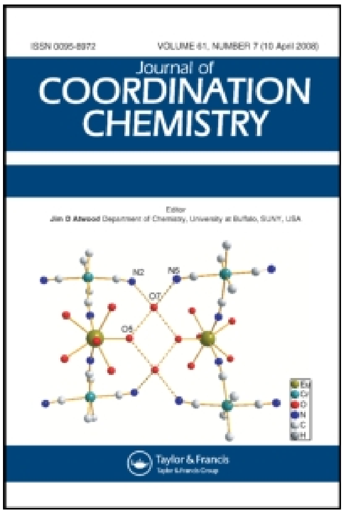

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Yash Paul[a]; Sushil K. Pandey[a]
[a] Department of Chemistry, University of Jammu, Jammu-180 006 (J & K), India

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Synthesis and characterization of cyclophosphazene complexes of zirconium(IV)

YASH PAUL and SUSHIL K. PANDEY*

Department of Chemistry, University of Jammu,
Baba Saheb Ambedkar Road, Jammu-180 006 (J & K) India

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Cyclophosphazene complexes of zirconium(IV) of the types $[\{N(PPh_2\overline{NR)_2\}_nZ}rCl_{4-n}]$ and $[\{N(PPh_2\overline{NR)_2\}_nZ}rCl_{2-n}(OPr^i)_2]$ (R = –Ph or –SiMe$_3$, $n = 1$ or 2) have been synthesized-and isolated by reactions of acyclic *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, or *bis*-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, with $ZrCl_4$ or $ZrCl_2(OPr^i)_2$ in different stoichiometries under anhydrous and inert conditions. These cyclozirconatriazadiphosphorines have been characterized by elemental analyses (C, H, N, Cl and Zr), molecular weight determination, IR and NMR (^1H, ^{13}C and ^{31}P) spectral studies, which indicated the monomeric nature of these complexes and a bidentate mode of bonding by the phosphazene ligand, leading to trigonal bipyramidal or octahedral geometries around the zirconium.

Keywords: Cyclozirconaphosphazenes; Heterometallacyclophosphazenes; Metallatriazadiphosphorines; Organophosphorus; Phosphazenes

1. Introduction

Phosphazene chemistry has experienced rapid growth and is a major part of the inorganic non-metallic field. The six-membered cyclotriazaphosphazene, $(NPCl_2)_3$, (2,2,4,4,6,6-hexasubstituted-1,3,5,2λ^5,4λ^5,6λ^5-triazatriphosphorines), is the most investigated phosphorus-nitrogen compound, particularly pertaining to its metathesis reactions with a wide variety of nucleophiles [1–4]. Several heterometallacyclophosphazenes have been synthesized from acyclic phosphazene ligands, with interesting structure and utility [5–9]. Phosphazene derivatives are potential precursors in the field of ceramic and inorganic polymer chemistry [8–11]. The phosphazene unit ($N{=}PR_2$) is isoelectronic to the siloxane group ($O{=}SiR_2$) that has a broad range of applications as fluids, greases, resins, elastomers and emulsions [12]. Transition metals as well as main group elements have been incorporated into the P–N ring system [13–16]. We have investigated phosphazene chemistry and incorporated several elements into the P–N ring skeleton using acyclic phosphazene ligands [17–22].

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*Corresponding author. Email: kpsushil@rediffmail.com

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These aminoiminophosphorane ligands are versatile chelating ligands, comparable in cone angle to $C_5Me_5^-$ [23]. Specific properties of the corresponding metal complexes can be tuned sterically and electronically by variation of the P-bonded organic group. Further, the presence of the silylated or phenylated substituents on nitrogen ensures solubility as well as steric protection of the coordinated metal ion. A literature survey shows the paucity of information on zirconium complexes with such nitrogen donor ligands [9, 13, 14, 24, 25]. Roesky *et al.* reported the synthesis and structure of $[\mathrm{PPh_2(\overline{NSiMe_3)_2Z}rCl_3}]$ and its acetonitrile adducts [9]. Compounds of this type are of interest as potential catalysts in organic synthesis [26]. It is expected that zirconium might produce promising results compared to titanium, as zirconium is larger than titanium [$r_{\mathrm{cov}} \approx 136$ (Ti), ≈ 148 pm (Zr)] [27]. The larger size and higher effective nuclear charge may result in more facile reactions. In view of the above, and knowing that $ZrCl_4$ and $ZrCl_2(OPr^i)_2$ are good synthones for preparing zirconium(IV) complexes, it was thought worthy to incorporate zirconium into the P–N–P ring system, we herein report the synthesis and characterization of cyclozirconaphosphazenes of the general formula $[\{\mathrm{N(PPh_2\overline{NR)_2\}_{\mathit{n}}Z}rCl_{4\text{-}\mathit{n}}}]$, and $[\{\mathrm{N(PPh_2\overline{NR)_2\}_{\mathit{n}}Z}rCl_{2\text{-}\mathit{n}}(OPr^i)_2}]$ by reactions of acyclic aminoiminophosphorane chelate, particularly *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, and *bis*-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, ligands with $ZrCl_4$ and $ZrCl_2(OPr^i)_2$.

2. Experimental

All manipulations were performed under anhydrous conditions under nitrogen using standard Schlenk technique. All glassware was dried in a preheated oven and solvents were distilled over sodium metal and degassed before use. The *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, and *bis*-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, ligands were prepared by literature methods [19, 28]. High purity $ZrCl_4$ was procured commercially (Aldrich) and used as received; $ZrCl_2(OPr^i)_2$ was prepared by 1 : 2 molar reaction of zirconiumtetrachloride with isopropanol in toluene.

2.1. *Synthesis of (N-(P,P-diphenyl-N-(trimethylsilyl)phosphorimidoyl-P, P-diphenylphosphorimidoyl)(trimethylsilyl)amino)zirconium(IV) chloride, $[\mathrm{N(PPh_2\overline{NSiMe_3)_2Z}rCl_3}]$ (1)*

A toluene solution (~30 mL) of 1.27 g (2.26 mmol) of acyclic *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, and triethylamine (0.23 g, 2.26 mmol) was added to a toluene solution (~30 mL) of 0.53 g (2.26 mmol) of $ZrCl_4$ at room temperature with constant stirring. The color changed to pale-yellow and precipitates of triethylaminehydrochloride formed after refluxing the contents for ~6 h. The contents were brought to room temperature and the triethylaminehydrochloride separated using a funnel fitted with G-4 sintered disc. Excess solvent was removed from filtrate under reduced pressure resulting in $[\mathrm{N(PPh_2\overline{NSiMe_3)_2Z}rCl_3}]$ (**1**) as pale-yellow solid in 93% yield. Similar methodology was applied for synthesis of **2**–**4**.

2.2. *Synthesis of (N-(P,P-diphenyl-N-(trimethylsilyl)phosphorimidoyl-P, P-diphenylphosphorimidoyl)(trimethylsilyl)amino)diisopropoxyzirconium(IV) chloride,* $[N(PPh_2\overline{NSiMe_3)_2Z}rCl(OPr^i)_2]$ *(5)*

A toluene solution (~30 mL) of 1.25 g (2.23 mmol) of *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, with triethylamine (0.22 g, 2.23 mmol) was added dropwise to a toluene solution (~30 mL) of 0.49 g (2.23 mmol) of $ZrCl_2(OPr^i)_2$ at room temperature with constant stirring. Triethylaminehydrochloride gets precipitated immediately. However, the reaction mixture was stirred for ~2 h at 60°C to complete the reaction. Triethylaminehydrochloride was filtered off using a funnel fitted with G-4 sintered disk followed by evaporation of solvent from the filtrate *in vacuo*. The complex $[N(PPh_2\overline{NSiMe_3)_2Z}rCl(OPr^i)_2]$ (**5**) was obtained as pale-yellow solid in 94% yield. Complexes **6**–**8** were prepared by similar method. The synthetic and analytical data of **1**–**8** are summarized in table 1.

3. Measurements

Elemental analyses (C, H and N) were carried out on a micro-elemental analyzer. Zirconium was estimated gravimetrically as ZrO_2. Chlorine was estimated by Volhard's method whereas isopropoxy was determined by potassium dichromate oxidation. Molecular weights were determined cryoscopically in freezing benzene. IR spectra were recorded in KBr mulls in the range 4000–200 cm^{-1} on a Perkin–Elmer 377 spectrophotometer. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker DRX 300 (120 MHz) spectrometer using TMS as the internal reference for ^1H NMR and 85% H_3PO_4 as an external reference for ^{31}P NMR.

4. Results and discussion

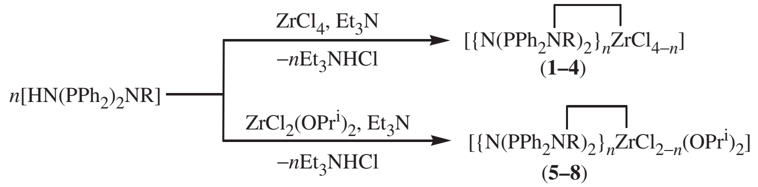
Reactions of acyclic *bis*-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, or *bis*-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, with $ZrCl_4$ or $ZrCl_2(OPr^i)_2$ in 1 : 1 and 2 : 1 molar ratio in the presence of equimolar triethylamine eliminated triethylaminehydrochloride (scheme 1) and afforded cyclozirconaphosphazene derivatives $[\{N(PPh_2\overline{NR)_2\}_nZ}rCl_{4-n}]$ and $[\{N(PPh_2\overline{NR)_2\}_nZ}rCl_{2-n}(OPr^i)_2]$ (R = –Ph or –$SiMe_3$, $n = 1$ or 2).

Reactions of $ZrCl_2(OPr^i)_2$ were facile compared to reactions using $ZrCl_4$ which required refluxing for 4–6 h. The reactions did not involve cleavage of trimethylsilyl and the complexes were obtained in 90–94% yield. These pale-yellow moisture sensitive solids are highly soluble in benzene, chloroform, dichloromethane, acetone and coordinating solvents like DMSO, DMF and THF, while insoluble in carbon tetrachloride and diethyl ether. These complexes decompose on heating under reduced pressure forming dark brown products, which could not be characterized. Molecular weight determination indicated the monomeric nature of these complexes. Elemental analyses of C, H, N, Cl and Zr were consistent with the composition of the complexes.

Table 1. Synthetic and analytical data of cyclophosphazene complexes of zirconium(IV).

	Reactants g (mmol)					Analysis (%) found (Calcd)				
S. No	LH*	$ZrCl_4/ZrCl_2\ (OPr^i)_2$	Product** Yield(%)	m.p. (°C)	M.W. Found (Calcd)	C	H	N	Cl	Zr
1	1.27	0.53	$[\mathrm{N(PPh_2\overline{NSiMe_3)_2Z}rCl_3}]$	92	750.41	47.71	5.12	5.63	14.01	12.15
	(2.26)	(2.26)	93		(755.72)	(47.64)	(5.06)	(5.55)	(14.06)	(12.06)
2	1.45	0.60	$[\mathrm{N(PPh_2\overline{NPh)_2Z}rCl_3}]$	82	752.65	56.61	3.79	5.55	13.81	11.73
	(2.58)	(2.58)	(94)		(763.72)	(56.58)	(3.96)	(5.49)	(13.92)	(11.94)
3	1.80	0.37	$[\{\mathrm{N(PPh_2\overline{NSiMe_3)_2\}_2Z}rCl_2}]$	76	1295.3	55.87	5.85	6.61	5.57	7.15
	(3.21)	(1.60)	(93)		(1287.22)	(55.32)	(5.99)	(6.52)	(5.54)	(7.08)
4	2.19	0.44	$[\{\mathrm{N(PPh_2\overline{NPh)_2\}_2Z}rCl_2}]$	78	1238.5	66.66	4.68	6.43	5.41	7.10
	(3.79)	(1.89)	(93)		(1295.2)	(66.76)	(4.67)	(6.48)	(5.47)	(7.13)
5	1.25	0.49	$[\mathrm{N(PPh_2\overline{NSiMe_3)_2Z}rCl(OPri)_2}]$	87	812.6	53.88	6.53	5.19	4.48	(11.23)
	(2.23)	(2.23)	(93)		(802.7)	(53.81)	(6.52)	(5.23)	(4.41)	11.35
6	1.45	0.56	$[\mathrm{N(PPh_2\overline{NPh)_2Z}rCl(OPr^i)_2}]$	72	803.4	62.11	5.42	5.23	4.29	11.19
	(2.55)	(2.55)	(90)		(810.7)	(62.17)	(5.47)	(5.18)	(4.37)	(11.24)
7	1.82 (3.25)	0.36 (1.62)	$[\{\mathrm{N(PPh_2\overline{NSiMe_3)_2\}_2Z}r(OPr^i)_2}]$	82	1315.4 (1325.2)	59.71 (59.74)	6.72 (6.84)	6.29 (6.33)	–	6.80 (6.87)
8	1.92	0.37	$[\{\mathrm{N(PPh_2\overline{NPh)_2\}_2Z}r(OPr^i)_2}]$	116	1340.8	64.96	5.49	6.24	–	1181
	(3.38)	(1.69)	(92)		(1333.2)	(65.01)	(5.72)	(6.30)		(11.76)

*LH=$[HN(PPh_2NR)_2]$ (where R = –Ph or $–SiMe_3$); **All the complexes are pale-yellow solid.



Scheme 1. Reactions of $[HN(PPh_2)_2NR]$ with $ZrCl_4$ and $ZrCl_2(OPr^i)_2$ (where R = –Ph or $-SiMe_3$, OPr^i = isopropoxy and $n = 1$ or 2).

Table 2. IR spectral data of cyclophosphazene complexes of zirconium(IV) (cm^{-1}).

Compound No.	νP=N	νP–N–P (Ring vibrations)	νZr–O	νZr–O	νZr–Cl
1	1430.5, vs	1220–1020, s	–	512, s	360, w
2	1432.3, vs	1200–1040, s	–	520, m	370, w
3	1495.2, vs	1203–1090, s	–	530, s	345, w
4	1440.3, vs	1280–1110, s	–	525, s	375, w
5	1436.4, vs	1205–1110, s	615, m	515, m	350, w
6	1420.3, vs	1285–1020, s	680, m	500, s	–
7	1410, vs	1220–1040, s	670, m	520, m	355, w
8	1425.5, vs	1210–1010, s	655, s	505, s	–

vs = very strong, s = strong, m = medium and w = weak.

IR spectra were interpreted on the basis of literature reports [8, 9, 16, 17, 28]. Absorptions due to νP–N were found between 1410–1495 cm^{-1}, in accord with the symmetric nature of the νP–N–P ring system. Disappearance of the νNH band at 3345 cm^{-1} and appearance of new band for νZr–N in the region 530–500 cm^{-1} indicates formation of Zr–N. Bands of medium intensity in the region 375–345 cm^{-1} may be ascribed to νZr–Cl. The strong νP=N vibrations found in the region 1495–1430 cm^{-1} show a shift of 60–40 cm^{-1} to lower frequency compared to the parent ligand. This shift might be due to bidentate chelation of the phosphazene ligand to zirconium. The relevant IR data are given in table 2.

The ^1H NMR spectra show the absence of –NH proton in the range 4.5–5.0 ppm, which is present in the parent ligands [17–22], indicating deprotonation of the phosphazene upon complexation to zirconium. The phenyl protons of $-PPh_2$ and –NPh in **2**, **4**, **6** and **8** were multiplets in the region 6.10–7.15 ppm and 7.10–8.40 ppm, respectively. The phenyl protons for PPh_2 in **1**, **3**, **5** and **7** were one multiplet in the region 7.20–8.40 ppm. The methyl protons of $-SiMe_3$ were a singlet at 0.12 ppm while methyl protons of isopropoxy are a doublet at 1.20–1.25 ppm. The presence of isopropoxy in the complexes was further supported by a multiplet due to –OCH in the region 3.35–4.80 ppm.

The ^{13}C NMR spectra (in $CDCl_3$) of these complexes do not show appreciable change in their chemical shifts. The chemical shift of $SiMe_3$ and isopropoxy were observed at 3.5–3.9 ppm and 25.5–27.9 ppm, respectively. The signal for the -OCH carbon was observed at 44.5–45.7 ppm. The resonances due to the phenyl carbons of both the $-PPh_2$ and –NPh moiety occurred in the region 130–138 ppm and 120–128 ppm, respectively.

In the ^{31}P spectra, only one singlet was observed in each complex with a downfield shift in the range 4–8 ppm compared to the parent ligand. Complexes of the

Table 3. ^{1}H, ^{13}C and ^{31}P NMR spectral data of cyclophosphazene complexes of zirconium(IV) in $CDCl_3$ (ppm).

		^{13}C Chemical shift					
Compound No.	^{1}H Chemical shift	$-SiMe_3$	$-PPh_2$	–NPh	$-CH_3$	–OCH	^{13}P Chemical shift
1	0.12, s, 18H(–SiMe3)	3.5, s	134–138, m	–	–	–	15.8, s
	7.20–8.30, m, 20H(–PPh2)	–	130–135, m	120–128	–	–	
2	6.20–6.95, m, 10H(–NPh)	3.9, s	134–138, m		–	–	16.2, s
	7.10–8.35, m, 20H(–PPh2)						
3	0.12, s, 36H(–SiMe3)	3.9, s	134–138, m	–	–	–	14.2, s
	7.20–8.40, m, 40H(–PPh2)						
4	6.20–7.15, m, 20H (–NPh)	–	130–135, m	120–126	–	–	15.3, s
	7.20–8.40, m, 40H (–PPh2)						
5	0.12, s, 18H(–SiMe3)	3.8, s	134–138, m	–	25.5, s	45.5, m	15.2, s
	1.25, d, 12H(–CH3)						
	3.57–4.20.10, m, 2H(–OCH)						
	7.20–8.40, m, 20H(–PPh2)						
6	1.25, d, 12H(–CH3)	–	130–135, m	121–128	26.5, s	45.7, m	14.9, s
	3.35–4.80, m, 2H(–OCH)						
	6.20–6.95, m, 10H(–NPh)						
	7.10–8.35, m, 20H(–PPh2)						
7	0.12, s, 36H(–SiMe3)	3.5, s	134–138, m	–	25.5, s	44.5, m	16.8, s
	1.20, d, 12H(–CH3)						
	3.35–4.80, m, 2H(–OCH)						
	7.10–8.30, m, 40H(–PPh2)						
8	1.24, d, 12H (CH3)	–	130–135, m	122–128	27.9, s	44.5, m	15.8, s
	3.60–4.20, m, 2H(–OCH)						
	6.10–6.95, m, 20H(–NPh)						
	7.10–8.35, m, 40H(–PPh2)						

s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet.

bis-phenylated phosphazene have more downfield shift (7–8 ppm) than derivatives of the *bis*-silylated phosphazene ligand (4–5 ppm). The chemical shifts occurred at 14.2–16.8 ppm. This downfield shift may be attributed to the bidentate linkage of the phosphazene with the zirconium. The occurrence of a singlet may also be correlated to the equivalence of the phosphorus nuclei as well as symmetric nature of the species.

The ^{1}H, ^{13}C and ^{31}P NMR spectral data of these complexes are summarized in table 3.

5. Structural features

Our efforts to get crystals for single crystal X-ray analysis were not successful. Therefore, it would not be possible to predict the precise structures of these complexes. However, on the basis of elemental analyses, molecular weight determinations and IR and NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopic studies and in conjunction with the literature reports [4–9, 13, 14], a trigonal bipyramidal geometry around zirconium in $[\mathrm{N(PPh_2\overline{NR)_2Z}rCl_3}]$ (**1** and **3**) and $[\mathrm{N(PPh_2\overline{NR)_2Z}rCl(OPr^i)_2}]$ (**5** and **7**) may plausibly be assigned whereas octahedral geometry around the zirconium in $[\{\mathrm{N(PPh_2\overline{NR)_2\}_2Z}rCl_2}]$ (**2** and **4**) and $[\{\mathrm{N(PPh_2\overline{NR)_2\}_2Z}r(OPr^i)_2}]$ (**6** and **8**) may be anticipated with the phosphazene moiety bound bidentate to zirconium (figures 1 and 2).

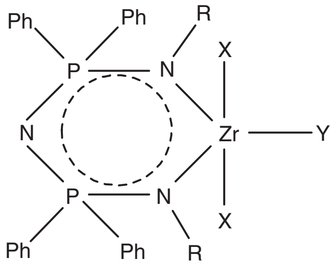


Figure 1. Trigonal bipyramidal geometry of $[\mathrm{N(PPh_2\overline{NR)_2Z}rCl_3}]$ (X and Y = Cl) and $[\mathrm{N(PPh_2\overline{NR)_2Z}rCl(OPr^i)_2}]$ (X = $\mathrm{OPr^i}$, Y = Cl) (where R = –Ph or –$\mathrm{SiMe_3}$).

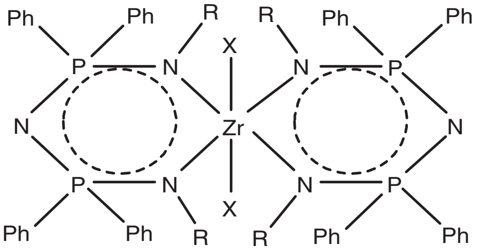


Figure 2. Octahedral geometry of $[\{\mathrm{N(PPh_2\overline{NR)_2\}_2Z}rX_2}]$ (X=Cl) and $[\{\mathrm{N(PPh_2\overline{NR)_2\}_2Z}rX_2}]$ (X = $\mathrm{OPr^i}$) (where R = –Ph or –$\mathrm{SiMe_3}$).

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