Synthesis and Molecular Structure of a Superbulky Tertiary Phosphine: Bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12)]phenylphosphine

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Bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12)]phenylphosphine (**2**) was obtained in 91% yield from phenyldichlorophosphine and two equivalents of 1-lithium-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) in ether and characterized by spectroscopy (^{31}P, ^{11}B, ^{1}H, ^{13}C NMR; IR) and by X-ray structure determination.

Introduction

Information about steric hindrance caused by substituents at phosphorus atoms is of great importance in understanding the chemical reactivity of organophosphorus compounds and their ability to act as ligands for transition metals [1]. Among dicarba-*closo*-dodecaborane(12) derivatives, 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12) has been regarded as too bulky for the preparation of the corresponding disubstituted tertiary phosphines. The reason for this conclusion was the report of an unsuccessful attempt to prepare bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12)]phenylphosphine (**2**) by reacting 1-lithium-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) with 1-chlorophenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**1**) (1:1) or dichlorophenylphosphine (2:1) [2].

We now report the successful high-yield synthesis of **2** and its characterization by ^{31}P, ^{11}B, ^{13}C and ^{1}H NMR spectroscopy and X-ray structure determination.

Results and Discussion

In the course of our investigations of dicarba-*closo*-dodecaborane(12)-containing organophosphorus compounds [3], we prepared 1-chlorophenylphosphino-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (**1**) according to the literature procedure by reaction of dichlorophenylphosphine with one equivalent of 1-lithium-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) [2]. However, besides **1** we also obtained bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12)]phenylphosphine (**2**) in 18% yield. When the reaction was carried out with two equivalents of 1-lithium-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) in diethylether **2** was obtained in 91% yield (eq. (1)).

*NMR spectra of bis[2-phenyl-1,2-dicarba-closo-dodecaboran-1-yl(12)]phenylphosphine (**2**)*

The ^{31}P NMR spectrum of **2** exhibits a singlet at 29.2 ppm. In the ^{11}B{^{1}H} NMR spectrum, three broad signals are observed for the 2-phenyl-1,2-dicarba-*closo*-dodecaboran-1-yl(12) clusters at 2.0, -3.1 and -8.0 ppm. On proton coupling, only the signals at 2.0 and -3.1 ppm split into doublets ($^{1}J_{B-H}$ = 150 and 138 Hz), while the other signal is too broad to allow observation of B-H coupling. In the ^{1}H NMR spectrum, the signals for the two phenyl groups overlap in the usual range for aromatic protons at 7.0 to 6.6 ppm.

The ^{13}C{^{1}H} NMR signals of the phenyl groups also overlap with each other and with those of the solvent (C_6D_6) and were observed at 138.8, 138.2, 137.5, 133.5, 132.9, 131.5, and 131.2 ppm. The signals of the carbon atoms of the *o*-carbaborane cluster appear as two doublets at 91.5 ppm ($^{3}J_{C-P}$ = 29 Hz) and 84.0 ppm ($^{1}J_{C-P}$ = 79 Hz).

*X-ray structure analysis of bis[2-phenyl-1,2-dicarba-closo-dodecaboran-1-yl(12)]phenylphosphine (**2**)*

Crystals of **2** were obtained by recrystallization from hexane at 0°C. **2** crystallizes in the ortho-

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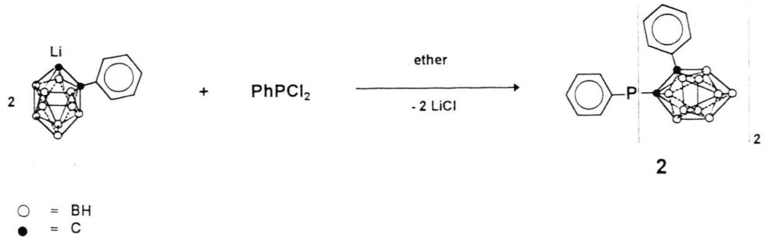

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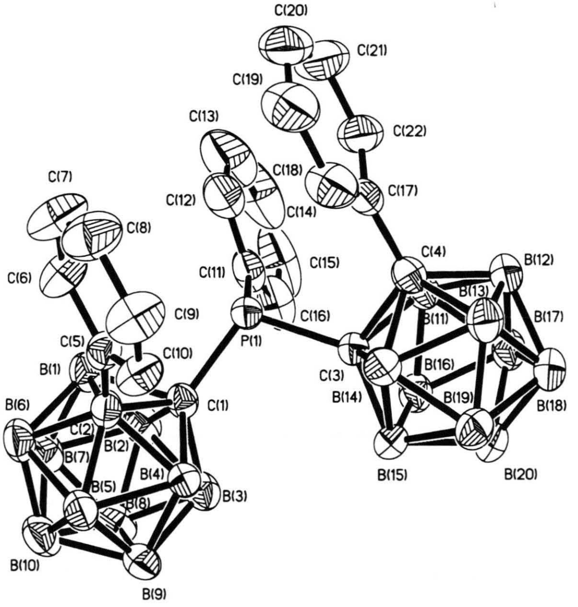

Fig. 1. Molecular structure of **2** showing the atom numbering scheme employed (ORTEP plot, 50 % probability, SHELXTL PLUS; XP [6]). H atoms omitted for clarity. Selected bond distances [Å] and angles [°]: P1-C1 1.867(2), P1-C3 1.896(2), P1-C11 1.825(3), C1-C2 1.780(3), C3-C4 1.761(3), C2-C5 1.505(3), C4-C17 1.506(3), C1-B1 1.744(4), C1-B2 1.715(4), C1-B3 1.708(4), C1-B4 1.724(3), C2-B1 1.733(4), C2-B4 1.731(3), C2-B5 1.694(4), C2-B6 1.706(4), C3-B11 1.744(4), C3-B14 1.733(3), C3-B15 1.713(4), C3-B16 1.726(4), C4-B11 1.740(4), C4-B12 1.708(4), C4-B13 1.708(4), C4-B14 1.729(4); C11-P1-C1 103.99(11), C11-P1-C3 103.53(11), C1-P1-C3 107.67(10), C4-C3-P1 107.50(14), C2-C1-P1 110.37(14), C17-C4-C3 119.1(2), C5-C2-C1 120.4(2).

rhombic space group $P2_12_12_1$ with four formula units in the unit cell.

The P atom in **2** is coordinated in a slightly distorted pseudo-tetrahedral fashion by two 2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) cluster fragments and the phenyl group (Fig. 1) with C-P-C angles between 103.5 and 107.7° (Table I). The B-B, C-C (Ph groups) and $C_{(cluster)}$-$C_{(Ph)}$ distances lie in the range observed for other known phosphorus compounds containing 1-substituted 1,2-dicarba-*closo*-dodecaboran-2-yl(12) substituents (Fig. 2, **3-6**) [4].

In **2**, the $C_{(cluster)}$-$C_{(cluster)}$ bond distance of one carbaboranyl substituent and the $C_{(cluster)}$-P bond distance in the other cluster unit lie at the higher end of the range of known C-C and C-P bond distances in comparable compounds (Table I). The bond angles at the P atom indicate the steric demand of the carbaboranyl groups [$C_{(cluster)}$-P-$C_{(cluster)}$ 107.67(10)°, $C_{(cluster)}$-P-$C_{(Ph)}$ 103.99(11), 103.53(11)°], which is, however, not as large as was previously assumed [2].

We are presently investigating the potential of **2** as a ligand in transition metal chemistry.

Experimental

All experiments were carried out under purified dry argon. Solvents were dried and freshly distilled under argon. NMR spectra (in C_6D_6): Avance DRX 400 (Bruker), standards: ^{1}H NMR (400 MHz): trace amounts of protonated solvent, C_6D_6, ^{13}C NMR (100.6 MHz): internal solvent, ^{31}P NMR (162 MHz): external 85% H_3PO_4, ^{11}B NMR: external $BF_3 \cdot Et_2O$. The IR spectrum was recorded as KBr mull on a Perkin-Elmer FT-IR spectrometer System 2000 in the range 350-4000 cm^{-1}. The melting point was determined in a sealed capillary and is uncorrected.

Preparation of bis[2-phenyl-1,2-dicarba-closo-dodecaboran-1-yl(12)]phenylphosphine (**2**)

At 0°C, a solution of 0.45 g (2.5 mmol) of $PhPCl_2$ in 25 cm^3 of diethylether was added to a solution of 1-lithium-2-phenyl-1,2-dicarba-*closo*-dodecaborane(12) (obtained from 1.11 g (5.0 mmol) of 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12) in 25 cm^3 of ether and BuLi (1.6 M solution in hexane, 5.5 mmol)). The solution was kept at 0°C for 1 h and then for 12 h at 20°C. The solvent was removed, the remaining solid dissolved in hexane/toluene and the solution filtered. Airstable colourless crystals of **2**

Table I. Selected bond distances [Å] and angles [°] in compounds **2**-**6**.

	2	**3**	**4**	**5**	**6**
	This work	[4a]	[4b]	[4c]	[4d]
P-$C_{(cluster)}$	1.896(2), 1.867(2)	1.879(3)	1.883(5), 1.869(5)	1.854(4), 1.850(4)	1.860(3)
$C_{(cluster)}$-$C_{(cluster)}$	1.780(3), 1.761(3)	1.769(4)	1.755(6), 1.732(6)	1.703(6), 1.722(5)	1.654(4), 1.656(4)
$C_{(cluster)}$-B	1.694(4) to 1.744(4)	1.710(5) to 1.731(5)	1.698(7) to 1.739(7)	1.692 to 1.736	1.716(4) to 1.736(5)
$C_{(cluster)}$-P-$C_{(cluster)}$	107.67(10)			114.2(2)	102.8(1)
$C_{(cluster)}$-P-$C_{(Ph/i-Pr)}$	103.99(11), 103.53(11)	104.4(2), 101.5(2)	102.6(2) to 104.4(2)		101.3(1), 101.5(1)
$C_{(Ph/i-Pr)}$-P-$C_{(Ph/i-Pr)}$		104.0(2)	105.2(2), 106.5(2)		

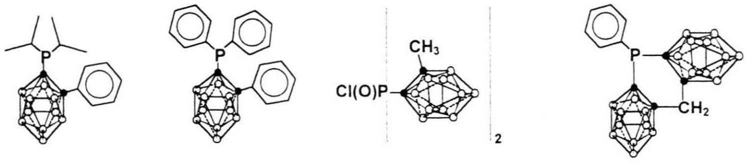

Fig. 2. Other known phosphorus compounds containing 1-substituted 1,2-dicarba-*closo*-dodecaboran-2-yl(12) substituents [4].

were obtained from hexane/toluene at 0°C; recrystallization from hexane gave crystals suitable for X-ray analysis. Yield 1.26 g (91%), m.p. 273-277°C.

Analysis for $C_{22}H_{35}B_{20}P$ (546.67)
Calcd C 48.35 H 6.41 %,
Found C 49.02 H 6.38 %.

IR (selected, cm^{-1}): 3062, 2960, 2928, 2870 (νC-H); 2654, 2578 (νB-H); 1956, 1889, 1800 (νPh).

Data collection and structure refinement of **2**

Experimental data (a total of 29167 reflections) were collected at T = 220 ± 2 K on a Siemens CCD (SMART) diffractometer between 3.4 and 56° 2Θ with monochromated Mo-Kα (λ = 0.71073 Å) radiation. This includes a total of 7096 unique reflections [R_{int} = 0.0600]. All observed reflections (2Θ range: 3.4-56°) were used for determination of the unit cell parameters. The studied specimen was a colourless single crystal of dimensions 0.4 × 0.3 × 0.2 mm. Crystal data for **2**: $C_{22}H_{35}B_{20}P$, M = 546.67, space group $P2_12_12_1$ (No. 19), orthorhombic, a = 11.521(2), b = 15.625(3), c = 17.587(4) Å, V = 3166.0(11) Å^3, at T = 220(2) K, Z = 4, D_c = 1.147 Mg m^{-3}, $F(000)$ = 1128, μ(Mo-Kα) = 0.103 mm^{-1}, absorption correction with SADABS [5].

Positions of P, C, and B atoms were located by using direct methods (SHELXTL PLUS) [6]. Subsequent least-squares refinement and difference electron density map calculations revealed positions of all H atoms. Final full-matrix least-squares refinement of 7095 parameters with a unit weighting scheme (P, C, and B atoms with anisotropic approximation, H atoms in B-H and Ph-H groups with isotropic approximation) converged to $R1$ = 0.0478, $wR2$ = 0.0998 (for reflections with $I > 2\sigma(I)$), $R1$ = 0.0865, $wR2$ = 0.1209 (all data). Further details of the X-ray structure analysis (thermal parameters, H atom coordinates, structure factors) have been deposited with the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany. This material may be requested by quoting the deposition number CSD 380170.

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