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The *tert*-butylaminomethyl(mesityl)phosphinic acid ester and formation of its zinc dichloride complex: syntheses and characterization

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Abstract: The syntheses and structures of *tert*-butylaminomethyl(mesityl)phosphinic acid ethyl ester **2** and its zinc dichloride complex **3** are reported. In the solid state, both compounds are dimeric via hydrogen bridges. In the complex **3**, the phosphinic acid ester **2** coordinates the zinc dichloride diastereoselectively.

Keywords: chelate ligand; diastereoselectivity; phosphinic acid ester; phosphorus; zinc.

Introduction

Diorganophosphinic acids R_2PO_2H (R =alkyl, aryl) are a fundamental class of phosphorus compounds. Together with their esters R_2PO_2R' and the corresponding anions $R_2PO_2^-$ they are rather popular phosphorus-based ligands in both main group and transition metal chemistry. The structural diversity of their metal complexes with a total number of more than 500 solid state structures has recently been reviewed (Carson et al., 2017). To the best of our knowledge, unsymmetrically substituted alkyl(aryl)-phosphinic acids and their corresponding derivatives (Korpiun et al., 1968; Onyido et al., 2005) as well as functionally substituted compounds have also received increased interest (Maier, 1992; Kaboudin et al., 2006; Demkowicz et al., 2016). Metal complexes with ligands containing phosphinic acid moieties have been reported as well (Lukeš et al., 2001; Cao et al., 2011; Ševčík et al., 2014). Herein, we present an organoaminomethyl(aryl)-phosphinic acid ester and demonstrate its behavior as a chelate ligand towards zinc dichloride.

Results and discussion

The *tert*-butylaminomethyl(mesityl)phosphinic acid ethyl ester *tert*-Bu(H)NCH₂(2,4,6-Me₃C₆H₂)P(O)OEt, **2**, was obtained as its racemate through the amination reaction of compound **1** with an excess of *tert*-butylamine according to Equation 1.

The reaction was performed under elevated pressure at 65°C in a teflon-sealed tube. In the course of the reaction, the precipitated white solid was identified by means of the melting point as *tert*-butylammonium iodide (220°C, lit. 218–220°C (Herrschaft and Hartl, 1989)). After a reaction time of 96 h, the conversion was complete and the reaction mixture was purified by performing acid base extraction. Compound **2** was obtained as a white solid material with a melting point of 67°C. A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of its solution in CDCl_3 showed a singlet resonance at δ 44.6 ppm that was low field shifted as compared with the signal of compound **1** [δ 38.0 ppm, CDCl_3 (Lutter and Jurkschat, 2018)]. A ^1H NMR spectrum revealed the characteristic singlet resonance of the *tert*-butyl protons at δ 0.89 ppm. An electrospray ionization (ESI) mass spectrum showed three mass clusters which were assigned to $[2 + \text{Na}]^+$ ($m/z = 617.3$), $[2 + \text{Na}]^+$ ($m/z = 320.1$) and $[2 + \text{H}]^+$ ($m/z = 298.1$). From its solution in acetone, colorless block-shaped crystals of compound **2** were obtained; the compound crystallized in the monoclinic space group $P2_1/n$ with four molecules in the asymmetric unit (Figure 1). Hydrogen bond distances and angles are given in the Figure caption. Crystallographic data are given in Table 1.

There exists a hydrogen bond ($\text{N1-H1} \cdots \text{O1}$ 3.001(3) Å, 170(3)°) between the PO and NH functional groups connecting two molecules. In the graph set analysis according to Etter and Bernstein (Bernstein et al., 1990, 1995a,b; Etter, 1990, 1991; Etter et al., 1990; Bernstein, 1991) the unitary elemental graph set is $\text{N}_1 = \text{R}_2^2(10)$, which is a

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Figure 1: The displacement ellipsoid (30% probability level) plot and the numbering scheme of the dimeric structure of compound **2** in the crystal.

C-H hydrogen atoms are omitted. Hydrogen bond distance [Å] and angle [°]: N(1)-H(1) $\cdots$ O(1A) 3.001(3), 170(3). Symmetry code: (A) 1-x, 1-y, 1-z.

ten-membered ring motif. In order to investigate the properties of compound **2** as a chelating ligand, the latter was reacted with zinc chloride in acetone according to Equation 2.

After the slow evaporation of the solvent, some colorless plate-shaped crystals of compound **3** were obtained. The washed (*iso*-hexane) and dried crystalline material of compound **3** was used for the acquisition of all analytical data.

A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (CDCl_3) showed one broad singlet resonance at δ 54.2 ppm ($\nu_{1/2} = 78.6$ Hz), which is low field shifted (9.6 ppm) as compared with the signal of compound **2**. The line width of the signal likely

Table 1: Crystallographic data for compounds **2** and **3**.

	2	3
Empirical formula	$\text{C}_{16}\text{H}_{28}\text{NO}_2\text{P}$	$\text{C}_{16}\text{H}_{28}\text{Cl}_2\text{NO}_2\text{PZn}$
Formula mass [$\text{g} \cdot \text{mol}^{-1}$]	297.36	433.63
T [K]	173(2)	173(2)
λ [Å]	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	10.6794 (12)	11.9168 (10)
b [Å]	11.9199 (13)	17.6511 (14)
c [Å]	14.0925 (16)	19.9614 (18)
α [°]	90	90
β [°]	105.742 (12)	102.971 (9)
γ [°]	90	90
V [Å ³]	1726.7 (3)	4091.6 (6)
Z	4	8
$\rho_{\text{calcd.}}$ [$\text{g} \cdot \text{cm}^{-3}$]	1.144	1.408
μ [mm^{-1}]	0.161	4.866
F(000)	648	1808
Crystal size [mm]	0.220 $\cdot$ 0.160 $\cdot$ 0.130	0.160 $\cdot$ 0.120 $\cdot$ 0.030
θ range [°]	2.617–27.499	3.381–68.981
Index ranges	$-13 \leq h \leq 13$ $-15 \leq k \leq 15$ $-17 \leq l \leq 18$	$-14 \leq h \leq 13$ $-20 \leq k \leq 21$ $-19 \leq l \leq 24$
No. of reflections collected	14583	29972
No. of independent reflections/ R_{int}	3888/0.0769	7611/0.0637
Completeness of θ_{max} [%]	99.9	100.0
Data/Restraints/parameters	3888/1/192	7611/2/437
GoF(F^2)	0.927	1.551
$R_1(F)$ [$I > 2\sigma(I)$]	0.0614	0.0635
$wR_2(F^2)$ (all data)	0.1615	0.1953
Largest difference peak/hole [$\text{e} \cdot \text{Å}^{-3}$]	0.253/–0.362	1.561/–1.090

Figure 2: The displacement ellipsoid (30% probability level) plot and the numbering scheme of the dimeric structure of compound **3** in the crystal.

The C-H hydrogen atoms are omitted. Selected interatomic distances [Å]: Zn(1)-Cl(1) 2.2417(12), Zn(1)-Cl(2) 2.2035(13), Zn(1)-O(1) 2.002(3), Zn(1)-N(1) 2.113(3), Zn(2)-Cl(3) 2.2346(12), Zn(2)-Cl(4) 2.2033(13), Zn(2)-O(3) 2.017(3), Zn(2)-N(2) 2.105(3). Selected interatomic angles [°]: Cl(1)-Zn(1)-Cl(2) 116.95(5), Cl(1)-Zn(1)-N(1) 107.64(11), Cl(1)-Zn(1)-O(1) 107.50(10), Cl(2)-Zn(1)-N(1) 121.71(11), Cl(2)-Zn(1)-O(1) 111.14(10), N(1)-Zn(1)-O(1) 87.44(13), Cl(3)-Zn(2)-Cl(4) 116.18(5), Cl(3)-Zn(2)-N(2) 110.34(11), Cl(3)-Zn(2)-O(3) 110.42(10), Cl(4)-Zn(2)-N(2) 119.88(11), Cl(4)-Zn(2)-O(3) 108.44(11), N(2)-Zn(2)-O(3) 87.66(14). Hydrogen bond distances [Å] and angles [°]: N(1)-H(1) $\cdots$ Cl3 3.502(4), 173(6); N(2)-H(2) $\cdots$ Cl1 3.470(4), 171(5).

indicates the kinetic lability of the complex **3** in solution and an equilibrium $2 + \text{ZnCl}_2 \rightleftharpoons 3$, which is on the onset of becoming slow on the NMR time scale. Alternatively, an epimerization induced by the rupture of either the P=O $\rightarrow$ Zn or N $\rightarrow$ Zn coordination could also account for the broadening of the ^{31}P NMR resonance. However, this was not investigated in further detail. A ^1H NMR spectrum showed an ABX pattern for the PCH_2N methylene protons at δ 3.13/3.39 ppm ($J_{\text{AB}} = 14.8$ Hz, $J_{\text{AX}} = 9.5$ Hz, $J_{\text{BX}} = 6.4$ Hz).

An ESI mass spectrum (positive mode) showed four mass peaks at $m/z = 320.17$, 298.19, 213.10, and 185.07, which are assigned to the cationic species $[2 + \text{Na}]^+$, $[2 + \text{H}]^+$, $[\text{MesPH}(\text{O})(\text{OEt}) + \text{H}]^+$, and $[\text{MesP}(\text{OH})_2 + \text{H}]^+$, respectively. The absence of the mass peak of the zinc complex **3** indicates that a positively charged zinc complex is not stable under the experimental ESI MS conditions employed.

From its solution in acetone, compound **3** precipitated as colorless plate-shaped crystals. The compound crystallized in the monoclinic space group $P2_1/c$ with eight molecules in the asymmetric unit (Figure 2). The hydrogen bond distances and angles are given in the figure caption. Crystallographic data are given in Table 1.

The Zn(1) and Zn(2) atoms are four-coordinated by Cl(1), Cl(2), O(1) and N(1), and Cl(3), Cl(4), O(3) and N(2), respectively, at distances of 2.2417(12), 2.2035(13), 2.002(3), and 2.113(3) Å, respectively, and 2.2346(12), 2.2033(13), 2.017(3) and 2.105(3) Å, respectively. The Cl(1) and Cl(3) atoms are involved in the hydrogen bonds (N1-H1 $\cdots$ Cl3 3.502(4), N2-H2 $\cdots$ Cl1 3.469(4) Å). Consequently, the Zn(1)-Cl(1) and Zn(2)-Cl(3) distances are slightly longer than the Zn(2)-Cl(2) and Zn(2)-Cl(4) distances. The zinc atom exhibits a distorted tetrahedral environment with angles

ranging between $121.71(11)^\circ$ (Cl2-Zn1-N1) and $87.44(13)^\circ$ (N1-Zn1-O1).

The graph set analysis of compound **3** gives two finite patterns on the unitary elemental level ($N_1 = \text{DD}$). The pattern on the binary elemental level is an eight-membered ring and can be described with $N_2(a, b) = R_2^2(8)$. Considering this eight-membered ring, the Cl(2) and Cl(4) atoms are *trans*, as are the five-membered Zn(1)-N(1)-C(10)-P(1)-O(1) and Zn(2)-N(2)-C(60)-P(2)-O(2) chelate rings.

Conclusion

When coordinated with the zinc dichloride, the nitrogen atom of *tert*-butylaminomethyl(mesityl)phosphinic acid ethyl ester **2** is a stereogenic center, in addition to the one at the phosphorus atom. This means that two diastereomers are possible for the resulting zinc dichloride complex **3**. However, apparently, the complexation proceeds diastereoselectively. Only one diastereomer was observed in the solid state. Although this has been established only for the single crystal actually measured, it is rather likely to hold also for the bulk material. The diastereomer with the *tert*-butyl substituents in *cis*-position should be less favored. This phenomenon needs to be evaluated by further experiments as well as DFT calculations. Nevertheless, the results demonstrate, to some extent, the high potential the title compound and related derivatives hold for such stereoselective reactions. In addition, the N-H function in both the ester **2** and the zinc dichloride complex **3** is involved in the hydrogen bridges and creates supramolecular structures.

Experimental

Crystallography

Intensity data for compound **2** were collected on an XcaliburS CCD diffractometer (Oxford Diffraction, Oxford, England) using Mo-K α radiation at 173(1) K with an Oxford Cryostream. The intensity data for compound **3** were collected on an APEX-II CCD diffractometer (Bruker Corporation, Billerica, MA, USA) using Cu-K α radiation at 100 K.

The structures were solved with direct methods using SHELXS-97 (compound **2**) or SHELXS-2014/7 (compound **3**) (Sheldrick, 2008, 2015) and refinements were carried out against F^2 by using SHELXL-2014/7 (Sheldrick, 2008, 2015). The C-H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. The NH protons of all compounds were located in the difference Fourier map and refined freely; the N-H distances were restrained to a fix value.

CCDC-1831583 (**2**) and CCDC-1831584 (**3**) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For the decimal rounding of numerical parameters and σ values, the rules of IUCr have been employed (Clegg, 2003). All Figures were generated using ORTEP III (Farrugia, 1997; Farrugia, 2012) visualization software. The graph sets were calculated using the calculation routine of Mercury (Macrae et al., 2006, 2008).

General

Solvents, including NMR solvents, were purified by distillation from the appropriate drying agents under argon and stored over molecular sieves. The NMR spectra were recorded at room temperature on a Bruker AV DPX 300. NMR chemical shifts were given in ppm and were referenced to Me $_4$ Si (^1H , ^{13}C) (using residual solvent signal: CDCl $_3$, ^1H 7.27 ppm, ^{13}C 77.0 ppm) and H $_3$ PO $_4$ (85%, ^{31}P). Elemental analyses were performed on a LECO-CHNS-932 analyzer (LECO Corporation, St. Joseph, MI, USA). The samples were weighted at air. The uncorrected melting points were measured on a Büchi M-560 (Büchi Labortechnik GmbH, Essen, Germany). The electrospray mass spectra were recorded with a Thermoquest-Finnigan instrument (Scientific Instrument Services, Ringoes, NJ, USA). The concentration was 0.1 mg/mL with a flow rate of 10 $\mu\text{L}/\text{min}$. The experimental isotopic pattern matched the theoretical ones. IR spectra (cm^{-1}) were measured on a Perkin Elmer Spectrum Two (ATR, PerkinElmer, Inc., Waltham, MA, USA). The synthesis of compound **1** has already been published. (Lutter and Jurkschat, 2018). The *tert*-butyl amine (98%) was purchased (abcr GmbH, Karlsruhe, Germany). The latter was dried (CaH $_2$) and distilled prior before use. The zinc chloride (97%) was purchased (abcr GmbH, Karlsruhe, Germany) and used without further purification.

N-(*tert*-butyl)aminomethyl(mesityl)phosphinic acid ethylester (**2**)

A stirring solution of iodomethylmesitylphosphinic acid ethylester (**1**) (3.520 g, 10.0 mmol) in freshly distilled *tert*-butyl amine (10.5 mL,

100.0 mmol) was heated (65°C) for 96 h under pressure. The resulting solid was filtered, washed with cold iso-hexane, dried and identified as *tert*-butylammonium iodide by means of the melting point (220°C). The volatiles of the filtrate were removed under reduced pressure. The residue was dissolved in dichloromethane (10 mL), acidified with diluted hydrochloric acid (10 mL, 1 M), and extracted with water (3 $\times$ 10 mL). The combined aqueous phases were treated with a diluted sodium hydroxide solution (1 M) to pH >10 and extracted with dichloromethane (3 $\times$ 10 mL). After drying the combined organic phases over magnesium sulphate and performing filtration, the volatiles of the resulting solution were removed under reduced pressure. Compound **2** (1.930 g, 6.5 mmol, 65%) was obtained as a colorless block-shaped crystalline solid with a melting point of 67°C.

^1H NMR: (300.13 MHz, CDCl $_3$, 298 K, 16 scans): δ 6.76 (d, $^4J(^1\text{H}-^{31}\text{P})=3.7$ Hz, 2H, C $_m\text{H}$), 4.15–4.02 (complex pattern, 1H, CH $_2$ CH $_3$), 3.89–3.76 (complex pattern, 1H, CH $_2$ CH $_3$), 3.02–2.85 (complex pattern, 2H, PCH $_2$ N), 2.51 (s, 6H, C $_o$ CH $_3$), 2.14 (s, 3H, C $_p$ CH $_3$), 1.20 (t, $^3J(^1\text{H}-^1\text{H})=7.1$ Hz, 3H, CH $_2$ CH $_3$), 0.89 (s, 9H, C(CH $_3$) $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR: (75.48 MHz, CDCl $_3$, 298 K, 640 scans): δ 143.1 (d, $^2J(^{13}\text{C}-^{31}\text{P})=11.2$ Hz, C $_o$), 141.2 (d, $^4J(^{13}\text{C}-^{31}\text{P})=2.8$ Hz, C $_p$), 130.3 (d, $^3J(^{13}\text{C}-^{31}\text{P})=12.7$ Hz, C $_m$), 123.6 (d, $^1J(^{13}\text{C}-^{31}\text{P})=120.4$ Hz, C $_i$), 60.0 (d, $^3J(^{13}\text{C}-^{31}\text{P})=6.5$ Hz, CH $_2$ CH $_3$), 50.3 (d, $^3J(^{13}\text{C}-^{31}\text{P})=14.6$ Hz, C(CH $_3$) $_3$), 43.0 (d, $^1J(^{13}\text{C}-^{31}\text{P})=110.1$ Hz, PCH $_2$ N), 28.1 (s, C(CH $_3$) $_3$), 22.9 (d, $^3J(^{13}\text{C}-^{31}\text{P})=2.3$ Hz, *ortho*-C $_o$ CH $_3$), 20.6 (d, $^5J(^{13}\text{C}-^{31}\text{P})=0.9$ Hz, *para*-C $_p$ CH $_3$), 16.1 (d, $^3J(^{13}\text{C}-^{31}\text{P})=6.4$ Hz, CH $_2$ CH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: (121.50 MHz, CDCl $_3$, 298 K, 128 scans): δ = 44.6 (s, $^1J(^{31}\text{P}-^{13}\text{C})=120.3$ Hz, $^1J(^{31}\text{P}-^{13}\text{C})=110.1$ Hz). Elemental analysis: calculated (found) for C $_{16}$ H $_{28}$ NO $_2$ P 64.6 (64.8)% C, 9.5 (9.3)% H, 4.7 (4.7)% N. ESI MS: (acetonitrile, m/z , positive mode): 617.3 [2 + Na] $^+$, 320.1 [2 + Na] $^+$, 298.1 [2 + H] $^+$. IR: (cm^{-1}): $\nu_{\text{N-H}}$ 3288, $\nu_{\text{P=O}}$ 1212.

N-(*tert*-butyl)aminomethyl(mesityl)phosphinic acid ethyl ester zinc chloride complex (**3**)

To a solution of the secondary amine **2** (0.120 g, 0.4 mmol) in acetone (5 mL) zinc chloride (0.550 g, 0.4 mmol) was added. After the slow evaporation of the solvent, the complex **3** was obtained as a colorless plate-shaped crystalline solid (0.164 g, 0.38 mmol, 95%) with a melting point of 180°C (decomposition).

^1H NMR: (300.13 MHz, CDCl $_3$, 297 K, 16 scans): δ 6.97 (d, $^4J(^1\text{H}-^{31}\text{P})=4.5$ Hz, 2H, C $_m\text{H}$), 4.34–3.97 (complex pattern, 2H, CH $_2$ CH $_3$), 3.39 (ABX pattern, $^3J(^1\text{H}-^1\text{H})=14.8$ Hz, $^3J(^1\text{H}-^{31}\text{P})=9.5$ Hz, 1H, PCH $_2$ N), 3.13 (ABX pattern, $^3J(^1\text{H}-^1\text{H})=14.8$ Hz, $^3J(^1\text{H}-^{31}\text{P})=6.4$ Hz, 1H, PCH $_2$ N), 2.59 (d, $^4J(^1\text{H}-^{31}\text{P})=1.2$ Hz, 6H, C $_o$ CH $_3$), 2.32 (s, 3H, C $_p$ CH $_3$), 1.38 (s, 9H, C(CH $_3$) $_3$), 1.36 (t, $^3J(^1\text{H}-^1\text{H})=7.1$ Hz, 3H, CH $_2$ CH $_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR: (75.47 MHz, CDCl $_3$, 297 K, 640 scans): δ 144.7 (d, $^4J(^{13}\text{C}-^{31}\text{P})=2.8$ Hz, C $_p$), 144.1 (d, $^2J(^{13}\text{C}-^{31}\text{P})=12.7$ Hz, C $_o$), 131.5 (d, $^3J(^{13}\text{C}-^{31}\text{P})=14.1$ Hz, C $_m$), 118.5 (d, $^1J(^{13}\text{C}-^{31}\text{P})=131.4$ Hz, C $_i$), 63.6 (d, $^2J(^{13}\text{C}-^{31}\text{P})=6.7$ Hz, CH $_2$ CH $_3$), 56.5 (d, $^3J(^{13}\text{C}-^{31}\text{P})=9.9$ Hz, C(CH $_3$) $_3$), 42.0 (d, $^1J(^{13}\text{C}-^{31}\text{P})=102.2$ Hz, PCH $_2$ N), 27.9 (s, C(CH $_3$) $_3$), 23.3 (d, $^3J(^{13}\text{C}-^{31}\text{P})=3.0$ Hz, C $_o$ CH $_3$), 21.2 (d, $^5J(^{13}\text{C}-^{31}\text{P})=0.8$ Hz, C $_p$ CH $_3$), 16.1 (d, $^3J(^{13}\text{C}-^{31}\text{P})=6.7$ Hz, CH $_2$ CH $_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: (121.50 MHz, CDCl $_3$, 297 K, 128 scans): δ = 54.2 (s, $\nu_{1/2}$ = 78.6 Hz). Elemental analysis: calculated (material from 1st synthesis found, material from 2nd synthesis found) for C $_{16}$ H $_{28}$ Cl $_2$ NO $_2$ PZn 44.3 (43.2, 43.5)% C, 6.5 (6.5, 6.5)% H, 3.2 (3.1, 3.1)% N. ESI MS: (material from 2nd synthesis, acetonitrile + water 1:1 + 0.1% trifluoro acetic acid, m/z , positive mode): 320.17 [2 + Na] $^+$, 298.19 [2 + H] $^+$, 213.10 [MesPH(O)(OEt) + H] $^+$, 185.07 [MesP(OH) $_2$ + H] $^+$. ESI MS: (material from 2nd synthesis, acetonitrile, m/z , positive mode): 595.38 [2 + H] $^+$, 298.19 [2 + H] $^+$. IR: (cm^{-1}): $\nu_{\text{N-H}}$ 3197, $\nu_{\text{P=O}}$ 1150.

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