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Preparation and molecular structure of 2,6-dimesitylphenyldichlorophosphane

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Owing to steric congestion, the phosphane unit within the title compound is dislocated from the central position which is associated with a difference in the P–C–C angles of 20.3(2)° and a compression of the Cl bond distance of the chlorine atom involved in this repulsive interaction. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; organophosphorus; terphenyl; steric protection

INTRODUCTION

Phosphorus ligands are of central importance for organic and organometallic synthesis with late transition metal catalysts, such as in alkene hydroformylation, the Heck reaction, cross-coupling and alkene hydrogenation.[1] The general synthetic access to phosphorus ligands, particularly tertiary phosphines, phosphinites and phosphonites, starts in most cases from the corresponding chlorophosphanes.[2,3] Dichlorophosphanes are important precursors for these $\sigma^3\lambda^3$ as well as for the low coordinated $\sigma^2\lambda^3$ phosphanes.[4,5] The latter class of compounds in which the trivalent phosphorus atom has only two coordination partners was initially studied to disprove the classical 'double bond rule'; however it recently also attracted considerable interest with respect to the potential of such compounds as novel electronic materials.[6,7] The title compound, 2,6-$(2,4,6\text{-Me}_3C_6H_2)_2C_6H_3PCl_2$ (**1**), is a sterically unusually crowded dichlorophosphane which has been employed to introduce the sterically protecting terphenyl ligand into low coordinated phosphorus compounds such as diphosphenes.[8,9] Employing dichlorophosphane **1**, very recently we succeeded in preparing the first metallocene bridged bisdiphosphenes which possess potential as a novel electroactive material.[10] Though compound **1** has been mentioned in the literature with some preliminary characterization, no detailed procedure for its preparation has been published to date.[8]

RESULTS AND DISCUSSION

2,6-Dimesitylphenyldichlorophosphane (**1**), was prepared in two synthetic steps from 2,6-dimesitylphenyliodide (Scheme 1). The latter is treated with an equimolar amount of *n*-butyllithium to effect a metal–halogen exchange, affording 2,6-dimesitylphenyllithium, which is subsequently reacted with phosphoroustrichloride, yielding 2,6-dimesitylphenyldichlorophosphane (**1**).

The molecular structure of **1** was established by spectroscopic methods and X-ray crystallography. In the crystal structure of **1** the phosphorus atom is almost coplanar to the central aryl ring, leaving the mesityl groups almost perpendicular to each side of the central ring plane (Fig. 1).

Owing to steric congestion between the chlorine atoms and one of the mesityl groups, the PCl_2 unit is bent away from this mesityl group to minimize the repulsive interaction. Consequently, the two P–C–C angles differ significantly by 20.3(2)°. The bond distances from phosphorus to the adjacent chlorine atoms also show differences and the bond length of the chlorine atom pointing directly towards the mesityl group, 2.0556(10) Å, is somewhat compressed compared with the chlorine atom pointing to the central cavity in the middle

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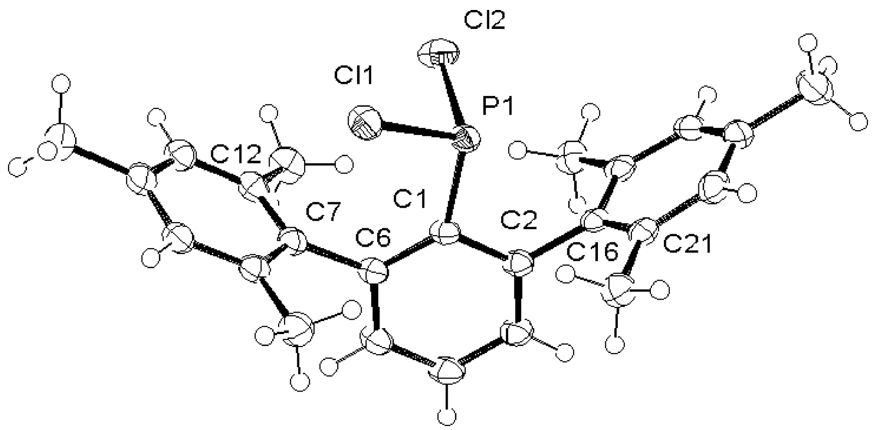
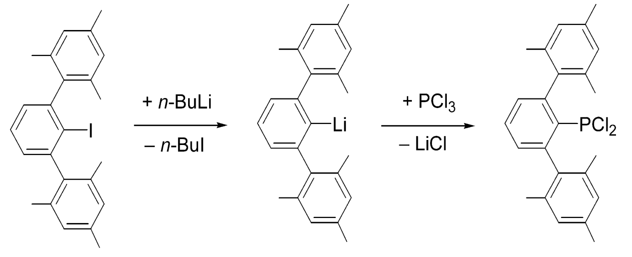


Figure 1. ORTEP plot of the molecular structure of **1**. Key geometric parameters: P1−Cl1 2.0556(10), P1−Cl2 2.0666(11), P1−C1 1.847(3), C1−C2 1.418(4), C1−C6 1.413(4), C6−C7 1.498(4), C2−C16 1.501(4) Å; C1−P1−Cl2 101.28(9)°, Cl1−P1−Cl2 98.77(5)°, C1−P1−Cl1 105.53(9)°, C2−C1−P1 109.87(19)°, C6−C1−P1 130.2(2)°, C1−C6−C7−C12 86.4(4)°, C1−C2−C16−C21 87.7(3)°.



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Scheme 1. Formation of 2,6-dimesitylphenyldichlorophosphane (**1**).

between both mesityl groups [2.0666(11) Å]. The Cl−P−Cl angle of 98.77(5)° is similar, but slightly smaller compared with a related terphenyl dichlorophosphane without any *ortho* substituents on the aryl groups [99.68(4)].[11]

In solution, the identity of dichlorophosphane **1** was confirmed by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy as well as by mass spectrometry. The ^{31}P NMR shift of **1** in benzene solution was observed at 161.3 ppm, which is close to the previously reported value. Unlike in the solid-state structure, in solution the ^{1}H and ^{13}C NMR spectra show that the two mesityl groups in **1** are effectively equivalent in symmetry. The splitting of the quarternary carbon atoms in the vicinity of the phosphorus atom can be attributed to coupling with the ^{31}P nucleus. An alternative explanation for the signal splitting based on chemical inequivalence of these carbon atoms due to hindered rotation of the $-PCl_2$ group and consequently lower symmetry can be ruled out, since the J_{CP} coupling constants have been confirmed by recording ^{13}C spectra at different magnetic field strengths.

EXPERIMENTAL

Materials

2,6-Dimesitylphenyliodide (1.76 g, 4 mmol; prepared according to a literature procedure)[12] in 20 ml *n*-hexane was reacted with 2.5 ml *n*-butyllithium solution (1.6 M in hexanes) at room temperature and stirred overnight. The resulting mixture was cooled to −78 °C and 0.55 ml PCl_3 (6 mmol) in 20 ml *n*-hexane were added dropwise. The temperature was maintained for 30 min, after which the reaction mixture was warmed to room temperature. The eliminated LiCl was removed by filtration and the solvent of the filtrate and excess PCl_3 were removed in vacuum. The remaining crude product (1.41g, 85%) was recrystallized from 10 ml toluene at 0 °C, yielding **1** as colorless crystalline solid (0.57 g, 34%). ^{31}P NMR (C_6D_6, δ ppm): 161.3. ^{1}H NMR (C_6D_6, δ ppm): 2.07 (s, 12H), 2.15 (s, 6H), 6.77 [dd, $^{1}J(^{1}H\text{-}^{1}H) = 7.4$ Hz, $^{1}J(^{1}H\text{-}^{31}P) = 3.1$ Hz, 2H], 6.81 (s, 4H), 7.07 [t, $^{1}J(^{1}H\text{-}^{1}H) = 7.4$ Hz, 1H]. ^{13}C NMR (C_6D_6, δ ppm): 20.34 (*o*-CH_3), 20.79 (*p*-CH_3), 128.17 (*m*-C_6H_3), 130.47 (*m*-C_6H_2), 132.85 (*p*-C_6H_3), 134.60 (d, $^{1}J_{CP} = 72$ Hz, C_q-aryl), 135.73 (d, $^{2}J_{CP} = 68$ Hz, C_q-aryl), 136.13 (C_q-aryl), 146.81 (d, $^{3}J_{CP} = 29$ Hz, C_q-aryl). MS(EI): 415 (2%, M^+), 400 (26%, M^+-CH_3), 399 (100%, M^+-CH_4), 344 (3%, $M^+-Cl-HCl$), 343 (8%, M^+-2HCl), 313 (3%, M^+-PCl_2).

Crystal structure determination

Intensity data were collected at 123 K on a Nonius Kappa CCD diffractometer for a colorless block 0.3 × 0.4 × 0.5 mm^3. $C_{24}H_{25}PCl_2$, $M = 415.31$, monoclinic, $P2_1/n$, $a = 8.9189(3)$, $b = 29.9942(11)$, $c = 9.0664(3)$ Å, $\beta = 118.075(2)°$, $V = 2140.01(13) Å^3$, $Z = 4$, 3523 unique data ($\theta_{max} = 25.0°$), 2883 data with $I > 2\sigma(I)$, $R = 0.045$ (observed data), $wR^2 = 0.111$ (all data). CCDC deposition no. = 607195. Programs used: SHELXS-97, SHELXL-97 and ORTEP.

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