Synthesis and structural characterization of zinc complexes of the imido–amido phosphate anions $OP[(NHR)_{3-x}(NR)]^{x-}$ (R = Me, *t*-Bu; *x* = 1–3) and $EP[(NH-t-Bu)_2(N-t-Bu)]^-$ (E = S, NSiMe₃)

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Abstract: The reaction of OP(NH-*t*-Bu)₃ with 1 equiv. of ZnMe₂ generates the dimeric eight-membered ring {MeZn[(μ -NH-*t*-Bu)(μ -N-*t*-Bu)P(NH-*t*-Bu)(μ -O)]}₂ (**5**) and the cubane {[MeZn]₃[OP(N-*t*-Bu)₃][OP(NH-*t*-Bu)₃]} (**6**), which contains the first known trisimidophosphate trianion. A related complex {Zn[ZnMe]₂[OP(N-*t*-Bu)(NH-*t*-Bu)₂]} (**6**), which contains the first known trisimidophosphate trianion. A related complex {Zn[ZnMe]₂[OP(N-*t*-Bu)(NH-*t*-Bu)₂]](OP(N-*t*-Bu)₃]}(**7**) is obtained by the reaction of OP(NH-*t*-Bu)₃ with ZnMe₂ in a 2:3 molar ratio. The treatment of OP(NHMe)₃ with 1 equiv. of ZnMe₂ produces the oxide-templated cluster {Zn₄(μ ₄-O)[OP(NMe)(NHMe)₂]₄[OP(NMe)₂-(NHMe)]}₂ (**8**). Each half of this centrosymmetric dimer contains a tetrahedral arrangement of four 4-coordinate Zn²⁺ ions surrounding the central μ ₄-O²⁻ anion. The reaction of SP(NH-*t*-Bu)₃ with ZnMe₂ in a 1:1 molar ratio generates the dimer {MeZn(μ -S)(μ -N-*t*-Bu)P(NH-*t*-Bu)₂]₂ (**10**), which has a ladder-type structure. When a 2:1 molar ratio of the same reagents is employed, the bis(*N*,*S*)-chelated complex {Zn[(μ -S)(μ -N-*t*-Bu)P(NH-*t*-Bu)₂]₂ (**11**) is obtained. The monomeric *N*,*N*'-chelated complex {MeZn[(μ -N-*t*-Bu)(μ -NSiMe₃)P(NH-*t*-Bu)₂]} (**12**) results from the reaction of Me₃SiNP(NH-*t*-Bu)₃ with 1 equiv. of dimethylzinc. All new compounds have been characterized by multinuclear (¹H, ¹³C, and ³¹P) NMR spectroscopy and, in the case of **5**, **6**, **7**, **8**, and **10**, by X-ray structural determinations.

Key words: zinc, phosphate, imido ligands, sulfur.

Résumé : La réaction du OP(NH-*t*-Bu)₃ avec un équivalent de ZnMe₂ conduit à la formation du cycle dimère à huit chaînons {MeZn[(μ -NH-*t*-Bu)(μ -N*t*-Bu)P(NH-*t*-Bu)(μ -O]]₂ (**5**) et du cubane {[MeZn]₃[OP(N-*t*-Bu)₃][OP(NH-*t*-Bu)₃]} (**6**) qui contient le premier trisimidophosphate connu. Le complexe apparenté {Zn[ZnMe]₂[OP(N-*t*-Bu)(NH-*t*-Bu)₃]} (**7**) est obtenu lors de la réaction du OP(NH-*t*-Bu)₃ avec du ZnMe₂ dans un rapport de 2 : 3. Le traitement du OP(NHMe)₃ avec un équivalent de ZnMe₂ conduit à la formation de l'agrégat avec gabarit d'oxyde {Zn₄(μ ₄-O)[OP(NMe)(NMe)₂]₄[OP(NMe)₂(NHMe)]₂ (**8**). Chacune des moitiés de ce dimère centrosymétrique comprend un arrangement tétraédrique de quatre ions Zn²⁺ tétracoordinés qui entourent l'anion μ ₄-O²⁻ central. La réaction du SP(NH-*t*-Bu)₃ avec du ZnMe₂ dans un rapport molaire de 1 : 1 génère la formation du dimère {MeZn(μ -S)(μ -N-*t*-Bu)P(NH-*t*-Bu)₂]₂ (**10**) dont la structure est en échelle. Quand on utilize un rapport 2 : 1 des même réactifs, on obtient le complexe bis-*N*,*S*-chélaté {Zn[(μ -S)(μ -N-*t*-Bu)P(μ -NH-*t*-Bu)₂]₂ (**11**). Le complexe *N*,*N'*-chélaté monomère {MeZn[(μ -N-*t*-Bu)₂]} (**12**) résulte de la réaction du Me₃SiNP(NH-*t*-Bu)₃ avec un équivalent de diméthylzinc. Tous les nouveaux composés ont été caractérisés par spectroscopie RMN (¹H, ¹³C et ³¹P) et dans les cas des composés **5**, **6**, **7**, **8** et **10**, par diffraction des rayons X.

Mots clés : zinc, phosphate, ligands imido, soufre.

Introduction

The preparation and structural characterization of imido analogues of common phosphorus oxoanions is an active area of main group chemistry (1, 2). The imido group $[NH]^{2-}$ is formally isoelectronic with the oxo $[O]^{2-}$ substituent;² partial or complete replacement of the oxygen atoms in an oxoanion such as orthophosphate $[PO_4]^{3-}$ by NH ligands generates a series of polyimido anions that are isoelectronic with phosphate. The introduction of an alkyl or aryl substituent on nitrogen is expected to result in polyimido anions whose metal complexes will exhibit significantly different structures and chemical properties compared with those of $[PE_4]^{3-}$ (E = O, NH). In addition, one or more of the oxo substituents in a polyimido phosphate can be replaced by a heavier chalcogen, such as sulfur, to create

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²The original definition of "isoelectronic" (isosteric) compounds restricts the term to species having the *same number of atoms* and the same number of electrons (I. Langmuir. J. Am. Chem. Soc. **41**, 1543 (1919)). Thus, according to this definition, N^{3-} is isoelectronic with O^{2-} . However, nitrides are compositionally different to oxides as a result of the different charges on the anions.

ligands with different coordinating properties as a result of the presence of both hard (N) and soft (S) binding sites.

In recent years, we have thoroughly investigated the reactivities of the triamidophosphates OP(NH-*t*-Bu)₃ (**1a**) (3, 4), SP(NHR)₃ (**2**, R = alkyl, aryl) (4, 5), and Me₃SiNP(NH-*t*-Bu)₃ (**3**) (3, 6) toward alkyllithium reagents. The mono- and di-lithium salts {Li[(μ -N-*t*-Bu)(μ -O)P(NH-*t*-Bu)₂]}₃.THF (**4**) and the double cubane {Li₂[OP(NH-*t*-Bu)(N-*t*-Bu)₂]}₂.4THF, isoelectronic with [H₂PO₄]⁻ and [HPO₄]²⁻, respectively, are readily obtained by treatment of **1a** with *n*-BuLi. However, complete deprotonation of **1a** to give the trianion [OP(N-*t*-Bu)₃]³⁻ could not be achieved (3, 4). The mono- and dianions [OP(N-*t*-Bu)_{*x*}(NH-*t*-Bu)_{3-*x*}]^{*x*-} (*x* = 1 or 2) are also produced from the reactions of **1a** with AlMe₃ or LiAlH₄ (7).

Similar reactivity was observed for the thiophosphates SP(NHR)₃ (**2a** (R = *t*-Bu), **2b** (R = *i*-Pr)) (4, 5). The monoand di-lithium salts of **2b** ({Li[(μ -N-*i*-Pr)(μ -S)P(NH-*i*-Pr)₂]}₂·2THF) and {[Li(TMEDA)]₂[SP(NH-*i*-Pr)(N-*i*-Pr)₂]}₂ have been isolated and characterized, as has a mixed monolithium–dilithium derivative of **2a**; attempts to generate [SP(N-*i*-Pr)₃]³⁻ resulted in sulfur extrusion. Trilithiation can be achieved, however, by replacement of the alkyl substituents by more electron-withdrawing *para*-tolyl groups; in this case, the trisimidothiophosphate {Li₃[SP(N*p*-tol)₃]} is readily obtained (4).

In sharp contrast to the somewhat limited reactivities of the chalcogen systems **1a** and **2** toward *n*-BuLi, both symmetrical and unsymmetrical tetraimidophosphates, $\{Li_3[P(NPh)_4]\}$ (8) and $\{Li_3[P(NR)_3(NSiMe_3)]\}$ (3) (R = *t*-Bu, Cy), respectively, are readily prepared by the reaction of the corresponding iminophosphorane (RNH)₃PNR with 3 equiv. of *n*-butyllithium.

Zinc phosphates are the second-largest family of the wellknown metal phosphate open-framework materials and have applications as both catalysts and molecular sieves. These materials are generally prepared under hydro- or solvothermal conditions; the three-dimensional structures of the products are highly dependent upon reaction conditions such as temperature and time, and the presence and shape of a templating agent (9–11). Consequently, it is of interest to explore the possibility of preparing a series of zinc imidophosphates. While the steric bulk of the imido groups is expected to hinder aggregation resulting in the formation of much smaller oligomers than the extended networks that are characteristic of metal-phosphate complexes (12), it remains to be seen whether these systems will exhibit similar dependencies on reaction conditions as do the zinc phosphates. In addition, it is germane to examine the modes of coordination of these multidentate ligands for comparison with their behaviour in the lithium derivatives (3–6). In an attempt to shed light upon these and other points, we have investigated the reactions of the triamidophosphates $OP(NHR)_3$ (R = Me, t-Bu), $SP(NH-t-Bu)_3$, and $Me_3SiNP(NH-t-Bu)_3$ towards dimethylzinc.

Experimental

Reagents and general procedures

All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Toluene, *n*-hexane, and diethyl ether were dried over Na/benzophenone, distilled, and stored over molecular sieves prior to use. Dimethylzinc (1.0 and 2.0 mol/L solutions in toluene) was used as received from Aldrich. Me₃SiNP(NH-*t*-Bu)₃ (3), OP(NHR)₃ (R = Me, *t*-Bu) (4), and SP(NH-*t*-Bu)₃ (5) were prepared according to the literature procedures.

Instrumentation

¹H, ⁷Li, ¹³C, and ³¹P NMR spectra were collected on a Bruker DRX-400 spectrometer with chemical shifts reported relative to Me₄Si in CDCl₃ (¹H and ¹³C), LiCl in D₂O (⁷Li), and 85% H₃PO₄ in D₂O (³¹P). All spectra were collected at 22 °C, with the exception of compound **10** (spectra recorded at -30 °C). Infrared spectra were recorded as Nujol mulls on KBr plates using a Nicolet Nexus 470 FT IR spectrometer in the range 4000–400 cm⁻¹. Mass spectra were recorded on a Bruker Esquire 3000 ESI ion trap mass spectrometer. Elemental analyses were provided by the Analytical Services Laboratory, Department of Chemistry, University of Calgary.

Preparation of $\{MeZn[(\mu-NH-t-Bu)(\mu-N-t-Bu)P(NH-t-Bu)(\mu-O)]\}_2$ (5) and $\{[MeZn]_3[OP(N-t-Bu)_3][OP(NH-t-Bu)_3]\}$ (6)

A solution of ZnMe₂ (0.70 mL, 2.0 mol/L, 1.40 mmol) in toluene was added to a slurry of OP(NH-*t*-Bu)₃ (0.366 g, 1.39 mmol) in toluene (20 mL) at 22 °C, resulting in a clear solution after 10 min. The reaction mixture was heated at 60 °C for 4 h; the solvent was then removed under vacuum to give a white powder (0.417 g). ³¹P{¹H} NMR (C₆D₆) δ : 46.8, 28.6, 24.3 (minor), 13.2 (minor), 11.3, 10.2, 9.3 (br), 8.1 (s).

Recrystallization of the product (72 mg) from toluene yielded colourless crystals of **5** (35 mg, 0.051 mmol, 21% based on ZnMe₂). ¹³C{¹H} NMR (solid state, 12 kHz) δ: 53.03 (s, NCMe₃), 52.28 (s, μ-HNCMe₃), 49.79 (s, HNCMe₃), 34.52 (s, NCMe₃), 32.05 (s, μ-HNCMe₃), 31.44 (s, HNCMe₃), -11.63 (s, MeZn). ³¹P{¹H} NMR (C₆D₆) δ: 9.3 (br), 8.1 (s). ³¹P{¹H} NMR (solid state, 5 kHz) δ: 7.4 (s). Anal. calcd. for $C_{38}H_{64}N_6O_2P_2Zn_2$: C 45.73, H 9.45, N 12.31; found: C 45.53, H 9.68, N 12.36.

Recrystallization of the product (51 mg) from Et₂O yielded colourless crystals of **6** (14 mg, 0.018 mmol, 32% based on ZnMe₂). ¹H NMR (C₆D₆) δ : 2.30 (br, 3H, NH), 1.38 (s, 9H, NCMe₃), 1.33 (s, 27H, NHCMe₃), 1.09 (s, 18H, NCMe₃), -0.12 (s, 9H, MeZn⁺). ³¹P{¹H} NMR (C₆D₆) δ : 46.8, 10.2. Anal. calcd. for C₂₇H₆₆N₆O₂P₂Zn₂: C 42.39, H 8.70, N 10.99; found: C 42.02, H 8.93, N 11.21.

Preparation of {Zn[MeZn]₂[OP(N-*t*-Bu)(NH-*t*-Bu)₂][OP(N-*t*-Bu)₃]} (7)

A solution of ZnMe₂ (5.34 mL, 1.0 mol/L, 5.34 mmol) in toluene was added dropwise to a solution of OP(NH-*t*-Bu)₃ (0.937 g, 3.56 mmol) in toluene (25 mL) at 22 °C. The toluene solution was refluxed at 113 °C for 18 h yielding a clear, colourless solution. The volume was reduced to 10 mL and after 1 day at 22 °C, colourless crystals of 7 had formed (0.601 g, 0.802 mmol, 45%). IR (cm⁻¹): 3279 (v(N-H)). ¹H NMR (C₆D₆) δ : 2.05 (br s, N*H*), 1.75–1.18 (numerous resonances, NCMe₃), 0.29 (s, ZnCH₃). ³¹P{¹H} NMR (C₆D₆) δ : 22.0 (s), 14.6 (s), 13.1 (s) (1:1:1), and additional minor resonances; solid state (10 kHz) δ : 22.0 (s), 13.5 (s). MS (ESI⁺): 549 (M⁺ - 199).

Preparation of $\{Zn_4(\mu_4-O)[OP(NMe)(NHMe)_2]_4[OP-(NMe)_2(NHMe)]\}_2$ (8)

A solution of ZnMe₂ (1.18 mL, 1.0 mol/L, 1.18 mmol) in toluene was added dropwise to a solution of OP(NHMe)₃ (0.162 g, 1.18 mmol) in toluene (25 mL) at 22 °C. The toluene solution was heated at reflux for 24 h. The volume of the solution was reduced to one-half and the concentrate was placed in the freezer. After 7 days at -15 °C, colourless crystals of **8**·C₇H₈ were recovered (0.144 g, 0.0718 mmol, 49% based on ZnMe₂). IR (cm⁻¹): 3323 (v(N-H)). ¹H NMR (C₆D₆) δ : 2.25 (s, NH*Me*), 2.22 (s, NH*Me*), 2.20 (s, NH*Me*), 2.16 (s, NH*Me*) (1:1:1:1), 1.36 (br s, N*Me*). ³¹P{¹H} NMR (C₆D₆) δ : 37.9 (s), 28.2 (s) (relative intensities ~1:3), and additional minor resonances; solid state (13 kHz) δ : 38.7 (s), 27.6 (s). Anal. calcd. for C₃₇H₁₁₆N₃₀O₁₂P₁₀Zn₈: C 22.15, H 5.83, N 20.94; found: C 22.02, H 6.05, N 19.96.

Preparation of [MeZn(µ-S)(µ-N-t-Bu)P(NH-t-Bu)₂]₂ (10)

A solution of ZnMe₂ (0.83 mL, 2.0 mol/L, 1.66 mmol) in toluene was added slowly to a slurry of SP(NH-*t*-Bu)₃ (0.461 g, 1.65 mmol) in toluene (20 mL) at 22 °C. The clear solution was stirred for 18 h; the solvent was then removed under vacuum to give **10** as a white powder (0.468 g, 0.652 mmol, 79%). ¹H NMR (C₆D₆) δ : 2.15 (br, N*H*), 1.48 (s, 9H, N), 1.31 (d, ${}^{4}J({}^{1}\text{H}-{}^{31}\text{P}) = 6.8$ Hz, 18H, NHCMe₃), -0.1 (s, 3H, MeZn⁺). ¹³C{}^{1}\text{H} NMR (C₆D₆) δ : 53.90 (d, CMe₃, ${}^{2}J({}^{13}\text{C}-{}^{31}\text{P}) = 44.4$ Hz), 51.63 (d, CMe₃, ${}^{2}J({}^{13}\text{C}-{}^{31}\text{P}) = 136.5$ Hz). ${}^{31}\text{P}{}^{1}\text{H}$ NMR (C₆D₆) δ : 39.3 (s). Anal. calcd. for C₂₆H₆₂N₆P₂S₂Zn₂: C 43.68, H 9.03, N 11.76; found: C 44.33, H 9.28, N 11.87.

Preparation of $\{Zn[(\mu-S)(\mu-N-t-Bu)P(NH-t-Bu)_2]_2\}$ (11)

A solution of ZnMe₂ (0.58 mL, 2.0 mol/L, 1.16 mmol) in toluene was added slowly to a slurry of SP(NH-*t*-Bu)₃ (0.648 g, 2.32 mmol) in toluene (20 mL) at 22°C. The resulting clear solution was stirred for 18 h; the solvent was then removed under vacuum to give **11** as an analytically pure white powder (0.710 g, 1.14 mmol, 98%). ¹H NMR (C₆D₆) δ : 2.12 (br, 2H, N*H*), 1.44 (s, 9H), 1.32 (s, 18H, CMe₃). ¹³C{¹H} NMR (C₆D₆) δ : 54.06 (d, CMe₃, ²J(¹³C-³¹P) = 43.5 Hz), 51.82 (d, CMe₃, ²J(¹³C-³¹P) = 9.9 Hz), 34.18 (d, CMe₃, ³J(¹³C-³¹P) = 38.7 Hz), 31.67 (d, CMe₃, ³J(¹³C-³¹P) = 17.1 Hz). ³¹P{¹H} NMR (C₆D₆) δ : 42.0 (s). Anal. calcd. for C₂₄H₅₈N₆P₂S₂Zn: C 46.33, H 9.40, N 13.51; found: C 45.30, H 10.64, N 13.48.

Preparation of {MeZn[(µ-N-t-Bu)(µ-NSiMe₃)P(NH-t-Bu)₂]} (12)

A solution of $ZnMe_2$ (0.53 mL, 2.0 mol/L, 1.06 mmol) in toluene was added slowly to a pale yellow solution of $Me_3SiNP(NH-t-Bu)_3$ (0.357 g, 1.07 mmol) in hexane

(20 mL) at 22 °C, resulting in an opaque yellow mixture. After 3 h, the solvent was removed under vacuum to give **12** as a yellow paste (0.400 g, 0.966 mmol, 91%). Washing with organic solvents did not improve the physical appearance of this highly soluble paste, which was shown to be pure **12** on the basis of spectroscopic and analytical data. ¹H NMR (C₆D₆) δ : 1.75 (br, N*H*), 1.22 (s, 27H, *CMe*₃), 0.27 (s, 9H, Si*Me*₃), -0.24 (s, 3H, *Me*Zn). ¹³C{¹H} NMR (C₆D₆) δ : 51.14 (d, *CMe*₃, ²*J*(¹³C-³¹P) = 8.9 Hz), 50.41 (d, *CMe*₃, ²*J*(¹³C-³¹P) = 34.2 Hz), 32.42 (d, *CMe*₃, ³*J*(¹³C-³¹P) = 15.5 Hz), 4.61 (d, Si*Me*₃, ³*J*(¹³C-³¹P) = 12.5 Hz), -15.0 (s, Zn*Me*). ³¹P{¹H} NMR (C₆D₆) δ : 9.1 (s). Anal. calcd. for C₁₆H₄₁N₄PSiZn: C 46.42, H 9.98, N 13.53; found: C 46.50, H 10.05, N 13.86.

X-ray analyses

Colourless crystals of **5**, **6**, **7**, **8**·C₇H₈, and **10** were coated with Paratone 8277 oil and mounted on a glass fibre. All measurements were made on a Nonius Kappa CCD diffractometer using graphite-monochromated molybdenum– K_{α} radiation. Crystallographic data are summarized in Table 1. The structures were solved by direct methods (13) and refined by full-matrix least-squares methods with SHELXL-97 (14). Hydrogen atoms were included at geometrically idealized positions and were not refined; the non-hydrogen atoms were refined anisotropically. Thermal ellipsoid plots were created using Diamond version 2.1 (15). Additional data are available in the Supporting information.³

Results and discussion

Reactions of OP(NHR)₃ with $ZnMe_2$ — Formation and structures of {MeZn[(μ -NH-*t*-Bu)(μ -N-*t*-Bu)P(NH-*t*-Bu)O]}₂ (5), {[MeZn]₃[OP(N-*t*-Bu)₃][OP(NH-*t*-Bu)₃]} (6), and {Zn[ZnMe]₂[OP(N-*t*-Bu)(NH-*t*-Bu)₂][OP(N-*t*-Bu)₃]} (7)

Initial attempts to conduct a thorough investigation of the reactivity of $ZnMe_2$ towards $OP(NHR)_3$ (1a (R = t-Bu), 1b (R = Me), 1c (R = Ad)) were confounded by the subtle dependence of these reactions upon both temperature and time. A mixture of products was observed by ³¹P NMR spectroscopy in all cases. Both the number and relative intensities of the resonances observed were strongly influenced by minor changes in the reaction conditions so that reproducible results were difficult to obtain, except for the reaction of 1a with 1 equiv. of dimethylzinc at 60 °C. The solid-state ³¹P NMR spectrum of the white powder produced in this reaction contains a single broad signal centred at 7 ppm. In solution at 22 °C, eight ³¹P NMR resonances of various intensities and linewidths were observed, suggesting the presence of multiple products. A variable-temperature NMR experiment showed that the linewidths, relative intensities, and indeed the number of resonances present are dependent upon temperature, indicating that this system is highly dynamic in solution and suggesting that different modes of ag-

³ Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 4056. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 269284–269287 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via 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 336033; or deposit@ccdc.cam.ac.uk).

Table 1. Crystallographic data.

	5	6	7	8	10
Formula	C ₂₆ H ₆₄ N ₆ P ₂ O ₂ Zn ₂	C ₂₇ H ₆₆ N ₆ P ₂ O ₂ Zn ₂	$C_{26}H_{62}N_6O_2P_2Zn_3$	C ₂₃ H ₆₂ N ₁₅ O ₆ P ₅ Zn ₄	C ₁₃ H ₃₂ N ₃ PSZn
fw (g)	685.51	764.97	748.87	1049.20	358.82
Space group	<i>P</i> 1	$Pna2_1$	$Pca2_1$	C2/c	$P2_1/c$
a (Å)	9.764(2)	22.936(5)	19.286(7)	17.5081(2)	11.854(3)
b (Å)	9.854(2)	10.445(2)	17.059(11)	23.6571(3)	9.678(2)
c (Å)	11.230(2)	16.213(3)	22.530(11)	21.4354(4)	17.108(6)
α (°)	64.54(3)	90	90	90	90
β (°)	71.01(3)	90	90	101.3377(5)	107.818(15)
γ (°)	72.64(3)	90	90	90	90
V (Å ³)	906.4(3)	3884.2	7412(7)	8705.1(2)	1868.5(9)
Ζ	1	4	8	4	2
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
$d_{\text{calcd}} \text{ (g cm}^{-3}\text{)}$	1.256	1.121	1.342	1.601	1.275
μ (mm ⁻¹)	1.441	1.340	2.042	2.410	1.505
<i>F</i> (000)	368	1400	3168	4336	768
R^a	0.035	0.0355	0.1198	0.040	0.0411
R _w ^b	0.093	0.0799	0.3503	0.107	0.0763

 ${}^{b}R_{w} = \{ [\Sigma w (F_{o}^{2} - F_{c}^{2})^{2}] / [\Sigma w (F_{o}^{2})^{2}] \}^{1/2}$ for all reflections.

gregation can occur for these products, even in the noncoordinating solvent d_8 -toluene.

Recrystallization of the white powder from toluene resulted in the isolation of colourless crystals, which were characterized by X-ray crystallography and multinuclear NMR spectroscopy; crystal data are compiled in Table 1. An X-ray structure, depicted in Fig. 1, showed the crystals to consist of the monoanion $[OP(N-t-Bu)(NH-t-Bu)_2]^-$ with a methylzinc counterion. The complex $\{MeZn[(\mu-NH-t-Bu)(\mu-t)]$ N-t-Bu)P(NH-t-Bu)(μ -O)]}₂ (5) exists as a centrosymmetric dimer. Each of the methylzinc cations is chelated by a t-BuNH and a t-BuN group of one monoanion, with a Zn-O bond serving to both link the zinc atom to the second monoanion and to complete the tetrahedral coordination sphere of the Zn atom. The second t-BuNH group on each phosphorus centre is not coordinated to either of the methylzinc cations.

Selected bond lengths and bond angles for 5 are summarized in Table 2. Three different P-N bond lengths and two distinct Zn-N distances are observed: the Zn(1)-N(1) bond length (1.980(9) Å) is substantially shorter than the Zn(1)— N(2) distance (2.430(8) Å), reflecting the greater strength of the zinc-imido linkage. Similarly, the P(1)-N(1) bond distance (1.590(8) Å) is considerably shorter than the P(1)-N(2) single-bond distance of 1.705(8) Å. The fact that N(3)is not coordinated to an electropositive zinc centre results in a shorter, stronger P-N bond (P(1)-N(3) 1.627(9) Å) than that observed for the coordinated N(2) atom. The Zn-O distances in 5 are slightly longer than those typically observed in zinc phosphates, with an average value of 2.001(7) Å, cf., mean values of 1.936(4) Å in the histidine complex $[Zn(HPO_4) \cdot (C_6H_9N_3O_2)]$ (9) and 1.933(2) Å in the aminobenzene-templated system [Zn(HPO₃)₂·C₆N₂H₁₀] (11). As expected, the bond angle at the sp² nitrogen atom ($\angle P(1)$ -N(1)-Zn(1), 102.5(5)°) is larger than the corresponding angle involving the sp³ amido nitrogen atom ($\angle P(1)$ -N(2)-

Fig. 1. Thermal ellipsoid plot of 5 (30% probability ellipsoids). Only α -carbon atoms of the *t*-Bu groups are shown.



Zn(1), 83.1(3)°), though both angles markedly deviate from ideal values, presumably owing to steric repulsions among the three *tert*-butyl groups attached to the nitrogen atoms.

The structure of 5 is a sharp contrast to the trimeric structure adopted by the lithium salt {Li[(µ-N-t-Bu)(µ-O)P(NH-t- $Bu_{2}]_{3}$ ·THF (4) (4), which contains the same monoanion. The Li⁺ cations in 4 are coordinated only by the oxo- and Nt-Bu ligands, while the NH-t-Bu groups are exocyclic. Whereas 5 is centrosymmetric, the trimer 4 displays C_1 symmetry, due in part to the presence of a molecule of THF coordinated to one Li⁺ cation. Some of these structural differences can be attributed to the high polarity of Li-E (E = N or O) units and their consequent propensity for aggregation to form ladder-type motifs.

The solid-state ³¹P and ¹³C NMR data for **5** were consistent with the X-ray structure; a major ³¹P resonance is observed at 7.4 ppm, and three distinct ¹³C signals for the

Bond lengths (Å)	
P(1)—O(1)	1.495(7)
P(1) - N(2)	1.705(8)
Zn(1) - O(1)	2.000(7)
Zn(1) - N(1)	1.980(9)
Zn(1) - C(25)	1.970(10)
P(1) - N(1)	1.590(8)
P(1)—N(3)	1.627(9)
Zn(1) - O(2)	2.001(7)
Zn(1) - N(2)	2.430(8)
Bond angles (°)	
P(1)-N(1)-Zn(1)	102.5(5)
P(1)-N(2)-Zn(1)	83.1(3)
P(1)-O(1)-Zn(2)	152.2(4)
O(1)-Zn(2)-C(26)	109.6(4)
P(1)-O(1)-Zn(2)	154.2(4)
O(1)-P(1)-N(1)	122.5(5)
N(1)-Zn(1)-O(2)	107.7(3)

106.8(4)

110.7(4)

Table 2. Selected bond lengths (Å) and bond angles (°) for **5**.



N(3)-P(1)-O(1)

N(2)-P(1)-N(3)

inequivalent CMe3 groups occur at 34.52, 32.05, and 31.44 ppm. In C_6D_6 solution, however, the ³¹P NMR spectrum consists of a sharp singlet at 8.1 ppm and a broader resonance at 9.3 ppm, possibly owing to an equilibrium between the dimer 5 and the corresponding monomer {[MeZn][(N-t-Bu)P(O)(NH-t-Bu)₂]}. A variable-temperature NMR experiment showed that, at low temperature $(-50 \, ^{\circ}\text{C})$, the 8.1 ppm species is predominant, while the intensity of the resonance at 9.3 ppm increases at higher temperatures, consistent with the proposed monomer-dimer equilibrium. The apparently facile dissociation of 5 into the corresponding monomer is somewhat surprising in light of its relatively strong Zn-O linkages (vide supra). Interestingly, the solidstate ³¹P NMR spectrum of 5 also displays a minor resonance at 9.8 ppm, which may be attributable to the presence of a small amount of the monomer.

When the product of the reaction of $OP(NH-t-Bu)_3$ with 1 equiv. of $ZnMe_2$ at 60 °C was recrystallized from diethyl ether rather than toluene, colourless crystals of a different product were obtained. An X-ray structure (Fig. 2) identified this compound as {[MeZn]₃[OP(N-t-Bu)₃][OP(NH-t-Bu)₃]} **Fig. 2.** Thermal ellipsoid plot of **6** (30% probability ellipsoids). Only α -carbon atoms of the *t*-Bu groups are shown.



(6), which is comprised of the trianion $[OP(N-t-Bu)_3]^{3-}$ and three MeZn⁺ counterions, with a neutral molecule of **1a** coordinated to two of the zinc centres. The formation of this previously unobserved trianion was somewhat unexpected given the lack of success encountered in attempts to generate $[OP(N-t-Bu)_3]^{3-}$ using organolithium reagents (4). In addition, the presence of unreacted $OP(NH-t-Bu)_3$ concomitant with the formation of this trianion is rather surprising; the generation of a mixture of mono- and di-anions would seem more probable.

In the solid state, 6 exists as a distorted PN₃Zn₃O cube, with the phosphorus and nitrogen atoms of the [OP(N-t- Bu_{3} ³⁻ trianion contributing four of the vertices, while the remaining positions are occupied by the three zinc cations and the oxygen atom O(2) of the neutral OP(NH-t-Bu)₃ molecule. While O(2) is coordinated to two of the methylzinc cations, the $=P(NH-t-Bu)_3$ fragment is pendant from the cube. Selected bond lengths and bond angles for 6 are given in Table 3. The oxo ligand of the trianion is exo to the cluster, with a P(1)—O(1) bond distance of 1.475(2) Å, cf., 1.474(3) Å in **1a** (4). In contrast, the P(2)—O(2) bond length is significantly longer (1.519(2) Å) because of coordination of this oxygen atom to two zinc atoms. The increase in this P=O distance has little effect on the P-N bond lengths in the neutral fragment; the average P(2)-N distance is 1.631(3) Å, cf., 1.637(3) Å in **1a** (4). The mean P-N bond length in the trianion is significantly longer (1.689(3) Å), since the nitrogen atoms in this moiety are four-coordinate.

Two of the zinc centres are four-coordinate, with two Zn—N bonds, one Zn—O linkage, and a methyl substituent, while the third zinc cation exhibits only a weak Zn—O contact (2.648(2) Å) and is thus considered three-coordinate. The zinc–oxygen distances for the two four-coordinate zinc atoms are Zn(1)—O(2) = 2.333(2) Å and Zn(2)—O(2) = 2.314(2) Å. These Zn—O distances are substantially longer than the mean values of 1.980(4) Å found in zinc-di(oxo)cyclodiphosph(V)azane systems (16), or the distances reported for the polymeric di(*tert*-butyl)phosphates {Zn[O₂P-(O-*t*-Bu)₂]₂[H₂N(CH₂)₆NH₂]_n and {Zn[O₂P(O-*t*-Bu)₂]₂]_n (range: 1.914(8)–1.929(6) Å) (17). The mean Zn—N dis-

Bond lengths (Å)	
P(1)—O(1)	1.476(2)
P(1)—N(2)	1.696(2)
P(2)—O(2)	1.519(2)
P(2)—N(5)	1.627(3)
Zn(1) - N(1)	2.091(2)
Zn(2)—N(2)	2.079(3)
Zn(1)—O(2)	2.333(2)
P(1)—N(1)	1.686(2)
P(1)—N(3)	1.684(3)
P(2)—N(4)	1.642(3)
P(2)—N(6)	1.625(3)
Zn(1)—N(3)	2.046(2)
Zn(2)—N(3)	2.074(2)
Zn(2)—O(2)	2.314(2)
Bond angles (°)	
N(1)-P(1)-N(2)	98.1(1)
N(2)-P(1)-N(3)	99.1(1)
N(1)-Zn(1)-O(2)	89.62(9)
N(2)-Zn(2)-N(3)	76.54(9)
N(3)-Zn(2)-O(2)	86.29(9)
Zn(1)-O(2)-Zn(2)	86.26(7)
N(1)-P(1)-N(3)	99.4(1)
N(1)-Zn(1)-N(3)	76.82(9)
N(3)-Zn(1)-O(2)	86.46(9)
N(2)-Zn(2)-O(2)	89.11(9)
N(1)-Zn(3)-N(2)	77.52(9)

Table 3. Selected bond lengths (Å) and bondangles (°) for 6.

tance for the three-coordinate zinc cation Zn(3) is 2.040(2) Å, cf., 2.073(2) Å for the four-coordinate zinc centres. The mean \angle N-P-N bond angle is 98.9(1)° while the \angle N-Zn-N and \angle N-Zn-O bond angles range from 76.54(9)° to 89.62(9)°.

A ³¹P NMR spectrum of **6** in C₆D₆ solution displayed two sharp singlets at 46.8 and 10.2 ppm, which are assigned to the $[OP(N-t-Bu)_3]^{3-}$ trianion and the neutral $OP(NH-t-Bu)_3$ ligand, respectively. Three resonances are observed in the ¹H NMR spectrum with relative intensities of 3:1:2, attributed to the three NH-t-Bu groups of the coordinated molecule of **1a** (27H) and the inequivalent N-t-Bu ligands of the trianion (9H and 18H), while a single broad resonance at -0.12 ppm is assigned to the methylzinc cations. These NMR data are consistent with the solid-state structure of **6**.

When the reaction of **1a** with dimethylzinc was carried out in a 2:3 molar ratio in boiling toluene, the ³¹P NMR spectrum of the resulting white powder indicated the formation of a mixture of products. However, recrystallization from toluene produced a single compound identified as $\{\text{Zn}[\text{ZnMe}]_2[\text{OP}(\text{N}-t-\text{Bu})(\text{NH})_2][\text{OP}(\text{N}-t-\text{Bu})_3]\}$ (7) by X-ray crystallography. Although the structure could not be satisfactorily refined ($R_1 = 0.12$) because of poor diffraction of the crystals and disorder of the *tert*-butyl substituents, the atom connectivities of **7** were established. Complex **7** is closely related to **6** in that its primary structural feature is a PN₃Zn₃O cube; however, in place of the neutral OP(NH-*t*-Bu)₃ ligand of **6**, complex **7** contains a monoanion [OP(N-*t*-Bu)(NH-*t*-Bu)₂]⁻ that is *N*,*O* chelated to a Zn²⁺ dication. The oxo substituent of this monoanion is coordinated to all three zinc centres, all of which are four-coordinate: the Zn^{2+} dication is also coordinated to nitrogen donors, while the other zinc atoms are also bound to two nitrogen atoms and a methyl substituent.



The solid-state ³¹P NMR spectrum of 7 consists of two singlets at 22.0 and 13.5 ppm, consistent with the X-ray structure. In C_6D_6 solution, the ³¹P NMR spectrum exhibits three major resonances at 22.0, 14.6, and 13.1 ppm, suggesting that more than one mode of aggregation occurs in solution; consistently, the solution ¹H NMR spectrum of 7 contains numerous resonances in the N-*t*-Bu region.

The contrasting structures of **5**, **6**, and **7** suggest that there are two different pathways possible for the reaction of dimethylzinc with OP(NH-*t*-Bu)₃. Complex **6** is clearly a precursor of **7**; in a separate experiment, it was shown by ³¹P NMR spectroscopy that crystalline **6** can, in fact, be converted to **7** by thermal elimination of methane under reduced pressure (Scheme 1). At the same time, **5** is clearly not a precursor of **6**, despite the fact that the first step in the formation of both **5** and **6** is likely the monodeprotonation of OP(NH-*t*-Bu)₃. In the case of **6**, the second step of the reaction results in the double deprotonation of one of the ligands.

The different coordination modes of the two ligands within both **6** and **7** are also noteworthy. The oxo unit of one ligand (the trianion) remains exo to the cubane, while the other oxygen atom plays an integral role in cluster formation, as it is coordinated to either two or three zinc centres in **6** and **7**, respectively. Additionally, two distinct modes of coordination for the $[OP(N-t-Bu)(NH-t-Bu)_2]^-$ monoanion are observed in these complexes, with *N*,*O* chelation displayed in **7**, whereas *N*,*N'* chelation prevails in **5**; similar *N*,*N'* coordination also occurs for the trianionic ligands in **6** and **7**, but in those two instances the oxo substituent remains non-coordinated.

Formation and X-ray structure of $\{Zn_4(\mu_4-O)-[OP(NMe)(NHMe)_2]_4[OP(NMe)_2(NHMe)]\}_2$ (8)

Following the successful generation of the trisimidophosphate trianion $[OP(N-t-Bu)_3]^{3-}$ utilizing dimethylzinc, similar reactions with tris(methylamido)phosphate $OP(NHMe)_3$ (**1b**) were investigated to determine the effect of the replacement of the bulky *tert*-butyl groups of **1a** with the much smaller NMe units on the size of the zinc imidophosphate clusters formed. The reaction of dimethylzinc with **1b** in a Scheme 1. Thermal conversion of 6 to 7.



Fig. 3. Thermal ellipsoid plot of 8 (30% probability ellipsoids). Hydrogen atoms of methyl groups are omitted.



1:1 ratio in boiling toluene led to the isolation of colourless crystals of the oxide-templated complex $\{Zn_4(\mu_4-O)-[OP(NMe)(NHMe)_2]_4[OP(NMe)_2(NHMe)]\}_2$ (8) in 49% yield.

An X-ray structure of **8** revealed that this complex is a centrosymmetric dimer, which crystallizes with a molecule of toluene in its lattice. A thermal ellipsoid plot is shown in Fig. 3, while the framework of the cluster is pictorially represented in Fig. 4. Each monomeric unit consists of four Zn^{2+} ions, four $[OP(NMe)(NHMe)_2]^-$ monoanions, one $[OP(NMe)_2(NHMe)]^{2-}$ dianion, and one oxide ligand; in each half of the cluster there is a tetrahedral core of four 4-coordinate Zn^{2+} ions that surround a central μ_4 -O²⁻ anion. The four monoanions bridge four edges of the Zn_4 tetrahedron. The two halves of the molecule are joined together by the two $[OP(NMe)_2(NHMe)]^{2-}$ dianions, while the NHMe

Fig. 4. Structural framework of 8. All methyl groups and noncoordinated NHMe groups are omitted for clarity.



group of each dianion does not participate in cluster bonding. Three of the four Zn^{2+} ions (Zn(1), Zn(2), and Zn(4)) interact with the two dianions and thus participate in linking together the two halves of the dimer. As a result of these linkages, there are numerous six-, eight-, ten-, and twelvemembered rings in the structure. The Zn and O atoms reside near the centre of the cluster, while the methyl groups of the phosphate anions point away from the central core.

The X-ray structure described in the preceding section is expected to give rise to five resonances in the ³¹P NMR spectrum of **8**. However, a solution ³¹P NMR spectrum in d_6 benzene revealed two dominant resonances at 37.9 and 28.2 ppm in an approximately 1:4 ratio, while the solid-state spectrum exhibited only two singlets centred at 38.7 and 27.6 ppm. These observations are tentatively attributed to the similar chemical environments experienced by the four crystallographically inequivalent [OP(NMe)(NHMe)2]⁻ monoanions, which result in the appearance of only one resonance for those four phosphorus atoms, along with a second resonance attributed to the [OP(NMe)₂(NHMe)₂]²⁻ dianion. The solution ¹H NMR spectrum of 8 exhibits four singlets of equal intensities at 2.25, 2.22, 2.20, and 2.16 ppm, assigned to the four different environments of the NHMe groups, while a single broad resonance centred at 1.36 ppm is observed for the indistinguishable NMe substituents. While no NH resonance could be detected in the ¹H NMR spectrum, the NHMe fragments were clearly identified by a sharp N-H stretch (3323 cm⁻¹) in the IR spectrum of **8**.

The formation of the much larger cluster 8, as compared with complexes 5, 6, and 7, is a direct consequence of the decrease in steric bulk of the NR groups, which allows for more extensive aggregation. Roesky and co-workers (18, 19) have reported the synthesis of a zinc complex of tertbutylphosphonic acid, $[Zn_2(THF)_2(EtZn)_6Zn_4(\mu_4-O)(t-BuPO_3)_8]$ (9), with a structure similar to that of 8: complex 9 contains a central $Zn_4(\mu_4-O)$ core, with the *tert*-butylphosphonate ligands radiating outwards from the centre of the dodecanuclear cluster. Selected bond lengths and bond angles for 8 are summarized in Table 4. The phosphorus-µ2-O bond lengths range from 1.498(3) to 1.532(2) Å (cf., 1.499(5)-1.527(5) Å in 9). The zinc- μ_4 -O distance is also similar to those of 9 (1.957(2)–2.026(2) Å in 8; 1.948(4)–2.073(4) Å in 9); however, the Zn— μ_2 -O distances are significantly longer in 8 than those in 9 (1.964(2)-2.055(1)) Å vs. 1.891(5)-1.990(5) Å, respectively).

The origin of the μ_4 -oxygen atom of **8** remains uncertain. It has been suggested that the presence of oxide in **9** results from the dehydration of *tert*-butylphosphonic acid induced by diethylzinc (19). However, this explanation is clearly not applicable to the reaction of ZnMe₂ with OP(NHMe)₃. Possible sources of the oxide ligand in the current case include (*a*) P=O bond cleavage during the course of the reaction, (*b*) the contamination of the reagent **1b** by water, or (*c*) the presence of "adventitious" water during the recrystallization process, as suggested for related systems (17, 20). As ³¹P NMR studies of the reaction mixtures gave no evidence for P=O bond cleavage, and the IR spectrum of **1b** showed that it was anhydrous, the most probable source of the oxide unit is the introduction of moisture during the recrystallization process.

Table 4. Selected bond lengths (Å) and bond angles (°) for **8**.

Rond longths (Å)	
Dona lengths (A) $\mathbf{Z}_{\mathbf{p}}(1) = \mathbf{N}(4)$	1.071(3)
$\frac{2n(1)-N(4)}{2n(1)}$	1.971(3) 1.000(3)
Zn(1) - N(1) Zn(1) - O(3)	2.005(3)
Zn(1) = O(5) Zn(1) = O(6)	2.005(3)
Zn(1) = O(0)	1.020(2)
Zn(2) = O(4)	1.969(3)
Zn(2) = O(2) Zn(2) = O(6)	1.907(2)
Zn(2) = O(0) Zn(2) = N(5)	2.045(2)
Zn(2) = N(3) Zn(3) = N(13)	1.958(3)
Zn(3) - O(6)	1.930(3) 1.989(2)
Zn(3) = N(10)	1.909(2) 1.992(3)
Zn(3) - O(1)	2.055(2)
Zn(4) - O(6)	1.974(2)
Zn(4) - N(7)	1.986(3)
Zn(4) - O(5)	2.045(2)
$Zn(4)$ — $N(5)^a$	2.079(2)
P(1) - O(1)	1.515(2)
P(1) - N(1)	1.605(3)
P(1) - N(2)	1.633(3)
P(1) - N(3)	1.650(3)
P(2)—O(2)	1.532(2)
P(2) - N(4)	1.602(3)
P(2) - N(6)	1.646(3)
P(2)—N(5)	1.667(3)
P(3)—O(3)	1.498(3)
P(3)—N(7)	1.607(3)
P(3)—N(8)	1.652(3)
P(3)—N(9)	1.660(3)
P(4)—O(4)	1.522(2)
P(4)—N(10)	1.598(3)
P(4)—N(11)	1.639(3)
P(4)—N(12)	1.649(4)
P(5)—N(13)	1.589(4)
P(5)—O(5)	1.515(2)
P(5)—N(14)	1.640(3)
P(5)—N(15)	1.671(3)
Bond angles (°)	
N(4)-Zn(1)-N(1)	124.56(11)
N(13)-P(5)-N(15)	117.63(16)
N(4)-Zn(1)-O(3)	106.27(10)
N(14)-P(5)-N(15)	100.88(16)
N(14)-P(5)-N(15)	100.88(16)
N(1)-Zn(1)-O(3)	98.83(11)
P(1)-O(1)-Zn(3)	121.67(14)
N(4)-Zn(1)-O(6)	109.48(10)
$P(2)-O(2)-Zn(2)^{a}$	133.13(12)
N(1)-Zn(1)-O(6)	108.6(1)
P(3)-O(3)-Zn(1)	130.67(16)
O(3)-Zn(1)-O(6)	107.51(9)
P(4)-O(4)-Zn(2)	125.79(14)
$U(b)$ -Zn(2)- $U(2)^{a}$	111.28(8)
P(5)-U(5)-Zn(4)	126.97(13)
U(b)-Zn(2)- $U(4)$	111.61(9)
Zn(2)-U(6)-Zn(4)	109.04(10)
$O(2)^{*}-Zn(2)-O(4)$	105.71(9)
Zn(2)-O(6)-Zn(3)	104.22(9)

 Table 4 (concluded).

D and an alog $(^{\circ})$	
Bond angles (1) $O(1)$ $T_{1}(2)$ $N(5)$	110 40(0)
O(0)-Zn(2)-N(3)	118.42(9)
2n(4)-O(6)-2n(3)	110.93(10)
$O(2)^{\alpha}-Zn(2)-N(5)$	103./1(9)
2n(2)-O(6)-2n(1)	110.67(9)
O(4)-Zn(2)-N(5)	105.07(10)
O(1)-P(1)-N(2)	110.45(15)
N(1)-P(1)-N(2)	107.12(16)
O(1)-P(1)-N(3)	104.80(15)
P(4)-N(10)-Zn(3)	116./5(15)
N(1)-P(1)-N(3)	110.10(16)
N(2)-P(1)-N(3)	108./1(16)
O(2) - P(2) - N(4)	108.48(12)
O(2)-P(2)-N(6)	114.66(13)
N(4)-P(2)-N(6)	109.53(14)
O(2)-P(2)-N(5)	105.23(12)
N(4) - P(2) - N(5)	114.35(13)
N(6)-P(2)-N(5)	104.66(13)
O(3)-P(3)-N(7)	110.36(15)
O(3)-P(3)-N(8)	107.33(16)
2n(4)-O(6)-2n(1)	108.18(9)
2n(3)-O(6)-2n(1)	113./1(10)
P(1)-N(1)-Zn(1)	113.64(16)
N(13)-Zn(3)-O(6)	117.01(10)
N(13)-Zn(3)-O(6) N(12)-Zn(2)-N(10)	117.01(10) 112.50(11)
N(13)-Zn(3)-N(10)	112.50(11)
O(6)-Zn(3)-N(10)	111.18(10)
N(13)-Zn(3)-O(1)	105.55(11) 100.56(0)
O(0)-Zn(3)-O(1)	109.50(9)
P(2)-N(4)-Zn(1)	116.69(15)
N(10)-Zn(3)-O(1)	99.34(10)
P(2)-N(3)-Zn(2) N(10), Zn(2), Zn(2)	105.20(15)
N(10)-ZII(3)-ZII(2) O(1), Zn(2), Zn(2)	106.91(7)
O(1)-Zn(3)-Zn(2)	100.81(7)
$P(2)-N(3)-ZH(4)^{n}$	114.07(15) 120.77(10)
O(0)-ZII(4)-IN(7) $Z_{P}(2) N(5) Z_{P}(4)^{a}$	120.77(10) 102.58(10)
$\Sigma_{II}(2) - IN(3) - \Sigma_{II}(4)$ $\Omega(6) Z_{II}(4) \Omega(5)$	103.36(10) 101.62(8)
N(7) Zn(4) O(5)	101.02(6) 101.50(10)
N(7) - Z II(4) - O(3) O(6) $Z p(4) N(5)^{a}$	101.39(10) 114.13(0)
$N(7) - Zn(4) - N(5)^{a}$	114.13(9) 114.42(10)
P(3)-N(7)-Zn(4)	120.41(16)
$\Omega(5) - 7n(4) - N(5)^{a}$	120.41(10) 00 70(0)
O(3)-ZII(4)-IN(3) O(1)-P(1)-N(1)	115 53(16)
N(7) - P(3) - N(8)	113.33(10) 114.25(16)
O(3) - P(3) - N(0)	114.25(10) 114.75(15)
N(7) - P(3) - N(9)	108.08(15)
N(8)-P(3)-N(9)	101.00(16)
O(4) - P(4) - N(10)	101.00(10) 110.00(14)
O(4) - P(4) - N(11)	107.17(15)
N(10)-P(4)-N(11)	116.08(16)
O(4)-P(4)-N(12)	112.26(15)
N(10)-P(4)-N(12)	108 23(16)
N(11)-P(4)-N(12)	103.01(17)
O(5)-P(5)-N(13)	109 46(14)
O(5)-P(5)-N(14)	115.83(14)
N(13)-P(5)-N(14)	108.36(16)
O(5)-P(5)-N(15)	104.78(14)

a - x + 1/2, -y + 1/2, -z.

Fig. 5. Thermal ellipsoid plot of **10** (30% probability ellipsoids). Only hydrogen atoms bonded to nitrogen atoms are shown.



Preparation and characterization of $[MeZn(\mu-S)(\mu-N-t-Bu)P(NH-t-Bu)_2]_2$ (10) and $\{Zn[(\mu-S)(\mu-N-t-Bu)P(NH-t-Bu)_2]_2\}$ (11)

The reaction of SP(NH-t-Bu)₃ with 1 equiv. of dimethylzinc produces {MeZn(μ -S)(μ -N-t-Bu)P(NH-t-Bu)₂}₂ (10) in 78% yield. An X-ray structure (Fig. 5) revealed that in the solid state, 10 exists as a centrosymmetric dimer in which each ligand is N,S chelated to a MeZn⁺ cation, with Zn-S bonds linking the two halves together into a stepshaped ladder motif. Each zinc atom is thus four-coordinate, with two Zn-S linkages, one Zn-C bond, and a Zn-N-t-Bu unit. Selected bond lengths and bond angles for 10 are given in Table 5. As expected, the mean P-N distances involving the pendant NH-t-Bu groups (1.650(2) Å) are longer than the P-N(t-Bu) linkage (1.592(2) Å). The substantial difference between the Zn(1)—N(1) (2.007(2) Å) and Zn(1)— S(1) (2.5849(9) Å) bond lengths, combined with the tetrahedral geometries of the phosphorus and zinc atoms, gives the four-membered PNSZn rings a distorted diamondoid shape. The Zn_2S_2 ring is closer to square-shaped, with bond angles of 97.10(3)° and 82.90(3)° at the zinc and sulfur centres, respectively. Two distinct Zn-S distances are observed with the shorter bond (2.4627(9) Å) linking the two monomeric units and contributing to the distortion of the ring.

The dimeric laddering arrangement exhibited by 10 has been observed for other complexes of imidophosphate monoanions. The lithium derivatives {Li[(µ-N-t-Bu)(µ- $NSiMe_3P(NH-t-Bu)_2]_2$ (6) and $\{Li[(\mu-N-i-Pr)(\mu-S)P(NH-i Pr_{2}$ Pr₂ $\frac{1}{2}$ · 2THF (5) both display this connectivity. The latter thiophosphate complex and 13 both exist in the trans conformation to minimize steric repulsions between the bulky tertbutyl substituents. The different mode of coordination of the heteroleptic imidophosphate ligand to zinc in 10 compared with that in 5 may be attributed, in part, to the greater affinity of zinc for the softer sulfur centre, resulting in N,S chelation, while N,N' coordination is observed for the Ocontaining ligand in 5. This, in turn, results in significantly different modes of oligomerization for these two dimers. It should be noted that the first transition-metal complexes of the monoanion [SP(N-t-Bu)(NH-t-Bu)₂]⁻ have been reported recently (21); interestingly, both N,S and N,N' chelation were observed in a single Ni(II) complex.

$\begin{array}{llllllllllllllllllllllllllllllllllll$	Bond lengths (Å)			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1)—N(1)	1.592(2)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1)—N(3)	1.651(2)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Zn(1) - S(1)	2.4627(9)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1)—N(2)	1.648(2)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	P(1)—S(1)	2.0501(11)		
Bond angles (°) $S(1)$ - $Zn(1)$ - $S(1)^a$ 97.10(3) $S(1)$ - $P(1)$ - $N(1)$ 101.66(9) $S(1)$ - $P(1)$ - $N(3)$ 108.51(9) $N(2)$ - $P(1)$ - $N(3)$ 100.42(12) $N(1)$ - $Zn(1)$ - $C(1)$ 121.18(10) $S(1)$ - $Zn(1)$ - $N(1)$ 82.90(3) $Zn(1)$ - $N(1)$ - $P(1)$ 106.22(12) $N(1)$ - $P(1)$ - $N(2)$ 110.49(13) $S(1)$ - $Zn(1)$ - $C(1)$ 121.18(10) $N(1)$ - $Zn(1)$ - $C(1)$ 75.19(7)	Zn(1)-C(1)	1.966(3)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Bond angles (°)			
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$S(1)-Zn(1)-S(1)^{a}$	97.10(3)		
$\begin{array}{llllllllllllllllllllllllllllllllllll$	S(1)-P(1)-N(1)	101.66(9)		
$\begin{array}{lll} N(2)-P(1)-N(3) & 100.42(12) \\ N(1)-Zn(1)-C(1) & 121.18(10) \\ S(1)-Zn(1)-N(1) & 82.90(3) \\ Zn(1)-N(1)-P(1) & 106.22(12) \\ N(1)-P(1)-N(2) & 110.49(13) \\ S(1)-Zn(1)-C(1) & 121.18(10) \\ N(1)-Zn(1)-S(1) & 75.19(7) \\ \end{array}$	S(1)-P(1)-N(3)	108.51(9)		
$\begin{array}{lll} N(1)-Zn(1)-C(1) & 121.18(10) \\ S(1)-Zn(1)-N(1) & 82.90(3) \\ Zn(1)-N(1)-P(1) & 106.22(12) \\ N(1)-P(1)-N(2) & 110.49(13) \\ S(1)-Zn(1)-C(1) & 121.18(10) \\ N(1)-Zn(1)-S(1) & 75.19(7) \end{array}$	N(2)-P(1)-N(3)	100.42(12)		
S(1)-Zn(1)-N(1)82.90(3)Zn(1)-N(1)-P(1)106.22(12)N(1)-P(1)-N(2)110.49(13)S(1)-Zn(1)-C(1)121.18(10)N(1)-Zn(1)-S(1)75.19(7)	N(1)-Zn(1)-C(1)	121.18(10)		
Zn(1)-N(1)-P(1)106.22(12)N(1)-P(1)-N(2)110.49(13)S(1)-Zn(1)-C(1)121.18(10)N(1)-Zn(1)-S(1)75.19(7)	S(1)-Zn(1)-N(1)	82.90(3)		
N(1)-P(1)-N(2)110.49(13)S(1)-Zn(1)-C(1)121.18(10)N(1)-Zn(1)-S(1)75.19(7)	Zn(1)-N(1)-P(1)	106.22(12)		
S(1)-Zn(1)-C(1)121.18(10)N(1)-Zn(1)-S(1)75.19(7)	N(1)-P(1)-N(2)	110.49(13)		
N(1)-Zn(1)-S(1) 75.19(7)	S(1)-Zn(1)-C(1)	121.18(10)		
	N(1)-Zn(1)-S(1)	75.19(7)		

Table 5. Selected bond lengths (Å) and bondangles (°) for 10.

^{*a*}Symmetry transformations used to generate equivalent atoms: -x + 1, -y + 1, -z.

The ³¹P NMR spectrum of **10** in C₆D₆ at 22 °C exhibits resonances at 41.1 and 39.6 ppm in an approximately 1:3 ratio, rather than the expected single peak; multiple resonances are observed in the ¹H NMR spectrum. Variable-temperature ³¹P NMR spectra were recorded at temperatures ranging from -30 to +40 °C. At higher temperatures, the minor signal at 41.1 ppm was observed to increase in intensity, while at lower temperatures this resonance became less intense and was not observed below -15 °C. This suggests that an equilibrium exists between the dimer 10 and the corresponding monomer. The ¹H and ¹³C NMR spectra of 10 at -30 °C showed the expected resonances for two inequivalent tertbutyl environments in a 2:1 ratio, as well as a singlet assigned to the two equivalent MeZn⁺ cations. Thus the lowtemperature NMR spectra are consistent with the presence of a single species consistent with the solid-state structure of 10.

When the reaction of SP(NH-*t*-Bu)₃ with dimethylzinc was carried out in a 2:1 molar ratio, a white powder was recovered and characterized by multinuclear NMR spectroscopy and CHN analysis. The ³¹P NMR spectrum of this product contained a singlet at 42.0 ppm, while the ¹H and ¹³C NMR spectra revealed two *tert*-butyl resonances with relative intensities of 1:2. No resonance for a MeZn⁺ cation was observed. These NMR data are consistent with the formation of $\{Zn[(\mu-S)(\mu-N-t-Bu)P(NH-t-Bu)_2]_2\}$ (11) in which a Zn²⁺ cation is *N*,*S* chelated by two monoanions. A peak at *m*/*z* 607 (M – Me⁺) is observed in the ESI mass spectrum of 11.

In contrast to the diverse reaction pathways and complex product mixtures in the reactions of $OP(NHR)_3$ with $ZnMe_2$, only monodeprotonation is observed in the corresponding reaction of $SP(NH-t-Bu)_3$. The lower reactivity of **2a** toward $ZnMe_2$ is unexpected, as previous studies have shown this thiophosphate to be much more reactive toward alkyllithium reagents than is the oxo analogue **1a** (3–5).



Preparation and characterization of {MeZn[(μ-N-*t*-Bu)-(μ-NSiMe₃)P(NH-*t*-Bu)₂]} (12)

The reaction of (t-BuNH)₃PNSiMe₃ with 1 equiv. of dimethylzinc generates {MeZn[(μ -N-*t*-Bu)(μ -NSiMe₃)P(NH-*t*-Bu)₂]} (**12**) as a yellow oil, which has been characterized by multinuclear NMR spectroscopy and CHN analysis. The ¹H NMR spectrum of **12** exhibits only three resonances with relative intensities of 9:3:1 assigned to the *t*-Bu groups, the SiMe₃ substituent, and the MeZn⁺ cation, respectively. Although the signals from the μ -N-*t*-Bu and NH-*t*-Bu groups are not resolved in the ¹H NMR spectrum, the ¹³C NMR spectrum shows two distinct sets of *t*-Bu resonances in an approximately 1:2 ratio. A singlet is observed at 9.1 ppm in the ³¹P NMR spectrum. Thus, the NMR data indicate a *N*,*N'*-chelated structure for **12**.



The reaction of **3** with $ZnMe_2$ in a 2:1 molar ratio produces a 1:1 mixture of **12** and unreacted **3**, indicating that dimethylzinc in only sufficiently basic to effect monodeprotonation of **3**. This result was somewhat surprising, given that **3** can be triply deprotonated by reactions with *n*-BuLi at room temperature; conversely, the trisamidophosphate **1a** can only be dilithiated regardless of reaction conditions, whereas reactions with dimethylzinc lead to the formation of triply deprotonated species such as **6** and **7**.

Conclusions

The reactivity of the triamidophosphates $EP(NHR)_3$ (E = O, S, NSiMe₃; R = alkyl) toward dimethylzinc markedly decreases on moving from oxygen to the heavier chalcogen sulfur. The higher basicity of the oxo ligand results in a tendency for coordination to numerous metal centres. Both the oxygen and sulfur systems display temperature-dependent solution dynamics. A further decrease in reactivity is observed when the chalcogen atom is replaced by an NSiMe₃ group; the only product observed is the monomer {[MeZn]- $[(\mu-N-t-Bu)(\mu-NSiMe_3)P(NH-t-Bu)_2]$ }, presumably because the steric bulk of the alkylimido groups impedes aggregation. Curiously, the reactivities of these triamidophosphates towards *n*-butyllithium decrease in the reverse order; threefold deprotonation of OP(NHR)₃ occurs only in reactions with dimethylzinc. The reactions of other organometallic reagents such as MgBu₂ with these triamidophosphates is worthy of investigation for comparison with the results observed for *n*-BuLi and ZnMe₂.

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