_{1/2} = 0.39\text{ V}$ ), indicating the stronger electron donating properties of the  $\text{Cp}^*$  ligand. A comparison of the voltammograms of **2a** and **2b** with those of the analo-

Table 3

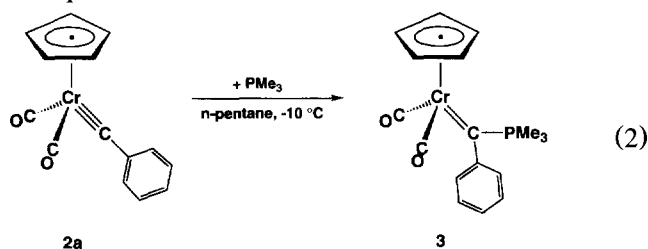
Selected bond lengths (pm) and bond angles (deg) with estimated standard deviations for **2a**

|                         |          |                                   |           |
|-------------------------|----------|-----------------------------------|-----------|
| $\text{Cr}-\text{C}1$   | 220.8(2) | $\text{Cr}-\text{C}14$            | 184.7(2)  |
| $\text{Cr}-\text{C}2$   | 220.4(2) | $\text{C}6-\text{C}7$             | 143.7(3)  |
| $\text{Cr}-\text{C}3$   | 221.0(2) | $\text{C}6-\text{Cr}-\text{C}13$  | 90.04(10) |
| $\text{Cr}-\text{C}4$   | 221.1(2) | $\text{C}6-\text{Cr}-\text{C}14$  | 87.55(10) |
| $\text{Cr}-\text{C}5$   | 221.7(3) | $\text{C}13-\text{Cr}-\text{C}14$ | 92.22(10) |
| $\text{Cr}-\text{Cp}^a$ | 186.0    | $\text{Cr}-\text{C}6-\text{C}7$   | 175.5(2)  |
| $\text{Cr}-\text{C}6$   | 170.5(2) | $\text{Cr}-\text{C}13-\text{O}1$  | 178.6(2)  |
| $\text{Cr}-\text{C}13$  | 186.0(3) | $\text{Cr}-\text{C}14-\text{O}2$  | 176.8(2)  |

<sup>a</sup>  $\text{Cp}$  denotes the center of the cyclopentadienyl ring.

gous aminocarbene complexes  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CN}^1\text{Pr}_2$  and  $\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{CN}^1\text{Pr}_2$ , which also undergo a reversible one-electron oxidation in  $\text{CH}_2\text{Cl}_2$  [12], reveals a 250 mV shift of the half-wave potential to lower values indicating in agreement with the spectroscopic data that the phenylcarbonyl ligand is a much stronger  $\pi$ -acceptor ligand than a diisopropylaminocarbonyl ligand (Table 4).

In order to compare the reactions of the chromium phenylcarbonyl complexes **2a** and **2b** with those of the analogous molybdenum and tungsten complexes, the compounds **2a** and **2b** were treated with  $\text{PMe}_3$ . The molybdenum and tungsten complexes ( $\eta^5\text{-C}_5\text{R}_5$ )(CO) $_2\text{M}\equiv\text{CR}'$  (R = H, Me; R' = aryl) have been previously shown to undergo with  $\text{PMe}_3$  a carbonyl–carbonyl coupling reaction to afford the  $\eta^2$  and  $\eta^1$  ketenyl complexes ( $\eta^5\text{-C}_5\text{R}_5$ )(CO)( $\text{PMe}_3$ ) $_n\text{M}[\text{C}(\text{R}')\text{CO}]$  ( $n = 1, 2$ ) [19]. The formation of the CO substitution products ( $\eta^5\text{-C}_5\text{R}_5$ )(CO)( $\text{PMe}_3$ ) $\text{M}\equiv\text{CR}'$  was also observed in some cases [20,21]. In contrast, the chromium phenylcarbonyl complex **2a** adds  $\text{PMe}_3$  at the carbonyl–carbon atom to give the  $\alpha$ -phosphonocarbene complex **3** (Eq. (2)).



This nucleophilic addition reaction at the carbonyl ligand of **2a** is surprising, since Cp-substituted Group VI metal carbonyl complexes of the type ( $\eta^5\text{-C}_5\text{R}_5$ )(CO) $_2\text{M}\equiv\text{CR}'$  (M = Cr, Mo, W; R = H, Me; R' = alkyl, aryl, amino) have been so far shown to add only electrophiles at the carbonyl–carbon atom [7,22], these reactions being charge-controlled [23]. Nucleophilic addition of  $\text{PMe}_3$  at the carbonyl–carbon has been observed only in cationic half-sandwich carbonyl complexes of the type  $[(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}\equiv\text{CPh}]\text{BCl}_4$  [24] and  $[(\eta^5\text{-C}_5\text{H}_4\text{R})(\text{CO})_2\text{M}\equiv\text{CPh}]\text{BCl}_4$  (R = H, Me; M = Mn, Re) [25]. These compounds have also been shown to add a variety of other nucleophiles at the

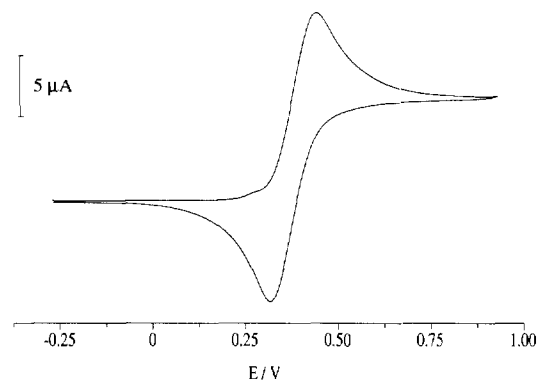


Fig. 2. Cyclic voltammogram of **2a** in  $\text{CH}_2\text{Cl}_2\text{-TBAPF}_6$  at  $-60^\circ\text{C}$ .  $\text{Fc}/\text{Fc}^+ = 0.0\text{ V}$ ; scan rate:  $100\text{ mV s}^{-1}$ .

carbonyl–carbon atom to afford carbene complexes [26], the reactions being frontier-orbital-controlled [27].

Evidence for the clean conversion of **2a** to **3** was given by the IR spectra of the *n*-pentane solutions, which showed a gradual decrease of the two  $\nu(\text{CO})$  absorptions of the starting material at 1999 and  $1937\text{ cm}^{-1}$ , the product **3** precipitating out of the solution. Complex **3** was isolated in 88% yield as a green, microcrystalline solid, that is soluble in  $\text{CH}_2\text{Cl}_2$ , acetone and THF, but insoluble in *n*-pentane. Complex **3** decomposes slowly in  $\text{CH}_2\text{Cl}_2$  or acetone at room temperature to give back the carbonyl complex **2a**, and starts decomposing in the solid state at  $104^\circ\text{C}$ . Two strong  $\nu(\text{CO})$  bands of almost equal intensity are observed in the IR spectra of the carbene complex **3**, which appear at considerably lower wavenumbers than those of the carbonyl complex **2a** (Table 1). This indicates that addition of  $\text{PMe}_3$  at the carbonyl–carbon atom of **2a** causes a dramatic increase of the electron density at the chromium center, in full agreement with the NMR spectroscopic data, the crystal structure and the electrochemical data of **3** which are presented below. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **3** displays a singlet resonance at  $\delta 7.9$  and the  $^1\text{H}$  NMR spectrum three multiplets for the phenyl protons at  $\delta 6.53$ ,  $7.03$  and  $7.21$ , a singlet Cp resonance at  $\delta 4.79$ , and a doublet resonance for the  $\text{PMe}_3$  protons at  $\delta 1.59$  (Table 2). The  $^2J(\text{HP})$  coupling constant of  $12.0\text{ Hz}$  is similar to that of the related  $\alpha$ -phosphonocarbene complexes

Table 4  
Voltammetric data of the complexes **2a**, **2b**, **3** and related aminocarbonyl complexes <sup>a</sup>

| Complex   | $E_{\text{pa}}$ (V) | $E_{\text{pc}}$ (V) | $E_{\text{pa}} - E_{\text{pc}}$ (mV) | $I_{\text{a}}/I_{\text{c}}$ | $E_{1/2}$ (V) | $T$ ( $^\circ\text{C}$ ) |
|---|---------------------|---------------------|--------------------------------------|-----------------------------|---------------|--------------------------|
| $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CPh}$ ( <b>2a</b> )         | 0.43                | 0.35                | 80                                   | 0.99                        | 0.39          | -60                      |
| $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CN}^1\text{Pr}_2$           | 0.16                | 0.08                | 80                                   | 1.00                        | 0.12          | +20                      |
| $\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{CPh}$ ( <b>2b</b> )       | 0.25                | 0.15                | 100                                  | 1.00                        | 0.20          | -60                      |
| $\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{CN}^1\text{Pr}_2$         | 0.00                | -0.10               | 100                                  | 0.98                        | -0.05         | +20                      |
| $\text{Cp}(\text{CO})_2\text{Cr}=(\text{PMe}_3)\text{CPh}$ ( <b>3</b> ) | -0.48               | -0.56               | 80                                   | 1.03                        | -0.52         | -60                      |
|   | 0.48                | —                   | —                                    | —                           | —             | —                        |

<sup>a</sup> All measurements were carried out in  $\text{CH}_2\text{Cl}_2\text{-TBAPF}_6$  with a scan rate of  $100\text{ mV s}^{-1}$ ; potentials are in volts against the ferrocene/ferrocenium redox couple.

$[(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}]\text{BCl}_4$  ( $^2J(\text{HP}) = 13.5$  Hz) [24] and *trans*- $\text{Br}(\text{CO})_4\text{Cr}=\text{C}(\text{PMe}_3)\text{Tol}$  ( $\text{Tol} = \text{C}_6\text{H}_4\text{Me-4}$ ) ( $^2J(\text{HP}) = 12.0$  Hz) [28], of the phosphonium salt  $[\text{PMe}_4]^+$  ( $^2J(\text{HP}) = 14.4$  Hz) [29] and the phosphorus ylide  $\text{PMe}_3\text{CH}_2$  ( $^2J(\text{HP}) = 12.5$  Hz) [30], which indicates the presence of a four-bonded phosphorus atom, bearing a positive charge. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** displays a doublet resonance for the  $\text{PMe}_3$  group at  $\delta$  13.1 ( $^1J(\text{CP}) = 54.9$  Hz), the chemical shift and the coupling constant comparing favorably with those of the related  $\alpha$ -phosphoniocarbene complex  $[(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}]\text{BCl}_4$  ( $\delta_{\text{Me}}$ : 11.6;  $^1J(\text{CP}) = 53.7$  Hz) [24]. In addition, two low-field resonances are observed in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** at  $\delta$  261.5 and 267.5. Both resonances appear as doublets due to  $^{13}\text{C}\text{-}^{31}\text{P}$  coupling, the more intense resonance at  $\delta$  267.5 being assigned to the two equivalent carbonyl ligands, and the other resonance being assigned to the carbene-carbon nucleus (Table 2). The carbonyl-carbon resonance of the  $\alpha$ -phosphoniocarbene complex **3** ( $\delta(\text{C}_{\text{carbonyl}})$ : 267.5), appears at considerably lower field than that of the carbyne complex **2a** ( $\delta(\text{C}_{\text{carbonyl}})$ : 238.1), indicating in good agreement with the IR data a stronger  $\text{Cr}(\text{d}\pi)\text{-CO}(\pi^*)$  back-bonding in the complex **3**. In contrast, the  $\text{CPh}$  resonance of **3** ( $\delta(\text{C}_{\text{carbene}})$ : 261.5) appears at considerably higher field than that of **2a** ( $\delta(\text{C}_{\text{carbyne}})$ : 325.7) (Table 2). A shielding of the  $\text{CPh}$  nucleus has also been observed previously upon addition of  $\text{PMe}_3$  to  $[(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}\equiv\text{CPh}]\text{BCl}_4$  ( $\delta(\text{C}_{\text{carbyne}})$ : 349.1) to afford  $[(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}]\text{BCl}_4$  ( $\delta(\text{C}_{\text{carbene}})$ : 307.3) [24].

The solid-state structure of **3** was determined by a single crystal X-ray diffraction study. Suitable crystals were obtained upon diffusion of  $\text{Et}_2\text{O}$  into a  $\text{CH}_2\text{Cl}_2$  solution of **3** at  $-30^\circ\text{C}$ . A ZORTEP plot of a single molecule with the atom-labeling scheme adopted is shown in Fig. 3. Selected bond lengths and angles are listed in Table 5.

Complex **3** has a distorted, 'three-legged piano-stool' structure, where the two legs are the carbonyl ligands and the third leg is the  $\alpha$ -phosphoniocarbene ligand. The Cp ligand is bonded in an  $\eta^5$  fashion to the chromium center, the  $\text{Cr}\text{-C}_{\text{cyclopentadienyl}}$  bonds ranging from 220.7(4) to 223.9(4) pm. The steric crowding caused by the carbene ligand on the chromium center opens the angles between the carbene and the carbonyl ligands to  $97.17(14)^\circ$  and  $100.22(14)^\circ$ . The carbonyl ligands are thereby pressed together as shown by the angle  $\text{C13}\text{-Cr}\text{-C14}$  of  $78.5(2)^\circ$ . The  $\text{Cr}\text{-C}_{\text{carbene}}$  bond of **3** is 190.5(3) pm long and compares favorably with that of the carbene complexes  $\text{Cp}(\text{CO})(\text{NO})\text{Cr}=\text{CPh}_2$  ( $\text{Cr}\text{-C}_{\text{carbene}} = 191.2(8)$  pm) [31] and  $(\eta^6\text{-C}_6\text{H}_6)(\text{CO})_2\text{Cr}=\text{C}(\text{OMe})\text{Ph}$  ( $\text{Cr}\text{-C}_{\text{carbene}} = 193.2(13)$  and  $193.9(12)$  pm, two independent molecules) [32]. It is shorter than a  $\text{Cr}\text{-C}$  single bond (e.g.

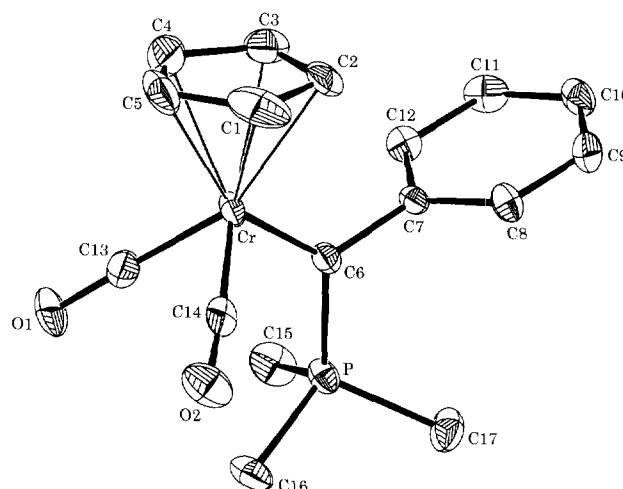


Fig. 3. ZORTEP plot of the structure of **3** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity reasons.

$(\text{tmeda})\text{Cr}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 214.6(3)$  pm [33];  $(\text{tmeda})\text{Cr}(\text{CH}_2\text{Ph})_2$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 217.7(2)$  pm [33]; *trans*- $\text{Cr}(\text{dmpe})_2\text{Me}_2$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 216.8(4)$  pm [34];  $\text{Cp}^*\text{Cr}(\text{PMe}_3)\text{Me}_2$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 206.7(5)$  pm [35];  $[\text{Cp}^*\text{Cr}(\text{py})_2\text{Et}]\text{PF}_6$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 209.4(12)$  pm [36];  $\text{CrCy}_4$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 200.9(4)$  and  $201.0(4)$  pm [37];  $\text{Cp}^*\text{Cr}(\text{O})_2\text{Me}$ :  $\text{Cr}\text{-C}_{\text{alkyl}} = 205.4(5)$  pm [38]) and longer than the  $\text{Cr}\text{-C}_{\text{carbyne}}$  triple bond of **2a** (170.5(2) pm) corresponding well to a chromium-carbon double bond. The carbene ligand is planar at the carbene-carbon atom as shown by the sum of the angles around the atom C6 ( $359.9^\circ$ ) or the dihedral angle of  $2.1^\circ$  between the planes defined by the atoms Cr, C7 and P, and C6, P and C7 respectively. The  $\text{C}_{\text{carbene}}\text{-P}$  bond of 176.7(3) pm is slightly shorter than the  $\text{C}_{\text{Me}}\text{-P}$  single bonds of  $\text{PMe}_3$  (179.2(3)–179.5(3) pm) due to the  $\text{sp}^2$  hybridization of the carbene-carbon atom and is considerably longer than the  $\text{C}\text{-P}$  bond of  $\text{PPh}_3\text{CH}_2$  ( $\text{C}_{\text{methylene}}\text{-P} = 166.1(8)$  pm) [39]. All these data indicate that the bond between the  $\alpha$ -phosphoniocarbene ligand and the chromium atom should be best described by the canonical form **A** (Fig. 4).

The plane of the carbene ligand defined by the atoms

Table 5  
Selected bond lengths (pm) and bond angles (deg) with estimated standard deviations for **3**

|                    |          |            |            |
|--------------------|----------|------------|------------|
| Cr–C1              | 221.5(4) | C6–P       | 176.7(3)   |
| Cr–C2              | 222.8(3) | C6–Cr–C13  | 97.17(14)  |
| Cr–C3              | 223.9(4) | C6–Cr–C14  | 100.22(14) |
| Cr–C4              | 221.6(4) | C13–Cr–C14 | 78.5(2)    |
| Cr–C5              | 220.7(4) | Cr–C6–C7   | 125.5(2)   |
| Cr–Cp <sup>a</sup> | 187.5    | Cr–C6–P    | 126.9(2)   |
| Cr–C6              | 190.5(3) | P–C6–C7    | 107.5(2)   |
| Cr–C13             | 180.2(4) | Cr–C13–O1  | 175.6(3)   |
| Cr–C14             | 180.1(4) | Cr–C14–O2  | 175.0(3)   |
| C6–C7              | 151.8(4) |            |            |

<sup>a</sup> Cp denotes the center of the cyclopentadienyl ring.

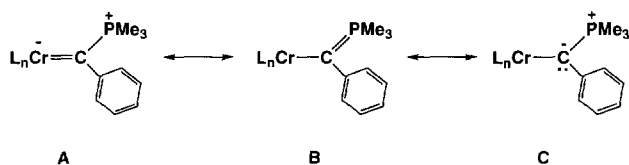


Fig. 4. Possible resonance formulae for the bonding of the  $\alpha$ -phosphino(carbene) ligand in **3**.

Cr, C6, C7 and P is almost perpendicular to the plane of the Cp ligand, the dihedral angle between the least-square planes being  $85.3^\circ$ . The same, 'upright' conformation is adopted by the carbene ligand in the complexes  $\text{Cp}(\text{CO})_2\text{Mn}=\text{CPh}_2$  [31] and  $\text{Cp}(\text{CO})_2\text{Mn}=\text{C}(\text{OEt})\text{Ph}$  [40] allowing an optimal  $\pi$ -interaction between the carbene ligand and the metal fragment [41]. The phenyl group points towards the Cp ligand and is oriented almost perpendicular to the carbene ligand plane, the torsional angle between the Cr–C6–C7–P and the C7–C8–C9–C10–C11–C12 planes being  $87.4^\circ$ . Thereby a steric repulsion between the phenyl and the cyclopentadienyl rings is avoided. The carbonyl ligands are approximately linear, the Cr–C–O bond angles being  $175.6(3)^\circ$  and  $175.0(3)^\circ$  respectively. The Cr–C<sub>carbonyl</sub> bonds (Cr–C13 =  $180.2(4)$  pm; Cr–C14 =  $180.1(4)$  pm) are shorter than those of  $\text{Cr}(\text{CO})_6$  ((Cr–C<sub>CO</sub>)<sub>av.</sub> =  $191.5(1)$  pm) [42] and of **2a** (Cr–C<sub>CO</sub> =  $184.7(2)$  and  $186.0(3)$  pm) (Table 3) indicating in full agreement with the IR and NMR spectroscopic data a strong Cr( $d\pi$ )–CO( $\pi^*$ ) back-bonding in **3** due to the presence of an electron-rich metal center. This is supported by the electrochemical properties of **3** obtained by cyclic voltammetry (Table 4). The voltammogram of **3** in  $\text{CH}_2\text{Cl}_2$  at  $-60^\circ\text{C}$  displays one reversible response on the anodic wave at  $E_p = -0.48$  V followed by an irreversible response at  $E_p = +0.48$  V (Fig. 5).

Reversibility of the first electron transfer step was demonstrated by the anodic to cathodic peak current ratio, which was  $1.03 \pm 0.05$ , the difference between the anodic and cathodic peak potentials (80 mV), which

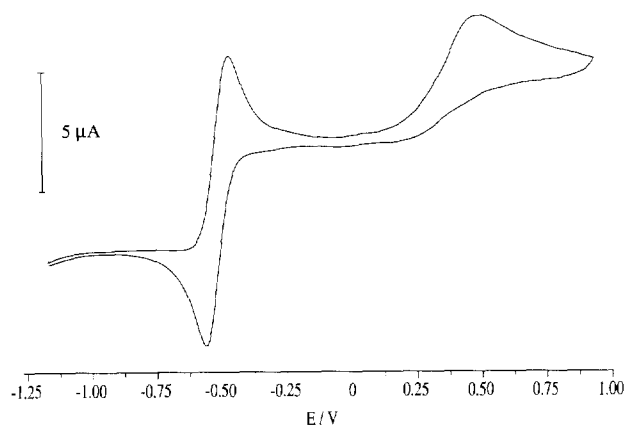
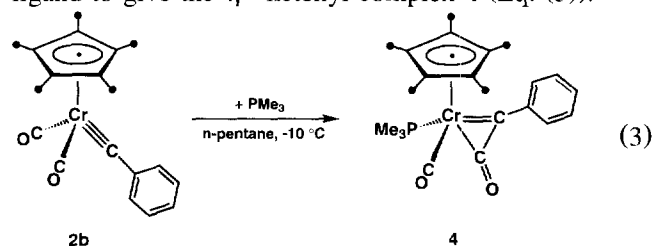


Fig. 5. Cyclic voltammogram of **3** in  $\text{CH}_2\text{Cl}_2$ -TBAPF<sub>6</sub> at  $-60^\circ\text{C}$ .  $\text{Fc}/\text{Fc}^+ = 0.0$  V; scan rate:  $100\text{ mV s}^{-1}$ .

was virtually identical with that of ferrocene measured under the same conditions (80 mV), and the anodic peak current, which was proportional to the square root of the scan rate [18]. The half-wave potential for the one-electron oxidation of the carbene complex **3** ( $E_{1/2} = -0.52$  V) is by 910 mV more negative than that of the phenylcarbyne complex **2a** ( $E_{1/2} = 0.39$  V) (Table 4) and is somewhat more positive than that of the electron-rich complexes  $\text{Cr}(\text{CNPh})_6$  ( $E_{1/2}^{0/+1}$  ( $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) =  $-0.83$  V vs.  $\text{Fc}/\text{Fc}^+$ ) [43], and  $[\text{Cr}(\text{CN}^t\text{Bu})_6]\text{PF}_6$  ( $E_{1/2}^{+1/+2}$  ( $\text{CH}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ) =  $-0.68$  V vs.  $\text{Fc}/\text{Fc}^+$ ) [12].

Addition of  $\text{PMe}_3$  to the phenylcarbyne complex **2b** induces a coupling of the carbyne with one carbonyl ligand to give the  $\eta^2$  ketenyl complex **4** (Eq. (3)).



IR monitoring of the course of the reaction reveals a clean conversion of the starting material **2b** to the product **4** which was isolated in 65% yield as a green solid and is soluble in  $\text{CH}_2\text{Cl}_2$ , acetone and  $\text{Et}_2\text{O}$ , but sparingly soluble in  $n$ -pentane. Complex **4** decomposes slowly in  $\text{CH}_2\text{Cl}_2$  or acetone solution at room temperature and in the solid state at  $90^\circ\text{C}$ . In the IR spectrum of **4** in  $\text{CH}_2\text{Cl}_2$  one strong absorption band is observed at  $1877\text{ cm}^{-1}$  for the terminal bonded CO ligand and one absorption of medium intensity at  $1721\text{ cm}^{-1}$ , which is assigned to the  $\nu(\text{C}=\text{O})$  vibration of the ketenyl ligand (Table 1). Both absorptions appear at smaller wavenumbers than those of the related molybdenum and tungsten complexes  $\text{Cp}^*(\text{CO})(\text{PMe}_3)\text{M}[\text{C}(\text{C}_6\text{H}_3\text{Me}_2-2,6)\text{CO}]$  (M = Mo:  $\nu(\text{CO}) = 1888\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O}) = 1733\text{ cm}^{-1}$ ; M = W:  $\nu(\text{CO}) = 1898\text{ cm}^{-1}$ ,  $\nu(\text{C}=\text{O}) = 1729\text{ cm}^{-1}$ ) [21]. Additional support for the proposed structure is given by the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **4** which shows a singlet resonance at  $\delta 33.7$  (Table 2). The  $^{31}\text{P}$  resonances of the related molybdenum and tungsten complexes  $\text{Cp}^*(\text{CO})(\text{PMe}_3)\text{M}[\text{C}(\text{C}_6\text{H}_3\text{Me}_2-2,6)\text{CO}]$  appear at  $\delta 12.7$  and  $-16.6$  respectively, as expected on the basis of the Group VI transition metal  $^{31}\text{P}$  shielding trend. The  $^1\text{H}$  NMR spectrum of **4** displays, besides the phenyl proton resonances, a singlet resonance for the  $\text{Cp}^*$  ring protons at  $\delta 1.74$  and a doublet resonance for the  $\text{PMe}_3$  protons at  $\delta 1.12$  (Table 2). The  $^2J(\text{HP})$  coupling constant of  $8.7\text{ Hz}$  and the  $^1J(\text{CP})$  coupling constant of  $26.1\text{ Hz}$  are smaller than those of the  $\text{PMe}_3$  ligand bonded to chromium. Finally, one singlet and two doublet low-field resonances are observed in the

$^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **4** at  $\delta$  216.1, 247.8 and 253.6 respectively. On the basis of the  $^{13}\text{C}$ – $^{31}\text{P}$  coupling constants and the relative chemical shift, these resonances are tentatively assigned to the terminal ketenyl-carbon, the carbonyl-carbon and the central ketenyl-carbon nucleus respectively [19]. The ketenyl complex **4** was found to be electrochemically inactive in the potential range of  $-1.5$  to  $1.0$  V.

The observed difference in the reactions of the chromium phenylcarbyne complexes **2a** and **2b** with  $\text{PMe}_3$  is surprising, since the analogous Cp- and Cp\*-substituted molybdenum and tungsten complexes show the same reactivity pattern towards  $\text{PMe}_3$  [19,21].

### 3. Conclusion

An efficient method for the synthesis of the half-sandwich chromium phenylcarbyne complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Cr}\equiv\text{CPh}$  ( $\text{R} = \text{H}, \text{Me}$ ) has been found involving a ligand substitution reaction of the easily accessible carbyne complex  $\text{cis-Br}(\text{CO})_2(\text{pic})_2\text{Cr}\equiv\text{CPh}$  with  $\text{NaCp}$  and  $\text{KCp}^*$  respectively. This has allowed the first studies on the reactivity of these compounds. Both carbyne complexes have been found to undergo in  $\text{CH}_2\text{Cl}_2$  a reversible one-electron oxidation, indicating that the  $17e^-$  phenylcarbyne complexes  $[(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Cr}\equiv\text{CPh}]^+$  are stable compounds on the cyclic voltammetry time scale. An unexpected difference in the reactions of  $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CPh}$  and  $\text{Cp}^*(\text{CO})_2\text{Cr}\equiv\text{CPh}$  was discovered. The cyclopentadienyl derivative adds  $\text{PMe}_3$  at the carbyne-carbon atom to afford the  $\alpha$ -phosphoniocarbene complex  $\text{Cp}(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}$ , whereas the pentamethylcyclopentadienyl complex undergoes with  $\text{PMe}_3$  a carbyne-carbonyl coupling reaction to give  $\text{Cp}^*(\text{CO})(\text{PMe}_3)\text{Cr}[\text{C}(\text{Ph})\text{CO}]$ , which is the first reported  $\eta^2$ -ketenyl complex of chromium. The formation of the  $\alpha$ -phosphoniocarbene complex  $\text{Cp}(\text{CO})_2\text{Cr}=\text{C}(\text{PMe}_3)\text{Ph}$  is unprecedented in the chemistry of Cp-substituted Group VI transition metal carbyne complexes, emphasizing the different chemistry of a first-row transition metal from that of a second- and a third-row transition metal. The availability of the carbyne complexes  $(\eta^5\text{-C}_5\text{R}_5)(\text{CO})_2\text{Cr}\equiv\text{CPh}$  facilitates exploration of their reactions, particularly those with oxidants and electrophiles, which are currently in progress.

## 4. Experimental section

### 4.1. General procedures

Standard inert-atmosphere techniques were used for all syntheses and sample manipulations. The solvents

were dried by standard methods (*n*-pentane over  $\text{CaH}_2$ ; THF and  $\text{Et}_2\text{O}$  over Na–benzophenone;  $\text{CH}_2\text{Cl}_2$  over  $\text{P}_2\text{O}_5$  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.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker AM-300 spectrometer. The  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  spectra were calibrated against the solvent signals (methylene- $d_2$ -chloride:  $\delta_{\text{H}}$  5.32 and  $\delta_{\text{C}}$  53.8 ppm) and the  $^{31}\text{P}\{^1\text{H}\}$  spectra against an external 85%  $\text{H}_3\text{PO}_4$  solution in water. Mass spectra were obtained with an HP 5995A spectrometer.  $m/z$  values refer to the  $^{52}\text{Cr}$  isotope. Melting points were determined using a Büchi 530 melting point apparatus and are corrected. The samples were sealed in capillary tubes under argon.

Cyclic voltammetry was carried out under nitrogen at  $-60^\circ\text{C}$  in 15 ml of  $\text{CH}_2\text{Cl}_2$  containing the substrate ( $0.1 \text{ mmol l}^{-1}$ ) and tetrabutylammonium hexafluorophosphate ( $\text{TBAPF}_6$ ) ( $0.1 \text{ mol l}^{-1}$ ). A 5 mm Pt wire (0.1 mm) was used as the working electrode and an  $\text{Ag}/\text{AgCl}/\text{CH}_3\text{CN}/[\text{NBu}_4]\text{Cl}$  electrode was used as the reference electrode, which was separated from the solution by a double fritted cartridge system (Metrohm). According to IUPAC recommendations [44] all potentials are given against the ferrocene/ferrocenium redox-couple ( $\text{Fc}/\text{Fc}^+$ ), which was used as internal standard ( $E_{\text{p}}^{\text{Fc}}$  (ferrocene,  $-60^\circ\text{C}$ ) = 0.72 V;  $E_{\text{p}}^{\text{Fc}}$  (ferrocene,  $-60^\circ\text{C}$ ) = 0.63 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, cold ( $-60^\circ\text{C}$ ) solution of the sample and the supporting electrolyte. The cell was then placed in a dry-ice–isopropanol bath and the temperature was kept at  $-60^\circ\text{C}$  during the experiment. The scan rate was  $100 \text{ mV s}^{-1}$ .

The complex  $\text{trans-Br}(\text{CO})_4\text{Cr}\equiv\text{CPh}$  was prepared following the procedure of Fischer and Kreis [45]. 4-Methylpyridine was distilled under argon and stored over 4 Å molecular sieves.  $\text{NaCp}$  was prepared as described previously [46].  $\text{KCp}^*$  was obtained from KH and  $\text{C}_5\text{Me}_5\text{H}$  [47].

### 4.2. Preparations

#### 4.2.1. $\text{cis-Br}(\text{CO})_2(\text{pic})_2\text{Cr}\equiv\text{CPh}$ (**1**)

3.57 g (10.72 mmol) of  $\text{trans-Br}(\text{CO})_4\text{Cr}\equiv\text{CPh}$  were dissolved in 80 ml of cold  $\text{CH}_2\text{Cl}_2$  ( $-78^\circ\text{C}$ ) and treated

with 3.29 ml (33.74 mmol) of 4-methylpyridine. The solution was then allowed to warm to 0°C and stirred for 3 h, whereby evolution of gas was observed and the color of the solution turned from yellow to red. Completion of the reaction was revealed by the disappearance of the  $\nu(\text{CO})$  absorptions of the starting material at 2116 and 2049  $\text{cm}^{-1}$  and the simultaneous appearance of the  $\nu(\text{CO})$  absorptions of **1** at 2000 and 1924  $\text{cm}^{-1}$ . The solution was concentrated in vacuo to a few milliliters and a cold  $\text{Et}_2\text{O}$ -*n*-pentane mixture (1:1) (−78°C) was added to complete precipitation of **1**. The supernatant solution was decanted off and the precipitate was washed twice with a cold  $\text{Et}_2\text{O}$ -*n*-pentane mixture (1:1) (−78°C) and dried in vacuo. Red-brown solid. M.p.: 114°C (dec.). Yield: 4.67 g (94%).  $\text{C}_{21}\text{H}_{19}\text{BrCrN}_2\text{O}_2$  (463.29). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{cm}^{-1})$ : 2000 (vs), 1924 (vs) [ $\nu(\text{CO})$ ]; 1622 (m) [ $\nu(\text{CN})_{\text{pic}}$ ].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , −40°C):  $\delta$  2.33 (s, 6 H, 2 × Me), 7.06 (d,  $^3J(\text{HH}) = 5.1$  Hz, 4 × H-3, pic), 7.32–7.54 (m, 5 H,  $\text{C}_6\text{H}_5$ ), 8.80 (d,  $^3J(\text{HH}) = 5.1$  Hz, 4 × H-2, pic).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , −40°C):  $\delta$  20.4 (Me), 124.8 (C-3, pic), 127.9, 128.5 ( $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$ ,  $\text{C}_6\text{H}_5$ ), 146.6 ( $\text{C}_{\text{ipso}}$ ,

$\text{C}_6\text{H}_5$ ), 149.3 (C-4, pic), 152.5 (C-2, pic), 230.3 (CO), 302.4 (Cr≡C).

#### 4.2.2. $\text{Cp}(\text{CO})_2\text{Cr}\equiv\text{CPh}$ (**2a**)

A mixture of 3.55 g (7.66 mmol) of **1** and 880 mg (9.99 mmol) of NaCp was suspended in 100 ml of cold THF (−60°C), warmed slowly to 0°C and stirred for 2 h at 0°C. Completion of the reaction was revealed by IR spectroscopy. The resulting brown solution was evaporated to dryness and the residue was purified by column chromatography on silica gel at −10°C. The product was eluted with *n*-pentane, the red eluate was concentrated in vacuo to a few milliliters and cooled to −78°C to afford complex **2a** as a red, microcrystalline solid. M.p.: 35–36°C (dec.). Yield: 1.27 g (63%). Anal. Found: C, 63.34; H, 3.67.  $\text{C}_{14}\text{H}_{10}\text{CrO}_2$  (262.22). Calc.: C, 64.13; H, 3.84%. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{cm}^{-1})$ : 1991 (vs), 1922 (vs) [ $\nu(\text{CO})$ ].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , −40°C):  $\delta$  5.14 (s, 5 H,  $\text{C}_5\text{H}_5$ ), 7.27–7.48 (m, 5H,  $\text{C}_6\text{H}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , −40°C):  $\delta$  89.6 ( $\text{C}_5\text{H}_5$ ), 128.1, 129.4, 129.6, 147.1 ( $\text{C}_o$ ,  $\text{C}_m$ ,  $\text{C}_p$ , and  $\text{C}_{\text{ipso}}$  of  $\text{C}_6\text{H}_5$ ), 238.1 (CO), 325.7 (Cr≡C). EI-MS (70 eV):  $m/z$  262 [ $\text{M}]^+$ ,

Table 6  
Summary of crystallographic data for the complexes **2a** and **3**

|  | <b>2a</b>                                | <b>3</b>   |
|--|--|--|
| Empirical formula                                | $\text{C}_{14}\text{H}_{10}\text{CrO}_2$ | $\text{C}_{17}\text{H}_{19}\text{CrO}_2\text{P}$ |
| Molecular weight                                 | 262.22                                   | 338.29   |
| Crystal color                                    | red                                      | green  |
| Crystal size ( $\text{mm}^3$ )                   | $0.45 \times 0.41 \times 0.38$           | $0.38 \times 0.38 \times 0.04$                   |
| Temperature (K)                                  | 190(2)                                   | 220(2)   |
| Crystal system                                   | monoclinic                               | orthorhombic                                     |
| Space group                                      | $P2_1/a$ (no. 14)                        | $Pbca$ (no. 61)                                  |
| $a$ (Å)  | 9.765(2)                                 | 11.162(2)  |
| $b$ (Å)  | 9.6853(13)                               | 13.581(2)  |
| $c$ (Å)  | 13.045(2)                                | 21.434(3)  |
| $\alpha$ (deg)                                   |  |  |
| $\beta$ (deg)                                    | 102.95(8)                                |  |
| $\gamma$ (deg)                                   |  |  |
| $V$ (Å <sup>3</sup> )                            | 1202.3(3)                                | 3249.2(8)  |
| $Z$  | 4  | 4  |
| $\rho_{\text{calcd.}}$ ( $\text{g cm}^{-3}$ )    | 1.449                                    | 1.383  |
| $\mu_{\text{Mo K}\alpha}$ ( $\text{mm}^{-1}$ )   | 0.936                                    | 0.782  |
| $F(000)$   | 536                                      | 1408   |
| Radiation (Mo K $\alpha$ ) (Å)                   | 0.71073                                  | 0.71073  |
| $2\theta$ min., max. (deg)                       | 3, 55                                    | 2, 49  |
| $hkl$ range                                      | −12, 12; 0, 12; 0, 16                    | 0, 12; 0, 15; 0, 24                              |
| Total data                                       | 2937                                     | 19466  |
| Data unique ( $I > 2\sigma I$ )                  | 2765 ( $R(\text{int}) = 0.0332$ )        | 2602 ( $R(\text{int}) = 0.1267$ )                |
| Min./max. density ( $\text{e}^- \text{Å}^{-3}$ ) | 0.274/−0.428                             | 0.340/−0.402                                     |
| No. of parameters refined                        | 194                                      | 190  |
| $R_1^a$  | 0.0338                                   | 0.0371   |
| $wR_2^b$   | 0.0830                                   | 0.0706   |
| GOF <sup>c</sup>                                 | 1.043                                    | 0.762  |

<sup>a</sup>  $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$ .

<sup>b</sup>  $wR_2 = \{\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]\}^{1/2}$ .

<sup>c</sup>  $\text{GOF} = S = \{\sum [w(F_o^2 - F_c^2)] / (n - p)\}^{1/2}$ .



234 [M – CO]<sup>+</sup>, 206 [M – 2CO]<sup>+</sup>, 117 [M – 2CO – CPh]<sup>+</sup>.

#### 4.2.3. $Cp^*(CO)_2Cr \equiv CPh$ (**2b**)

Following the procedure described above for **2a**, complex **2b** was obtained as a purple microcrystalline solid, after the reaction of 1.27 g (2.74 mmol) of **1** with 620 mg (3.56 mmol) of  $KCp^*$  in THF at 0 °C. M.p.: < 20 °C (dec.). Yield: 460 mg (50%).  $C_{19}H_{20}CrO_2$  (332.36). IR (THF)  $\nu(\text{cm}^{-1})$ : 1976 (vs), 1908 (vs) [ $\nu(\text{CO})$ ].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –40 °C):  $\delta$  1.96 (s, 15 H,  $C_5Me_5$ ), 7.23–7.34 (m, 5 H,  $C_6H_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –40 °C):  $\delta$  11.1 ( $C_5Me_5$ ), 102.5 ( $C_5Me_5$ ), 127.9, 128.5, 128.7, 146.6 ( $C_o$ ,  $C_p$ ,  $C_m$ , and  $C_{\text{ipso}}$  of  $C_6H_5$ ), 241.2 (CO), 323.7 (Cr≡C).

#### 4.2.4. $Cp(CO)_2Cr = C(PMe_3)Ph$ (**3**)

A solution of 290 mg (1.11 mmol) of **2a** in 20 ml of *n*-pentane was treated at –10 °C with 0.17 ml (1.67 mmol) of  $PMe_3$  and stirred for 8 h. During this time the initially red solution turned green and precipitation of a green solid was observed. Completion of the reaction was monitored by IR spectroscopy. The mixture then was cooled to –78 °C, the supernatant solution was decanted off and the precipitate was washed once with cold *n*-pentane (–78 °C) and dried in vacuo at –10 °C. Green, microcrystalline solid. M.p.: 104 °C (dec.). Yield: 330 mg (88%). Anal. Found: C, 59.78; H, 6.02.  $C_{17}H_{19}CrO_2P$  (338.29). Calc.: C, 60.36; H, 5.66%. IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{cm}^{-1})$ : 1889 (vs), 1787 (vs) [ $\nu(\text{CO})$ ].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –30 °C):  $\delta$  1.59 (d, 9 H,  $^2J(\text{PH}) = 12.0$  Hz,  $PMe_3$ ), 4.79 (s, 5 H,  $C_5H_5$ ), 6.53 (m, 2 H,  $C_6H_5$ ), 7.03 (m, 1 H,  $C_6H_5$ ), 7.21 (m, 2 H,  $C_6H_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –30 °C):  $\delta$  13.1 (d,  $^1J(\text{PC}) = 54.9$  Hz,  $PMe_3$ ), 94.2 ( $C_5H_5$ ), 123.3 (d,  $^3J(\text{PC}) = 4.8$  Hz,  $C_p$  of  $C_6H_5$ ), 124.2 (d,  $^3J(\text{PC}) = 8.0$  Hz,  $C_o$  of  $C_6H_5$ ), 127.0 (d,  $^4J(\text{PC}) = 4.8$  Hz,  $C_m$  of  $C_6H_5$ ), 161.4 (d,  $^2J(\text{PC}) = 9.6$  Hz,  $C_{\text{ipso}}$  of  $C_6H_5$ ), 261.5 (d,  $^1J(\text{PC}) = 8.0$  Hz, Cr=C), 267.5 (d,  $^3J(\text{PC}) = 6.3$  Hz, CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –30 °C):  $\delta$  7.9.

#### 4.2.5. $Cp^*(CO)(PMe_3)Cr[C(Ph)CO]$ (**4**)

A solution of 230 mg (0.69 mmol) of **2b** in 30 ml of *n*-pentane was treated with 0.12 ml (1.18 mmol) of  $PMe_3$  and stirred at –10 °C for 12 h. During this time the color of the solution turned from red to green and precipitation of a green solid was observed. Completion of the reaction was monitored by IR spectroscopy. The suspension then was cooled to –78 °C, the supernatant solution was decanted off and the green precipitate was washed once with cold *n*-pentane (–78 °C) and dried in vacuo at –10 °C. Green, microcrystalline solid. M.p.: 90 °C (dec.). Yield: 185 mg (65%).  $C_{22}H_{29}CrO_2P$  (408.44). IR ( $\text{CH}_2\text{Cl}_2$ )  $\nu(\text{cm}^{-1})$ : 1877 (vs) [ $\nu(\text{CO})$ ]; 1721 (m) [ $\nu(\text{C}=\text{O})_{\text{ketenyl}}$ ].  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –40 °C):  $\delta$  1.12 (d, 9 H,  $^2J(\text{PH}) = 8.7$  Hz,  $PMe_3$ ), 1.74 (s, 15 H,

$C_5Me_5$ ), 7.16–7.45 (m, 5 H,  $C_6H_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –40 °C):  $\delta$  10.9 ( $C_5Me_5$ ), 18.6 (d,  $^1J(\text{PC}) = 26.1$  Hz,  $PMe_3$ ), 104.7 ( $C_5Me_5$ ), 125.3, 127.1, 128.4, 142.8 ( $C_o$ ,  $C_p$ ,  $C_m$ , and  $C_{\text{ipso}}$  of  $C_6H_5$ ), 216.1 (C(Ph)CO), 247.8 (d,  $^2J(\text{PC}) = 33.9$  Hz, CO), 253.6 (d,  $^2J(\text{PC}) = 20.4$  Hz, CrC(Ph)CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , –40 °C):  $\delta$  33.7.

#### 4.2.6. Crystal structure determinations of **2a** and **3**

A summary of the crystal data, data collection and refinement for **2a** and **3** is given in Table 6.

Data collection for **2a** was performed on a Stoe STADI4 four circle diffractometer and for **3** on a Stoe IPDS diffractometer, both equipped with a low temperature device. Lattice parameters derived for **2a** from the setting angles of 32 reflections in the range of  $30 \leq 2\theta \leq 32^\circ$  and for **3** from 2000 reflections after data collection. Data were collected in the  $\omega$ - $2\theta$  scan mode. The crystal of **3** was oscillated in  $2.0^\circ$  steps to yield 100 exposures and each of them was irradiated for 10 min. After every 2 h three standard reflections were monitored for **2a** and the crystal reoriented in case of deviation between  $0.1^\circ$  and  $0.15^\circ$ . Intensity data for **2a** were corrected for Lorentz and polarization effects. Intensity data for **3** were integrated and converted into a SHELX hkl-file with the Stoe IPDS software [48]. The input files for the SHELX programs were prepared with the program UTILITY [49]. Structure solution was performed with Patterson methods (SHELXS-86) [50] and subsequent difference-Fourier synthesis (SHELXL-93) [51]. 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

Table 7  
Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^7$ ) for **2a**

| Atom  | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{eq}}^a$ |
|-------|----------|----------|----------|-------------------|
| Cr    | 7774(1)  | 98(1)    | 8124(1)  | 28(1)             |
| C(1)  | 7858(3)  | 478(3)   | 9805(2)  | 44(1)             |
| C(2)  | 8342(3)  | 1658(2)  | 9378(2)  | 40(1)             |
| C(3)  | 7249(3)  | 2189(3)  | 8595(2)  | 46(1)             |
| C(4)  | 6079(3)  | 1347(3)  | 8536(2)  | 56(1)             |
| C(5)  | 6441(3)  | 281(3)   | 9287(2)  | 56(1)             |
| C(6)  | 9028(2)  | 318(2)   | 7414(2)  | 31(1)             |
| C(7)  | 10123(2) | 396(2)   | 6842(2)  | 30(1)             |
| C(8)  | 11238(2) | –554(2)  | 7059(2)  | 36(1)             |
| C(9)  | 12312(3) | –467(3)  | 6524(2)  | 44(1)             |
| C(10) | 12299(3) | 566(3)   | 5789(2)  | 46(1)             |
| C(11) | 11209(3) | 1500(3)  | 5572(2)  | 48(1)             |
| C(12) | 10129(2) | 1428(2)  | 6093(2)  | 40(1)             |
| C(13) | 6514(2)  | –509(3)  | 6919(2)  | 37(1)             |
| O(1)  | 5751(2)  | –865(2)  | 6166(1)  | 56(1)             |
| C(14) | 8479(2)  | –1659(2) | 8437(2)  | 36(1)             |
| O(2)  | 8974(2)  | –2729(2) | 8621(2)  | 54(1)             |

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 8

Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{pm}^2 \times 10^7$ ) for **3**

| Atom  | x        | y       | z       | $U_{\text{eq}}^a$ |
|-------|----------|---------|---------|-------------------|
| Cr    | 406(1)   | 1183(1) | 1467(1) | 19(1)             |
| C(1)  | 807(4)   | -254(3) | 1025(2) | 46(1)             |
| C(2)  | 1189(3)  | 498(3)  | 615(2)  | 31(1)             |
| C(3)  | 2094(4)  | 1021(3) | 913(2)  | 35(1)             |
| C(4)  | 2274(4)  | 636(3)  | 1502(2) | 45(1)             |
| C(5)  | 1493(4)  | -164(3) | 1573(2) | 54(2)             |
| C(6)  | -63(3)   | 2386(2) | 1080(2) | 18(1)             |
| C(7)  | 399(3)   | 2767(2) | 460(1)  | 17(1)             |
| C(8)  | -196(3)  | 2515(2) | -93(2)  | 23(1)             |
| C(9)  | 199(3)   | 2893(3) | -658(2) | 28(1)             |
| C(10) | 1181(3)  | 3502(2) | -688(2) | 26(1)             |
| C(11) | 1779(3)  | 3741(2) | -145(2) | 27(1)             |
| C(12) | 1398(3)  | 3372(2) | 425(2)  | 23(1)             |
| C(13) | 408(3)   | 1625(2) | 2260(2) | 24(1)             |
| O(1)  | 352(2)   | 1868(2) | 2786(1) | 42(1)             |
| C(14) | -1026(4) | 752(2)  | 1742(2) | 23(1)             |
| O(2)  | -1918(2) | 439(2)  | 1959(1) | 38(1)             |
| P     | -1020(1) | 3295(1) | 1395(1) | 20(1)             |
| C(15) | -167(3)  | 4295(2) | 1714(2) | 33(1)             |
| C(16) | -2003(3) | 2898(2) | 2005(2) | 29(1)             |
| C(17) | -1986(3) | 3820(2) | 814(2)  | 30(1)             |

<sup>a</sup>  $U_{\text{eq}}$  is defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

atoms for **2a** were refined isotropically, whereas the hydrogen atoms of **3** were included using a riding model with  $d(\text{C-H}) = 96 \text{ pm}$  and  $U_{\text{ISO}} = 600 \text{ pm}^2$ . Neutral atom scattering factors were taken from Cromer and Mann [52]. Illustrations were performed with ZORTEP [53]. Final positional and equivalent isotropic thermal parameters are given in Table 7 for **2a** and in Table 8 for **3**.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge on application to the Director CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) (0)1223 336 033; e-mail: teched@chemcrs.cam.ac.uk).

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