

Note

# Synthesis and structural characterization of a terphenyl substituted phosphalkyne, $\text{P}\equiv\text{C}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\text{-}2,6\}$

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## Abstract

In attempts to form group 15 heteroalkynes, the reactions of  $\text{Ar}'\text{C}(\text{O})\text{Cl}$  ( $\text{Ar}' = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3^i\text{-}2,4,6)_2\text{-}2,6$ ) or  $\text{Ar}''\text{C}(\text{O})\text{Cl}$  ( $\text{Ar}'' = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\text{-}2,6$ ) with  $[\text{LiE}(\text{SiMe}_3)_2]$  ( $\text{E} = \text{P}, \text{As}$  or  $\text{Sb}$ ) have been carried out. No reactions occurred with the bulkier acid chloride,  $\text{Ar}'\text{C}(\text{O})\text{Cl}$ , whilst reactions only occurred with  $\text{Ar}''\text{C}(\text{O})\text{Cl}$  at elevated temperatures. One of these afforded the first terphenyl substituted phosphalkyne,  $\text{P}\equiv\text{CAr}''$ , as an air stable, crystalline solid. The X-ray crystal structure of this compound was obtained. © 2007 Elsevier B.V. All rights reserved.

**Keywords:** Phosphalkyne; Terphenyl; Low coordination; Multiple bonding; Crystal structure

## 1. Introduction

The chemistry of phosphalkynes,  $\text{P}\equiv\text{CR}$ , is very well developed and these compounds have been utilized as building blocks in the formation of a wide variety of organophosphorus cage, heterocyclic and acyclic compounds [1]. In addition, the metal coordination chemistry of phosphalkynes has been the subject of many studies, the results of which have highlighted the alkyne like reactivity of this important class of compound [1]. It is perhaps surprising that although more than 450 papers have detailed their chemistry [2], only seven phosphalkynes have been crystallographically characterized in the free state [3]. In contrast to phosphalkynes, only a handful of publications detailing the chemistry of arsaalkynes,  $\text{As}\equiv\text{CR}$ , have appeared [4] and only one such compound has been structurally authenticated,  $\text{As}\equiv\text{CMes}^*$  ( $\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}_3^i\text{-}$

$2,4,6$ ) [4c]. Corresponding stibaalkynes,  $\text{Sb}\equiv\text{CR}$ , are unknown, though attempts to prepare sterically hindered examples have led to compounds containing rare examples of crystallographically elucidated  $\text{Sb}=\text{C}$  bonds, *viz.* the 2,3-distibabutadienes,  $(\text{Me}_3\text{SiO})(\text{R})\text{C}=\text{SbSb}=\text{C}(\text{R})(\text{OSiMe}_3)$ ,  $\text{R} = \text{Mes}^*$  or mesityl [5].

We are interested in preparing examples of stibaalkynes, in addition to extending the known range of both arsaalkynes and phosphalkynes. It is beyond question that very bulky substituents will be required for the preparation of ambient temperature stable stibaalkynes and arsaalkynes. In recent years, the groups of Power and others have utilized bulky terphenyl substituents to great effect for the stabilization of systems containing multiple bonds between heavier p-block elements, e.g.  $\text{RE}=\text{ER}$ ,  $\text{E}=\text{As}$  or  $\text{Sb}$ ;  $\text{R} = \text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Pr}_3^i\text{-}2,4,6)_2\text{-}2,6(\text{Ar}')$  or  $\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3\text{-}2,4,6)_2\text{-}2,6(\text{Ar}'')$  [6]. It seemed to us that the terphenyl substituents,  $\text{Ar}'$  and  $\text{Ar}''$ , could stabilize heavy group 15 alkyne analogues. In this note we report our attempts to prepare such compounds which, though largely unsuccessful, have led to the synthesis and structural characterization of the first terphenyl substituted phosphalkyne.

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## 2. Results and discussion

The supermesityl substituted heteroalkynes,  $E\equiv CMe_s^*$ ,  $E=P$  or  $As$ , are prepared by reaction of the lithium pnictides,  $LiE(SiMe_3)_2$ , with the acid chloride,  $Me_s^*C(O)Cl$  [4b,7]. These reactions presumably proceed *via* the heteroalkenes,  $(Me_3Si)E=C(Me_s^*)(OSiMe_3)$ , which spontaneously eliminate hexamethyldisiloxane,  $(Me_3Si)_2O$ , yielding the heteroalkyne. In consideration of this, similar synthetic methodologies were chosen to access the target heteroalkynes of this study. As the terphenyl acid chloride,  $Ar'C(O)Cl$ , was unknown, a synthetic route to it was devised, whereby a diethyl ether solution of the known lithium aryl,  $[Ar'Li(OEt_2)]$ , was treated with freshly sublimed dry ice which, following aqueous work-up, yielded the new acid,  $Ar'COOH$ , in high yield. Heating a solution of this in neat thionyl chloride at 80 °C overnight afforded a high yield of  $Ar'C(O)Cl$ . Both compounds were fully spectroscopically characterized. The less bulky acid,  $Ar''COOH$ , had been previously reported [8] and was readily converted to  $Ar''C(O)Cl$  by heating in thionyl chloride.

Treatment of the lithium pnictides,  $LiE(SiMe_3)_2$ ,  $E=P$ ,  $As$  or  $Sb$ , with  $Ar'C(O)Cl$  in DME at 20 °C led to no reaction after stirring overnight. This is surprising and probably results from the significant steric bulk of the terphenyl acid chloride which prevents attack of the pnictide center at the acid chloride functionality. When the reaction solutions were heated to 80 °C for 4 h, no reaction occurred for  $E=P$ , whilst the pnictide salt thermally decomposed for  $E=As$  or  $Sb$  and the acid chloride was recovered unreacted.

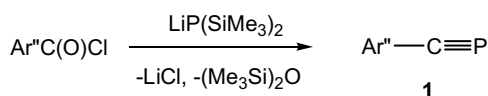
The lithium pnictides were then treated with the less bulky acid chloride,  $Ar''C(O)Cl$ , and again no reactions occurred at ambient temperature. However, when the reaction mixture involving  $LiP(SiMe_3)_2$  was heated to 80 °C for 4 h, the new phosphalkyne, **1**, was isolated in low to moderate yield after chromatographic work-up (Scheme 1). Following this reaction by  $^{31}P$  NMR spectroscopy revealed no signals corresponding to probable reaction intermediates, e.g.  $(Me_3Si)P=C(Ar'')(OSiMe_3)$ . In this respect, reactions of aryl substituted acid chlorides with  $LiP(SiMe_3)_2$  have previously been reported to lead directly to phosphalkynes [3b]. In contrast, when the reaction mixtures incorporating the arsenide and antimonide starting materials were heated, decomposition occurred leading to intractable mixtures of products which did not include  $Ar''C(O)Cl$ . This suggests that the acid chloride does react with these pnictides at elevated temperatures, but the resulting heteroalkynes or reaction intermediates are unstable under the conditions employed. In an attempt to

increase the rates of these reactions at room temperature, one equivalent of 12-crown-4 was added to them to potentially increase the reactivity of the pnictide salt. Unfortunately, this had no effect.

The phosphalkyne, **1**, is a colourless crystalline solid which is indefinitely air stable at room temperature. Its spectroscopic data are consistent with its proposed formulation. The  $^{31}P\{^1H\}$  NMR spectrum of the compound exhibits a singlet at  $\delta -8.0$  ppm (*cf.*  $P\equiv CMe_s^*$   $\delta$  34.4 ppm [7]), whilst its  $^{13}C\{^1H\}$  NMR spectrum displays a doublet alkyne resonance at  $\delta$  161.4 ppm,  $^1J_{PC} = 50.8$  Hz (*cf.*  $P\equiv CMe_s^*$   $\delta$  168.7 ppm,  $^1J_{PC} = 53.2$  Hz [7]).

X-ray quality crystals of **1** proved difficult to obtain, though upon recrystallization of the product mixture from one reaction, several large prismatic crystals were isolated from the bulk crystalline material. A crystallographic analysis of one of these showed it to be a co-crystallized mixture of  $P\equiv CAr''$  (81%) and  $Ar''I$  (19%) [9] which were disordered over the same site in the crystal lattice. This disorder was successfully modelled, thus allowing comment on the structural parameters of **1**. It should be noted that the  $Ar''I$  contaminant originates from the preparation of the  $Ar''COOH$  precursor to the acid chloride,  $Ar''C(O)Cl$ . Also, spectroscopic analysis of bulk crystalline **1** did not reveal detectable amounts of  $Ar''I$ , suggesting this is a very minor contaminant.

The molecular structure of **1** is depicted in Fig. 1 and shows it to be monomeric with a near linear CCP fragment. Its C–P distance [1.539(6) Å] is consistent with a localized triple bond and is in the known range (1.522–1.558 Å [3]) for free phosphalkynes. The other geometrical parameters



Scheme 1.  $Ar' = C_6H_3(C_6H_2Me_3-2,4,6)_2-2,6$ .

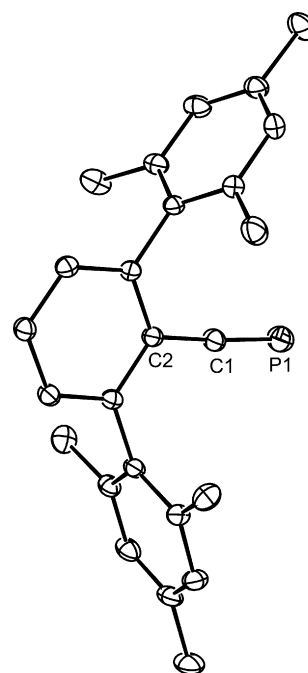


Fig. 1. Molecular structure of **1** (30% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): P(1)–C(1) 1.539(6), C(1)–C(2) 1.396(7), C(2)–C(1)–P(1) 176.6(4).

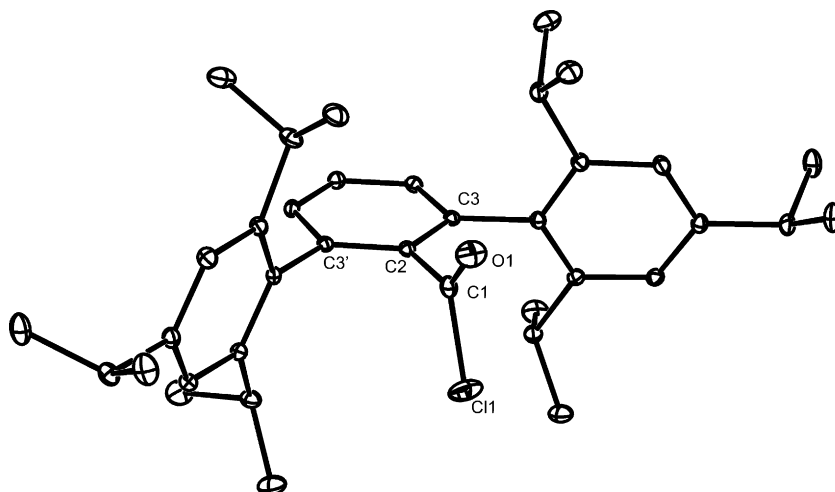


Fig. 2. Molecular structure of  $\text{Ar}'\text{C}(\text{O})\text{Cl}$  (30% probability ellipsoids; hydrogen atoms omitted for clarity). Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ):  $\text{C}(1)\text{--Cl}(1)$  1.765(4),  $\text{C}(1)\text{--O}(1)$  1.178(5),  $\text{C}(1)\text{--C}(2)$  1.511(5),  $\text{O}(1)\text{--C}(1)\text{--C}(2)$  126.7(4),  $\text{O}(1)\text{--C}(1)\text{--Cl}(1)$  119.5(3),  $\text{C}(2)\text{--C}(1)\text{--Cl}(1)$  113.8(3). Symmetry operation:  $'x, y, -z + 1/2$ .

of the molecule are unexceptional. As the crystal structure of the acid chloride,  $\text{Ar}'\text{C}(\text{O})\text{Cl}$ , was obtained during the course of this study, its molecular structure is included here (Fig. 2). This shows it to be monomeric and to sit on a mirror plane. There are no extraordinary geometrical features of the structure but it is obvious that the steric protection afforded to its acid chloride fragment leads to its lack of reactivity towards the pnictide salts employed in this study.

### 3. Conclusion

In summary, the first example of a terphenyl substituted phosphalkyne has been prepared and structurally characterized. All attempts to prepare terphenyl substituted arsaalkynes and stibaalkynes met with failure, apparently because the acid chlorides utilized were too bulky to react with the silylated pnictide starting materials. Efforts continue in our laboratory to access stibaalkynes *via* alternative routes.

### 4. Experimental

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon. DME and hexane were distilled over potassium, whilst diethyl ether was distilled over Na/K then freeze/thaw degassed prior to use.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}\{^1\text{H}\}$  spectra were recorded on either a Bruker DXP400 or Jeol Eclipse 300 spectrometer, and were referenced to the residual  $^1\text{H}$  or  $^{13}\text{C}$  resonances of the solvent used or 85% external  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}\{^1\text{H}\}$  NMR). Mass spectra were obtained from the EPSRC National Mass Spectrometry Service at Swansea University. IR spectra were recorded using a Nicolet 510 FT-IR spectrometer as Nujol mulls between NaCl plates. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Microanalyses were carried out by Medac

Ltd. [ $\text{Ar}'\text{Li}(\text{OEt}_2)$ ] [9],  $\text{Ar}''\text{C}(\text{O})\text{Cl}$  [8] and [ $\text{LiP}(\text{SiMe}_3)_2(\text{DME})$ ] [10] were prepared by variations of literature procedures. All other reagents were used as received.

#### 4.1. $\text{Ar}'\text{COOH}$

[ $\text{Ar}'\text{Li}(\text{OEt}_2)$ ] (920 mg, 1.64 mmol) in diethyl ether (20 ml) was added to freshly sublimed dry ice over 30 min. The resultant suspension was warmed to room temperature over a period of two hours whereupon a deoxygenated aqueous HCl solution (1 M, 100 ml) was added. A solution of  $\text{NaHCO}_3$  (1 M) was then added until the aqueous layer attained a pH of 7. The organic layer was dried with  $\text{MgSO}_4$ , filtered, and volatiles removed from the filtrate to give  $\text{Ar}'\text{COOH}$  as an off-white solid (650 mg, 75%), m.p. 247–248  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300.5 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  0.95 (d,  $^3J_{\text{HH}} = 6.7$  Hz, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 1.04 (d,  $^3J_{\text{HH}} = 6.7$  Hz, 12H, *o*- $\text{CH}(\text{CH}_3)_2$ ), 1.25 (d,  $^3J_{\text{HH}} = 6.8$  Hz, 12H, *p*- $\text{CH}(\text{CH}_3)_2$ ), 2.46 (sept,  $^3J_{\text{HH}} = 6.7$  Hz, 4H, *o*- $\text{CHMe}_2$ ), 2.86 (sept,  $^3J_{\text{HH}} = 6.8$  Hz, 2H, *p*- $\text{CHMe}_2$ ), 6.91 (s, 4H, *m*-Trip), 7.15 (t,  $^3J_{\text{HH}} = 7.5$  Hz, 2H, *m*-Ph), 7.41 (d,  $^3J_{\text{HH}} = 7.5$  Hz, 1H, *p*-Ph), 10.10 (br.s, 1H, OH);  $^{13}\text{C}$  NMR (75.6 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  23.0 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 24.1 (*p*- $\text{CH}(\text{CH}_3)_2$ ), 25.4 (*o*- $\text{CH}(\text{CH}_3)_2$ ), 30.9 (*o*- $\text{CHMe}_2$ ), 32.4 (*p*- $\text{CHMe}_2$ ), 120.2, 120.5, 129.0, 133.0, 134.3, 139.7, 146.6, 148.0 (Ar-C), 172.8 (COOH); IR (Nujol)  $\nu$  ( $\text{cm}^{-1}$ ): 3030 (OH), 1695 (C=O); MS/EI  $m/z$ (%): 527 ( $\text{M}^+$ , 100); accurate mass MS (ES+) calc. mass for  $\text{C}_{37}\text{H}_{50}\text{O}_2$ : 527.3884; measured mass: 527.3895. Anal. Calc. for  $\text{C}_{37}\text{H}_{50}\text{O}_2$ : C, 84.36; H, 9.57. Found: C, 84.32; H, 9.50%.

N.B.: Trip = the  $\text{C}_6\text{H}_2\text{Pr}_3^{2,4,6}$  substituent.

#### 4.2. $\text{Ar}'\text{C}(\text{O})\text{Cl}$

A solution of  $\text{Ar}'\text{COOH}$  (650 mg, 1.24 mmol) in thionyl chloride (20 ml) was heated to 80  $^\circ\text{C}$  for 16 h. Volatiles were then removed *in vacuo* to give an off-white solid. This was

recrystallized from hexane (30 ml) to give colorless crystals of Ar'C(O)Cl (550 mg, 81%), m.p. 204–205 °C. <sup>1</sup>H NMR (300.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 1.10 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.20 (d, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 12H, *p*-CH(CH<sub>3</sub>)<sub>2</sub>), 1.40 (d, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 12H, *o*-CH(CH<sub>3</sub>)<sub>2</sub>), 2.80 (sept, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz, 2H, *p*-CHMe<sub>2</sub>), 2.89 (sept, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4H, *o*-CHMe<sub>2</sub>), 7.12 (tr, 1H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *p*-Ph), 7.14 (d, 2H, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, *m*-Ph), 7.20 (s, 4H, *m*-Trip); <sup>13</sup>C NMR (75.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 22.6 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 24.0 (*p*-CH(CH<sub>3</sub>)<sub>2</sub>), 25.9 (*o*-CH(CH<sub>3</sub>)<sub>2</sub>), 31.3 (*o*-CHMe<sub>2</sub>), 34.5 (*p*-CHMe<sub>2</sub>), 121.0, 129.2, 129.8, 132.9, 137.3, 139.0, 147.3, 149.6 (Ar–C), 168.5 (C(O)Cl); IR (Nujol) ν cm<sup>-1</sup>: 1792 (C=O); MS/EI *m/z*(%): 545 (M<sup>+</sup>, 100); accurate mass MS (EI) calc. mass for C<sub>37</sub>H<sub>49</sub>ClO: 544.3466; measured mass: 544.3464. Anal. Calc. for C<sub>37</sub>H<sub>49</sub>ClO: C, 81.51; H, 9.06. Found: C, 81.48; H, 8.99%.

#### 4.3. P≡CAr''(1)

A solution of [LiP(SiMe<sub>3</sub>)<sub>2</sub>(DME)] (403 mg, 1.47 mmol) in DME (20 ml) was added to a solution of Ar''C(O)Cl (800 mg, 1.47 mmol) in DME (20 ml) at 0 °C. The resultant suspension was allowed to warm to room temperature, stirred overnight, then heated at 80 °C for 4 h. Volatiles were then removed *in vacuo* and the residue extracted into hexane (5 ml). The extract was chromatographed (silica/hexane) and the single colorless band collected. Concentration of this band to *ca.* 3 ml and cooling to –30 °C afforded colorless crystals of **1** (150 mg, 30%), m.p. 160–163 °C (decomp.). <sup>1</sup>H NMR (300.5 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 2.15 (s, 12H, *o*-Me), 2.18 (s, 6H, *p*-Me), 6.76–7.15 (m, 7H, Ar–H); <sup>13</sup>C NMR (75.6 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 20.2 (*o*-Me), 20.7 (*p*-Me), 129.4, 135.1, 135.4, 136.7, 137.8, 139.0, 147.7 (Ar–C), 146.9 (d, <sup>2</sup>J<sub>PC</sub> = 6.9 Hz, *ipso*-Ar), 161.4 (d, <sup>1</sup>J<sub>PC</sub> = 50.8 Hz, C≡P); <sup>31</sup>P {<sup>1</sup>H} NMR (121.7 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ –8.0 (s, C≡P); MS/EI *m/z*(%): 357 (M<sup>+</sup>, 53); accurate mass MS (EI) calc. mass for C<sub>25</sub>H<sub>25</sub>P: 356.1688 measured mass: 356.1691. Anal. Calc. for C<sub>25</sub>H<sub>25</sub>P: C, 84.24; H, 7.07. Found: C, 84.01; H, 7.00%.

N.B. identical reaction conditions were employed in attempts to prepare E≡CAr'' (E = As or Sb) from [LiE(SiMe<sub>3</sub>)<sub>2</sub>(DME)] and Ar''C(O)Cl. These reactions were unsuccessful.

#### 4.4. Crystallographic studies

Crystals of **1** and Ar'C(O)Cl suitable for X-ray crystal structure determination were mounted in silicone oil. Crystallographic measurements were made using a Nonius Kappa CCD diffractometer. The structures were solved by direct methods and refined on *F*<sup>2</sup> by full matrix least squares (SHELX97) [11] using all unique data. The crystal of **1** chosen for the crystallographic experiment was found to be a co-crystal of **1** (81%) and Ar''I (19%) which were disordered over the same site in the crystal lattice. This disorder was successfully modelled. Crystal data, details of data collections and refinement are given in Table 1.

Table 1  
Crystal data for compounds **1** and Ar'C(O)Cl

	<b>1</b>	Ar'C(O)Cl
Chemical formula	C <sub>24.81</sub> H <sub>25</sub> I <sub>0.19</sub> P <sub>0.81</sub>	C <sub>37</sub> H <sub>49</sub> ClO
Formula weight	372.36	545.21
<i>T</i> (K)	150(2)	150(2)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>C</i> 2/ <i>c</i>	<i>Pbcm</i>
<i>a</i> (Å)	14.933(3)	10.981(2)
<i>b</i> (Å)	9.2055(18)	12.094(2)
<i>c</i> (Å)	31.399(6)	25.429(5)
β (°)	102.42(3)	90
<i>V</i> (Å <sup>3</sup> )	4215.3(15)	3377.1(12)
<i>Z</i>	8	4
μ (Mo Kα) (mm <sup>-1</sup> )	0.399	0.138
Reflections collected ( <i>R</i> <sub>int</sub> )	6726 (0.0331)	19006 (0.0614)
Unique reflections	3629	3118
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0788	0.0752
w <i>R</i> <sub>2</sub> ' (all data)	0.2550	0.2046

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#### Appendix A. Supplementary material

CCDC 648225 and 648226 contain the supplementary crystallographic data for **1** and Ar'C(O)Cl. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.07.021.

#### References

- [1] K.B. Dillon, F. Mathey, J.F. Nixon, Phosphorus: The Carbon Copy, Wiley, Chichester, 1998, and references therein.
- [2] Results of a literature survey using SciFinder® Scholar, May, 2007.
- [3] (a) G. Becker, H. Brombach, S.T. Horner, E. Niecke, W. Schwarz, R. Streubel, E.-U. Wurthwein, Inorg. Chem. 44 (2005) 3080; (b) A.M. Arif, A.R. Barron, A.H. Cowley, S.W. Hall, Chem. Commun. (1988) 171; (c) M.Yu. Antipin, A.N. Chernega, K.A. Lysenko, Yu.T. Struchkov, J.F. Nixon, Chem. Commun. (1995) 505; (d) G. Becker, M. Bohringer, R. Gleiter, K.-H. Pfeifer, J. Grobe, D. Le Van, M. Hegemann, Chem. Ber. 127 (1994) 1041; (e) A.N. Chernega, G.N. Koidan, A.P. Marchenko, A.A. Korokin, Heteroatom Chem. 4 (1993) 365; (f) M. Brym, C. Jones, Dalton Trans. (2003) 3665; (g) K. Toyota, S. Kawasaki, M. Yoshifuji, J. Org. Chem. 69 (2004) 5065.
- [4] (a) P.B. Hitchcock, J.A. Johnson, J.F. Nixon, Angew. Chem., Int. Ed. Engl. 32 (1993) 103; (b) G. Märkl, H. Sejpka, Angew. Chem., Int. Ed. Engl. 25 (1986) 264;

- (c) P.B. Hitchcock, C. Jones, J.F. Nixon, *J. Chem. Soc., Chem. Commun.* (1994) 2061;
- (d) M.D. Francis, D.E. Hibbs, M.B. Hursthouse, C. Jones, K.M.A. Malik, *J. Chem. Soc., Chem. Commun.* (1996) 631;
- (e) C. Jones, T.C. Williams, *J. Organomet. Chem.* 689 (2004) 1648;
- (f) L. Lassalle, S. Lepoupy, J.-C. Guillemin, *Inorg. Chem.* 34 (1995) 5694.
- [5] (a) C. Jones, J.W. Steed, R.C. Thomas, *J. Chem. Soc., Dalton Trans.* (1999) 1541;
- (b) P.B. Hitchcock, C. Jones, J.F. Nixon, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 492.
- [6] B. Twamley, C.D. Sofield, M.M. Olmstead, P.P. Power, *J. Am. Chem. Soc.* 121 (1999) 3357.
- [7] G. Märkl, H. Sejka, *Tetrahedron Lett.* 27 (1986) 171.
- [8] J.R. Hagadorn, L. Que Jr., W.B. Tolman, *J. Am. Chem. Soc.* 120 (1998) 13531.
- [9] B. Schiemenz, P.P. Power, *Organometallics* 15 (1996) 958.
- [10] G. Fritz, W. Hölderich, *Z. Anorg. Allg. Chem.* 422 (1976) 104.
- [11] G.M. Sheldrick, *SHELX-97*, University of Göttingen, 1997.