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Cyclometallaphosphazene Complexes of Titanium(IV)

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Cyclometallacyclophosphazene complexes of titanium(IV) corresponding to $[{N(PPh_2NR)_2}_nTiCl_{4-n}], [{N(PPh_2NR)_2}_nTiCl_{2-n}]$ $(OPr^{i})_{2}$], and $[{N(PPh_{2}NR)_{2}}_{n}^{\dagger} TiOGO(OPr^{i})_{2-n}](R = Ph \text{ or } SiMe_{3}, G = CH_{2}CH_{2}, n=1 \text{ or } 2)$ have been synthesized under anhydrous and inert conditions by the reaction of acyclic bis-silylated phosphazene ligand (A), [HN(PPh₂NSiMe₃)₂], or bis-phenylated ligand (B), [HN(PPh₂NPh)₂] phosphazene with TiCl₄. TiCl₂(OPrⁱ)₂ or TiOGO(OPrⁱ)₂ in 1:1 and 2:1 molar ratios. These titanatriazadiphosphorines were characterized by elemental analyses (C, H, N, Cl and Ti), molecular weight determination, and spectral studies including IR and NMR (¹H, ¹³C, and ³¹P), which have indicated monomeric nature of the complexes and bidentate mode of bonding by phosphazene moiety leading to a trigonal bipyramidal and octahedral geometries around the

Keywords metallatriazadiphosphorines, heterometallacyclophosphazenes, cyclotitanaphosphazenes, bis-silylated and bis-phenylated phosphazenes

titanium atom in 5 and 6 coordination numbers.

INTRODUCTION

Phosphazene chemistry has experienced a rapid growth during the past decade, stimulated by the wide interest into its fundamental as well as technological aspects, and perhaps represents next to the silicones which are the most intensively investigated inorganic non-metallic field. The 6-membered cyclotriazaphosphazene, (NPCl₂)₃, (2,2,4,4,6,6-hexasubstituted-1,3,5,2 λ^5 ,4 λ^5 ,6 λ^5 -triazatriphosphorines), is by far the

most investigated phosphorus-nitrogen compound, particularly, in view to its metathesis reactions with a wide variety of nucleophiles.^[1-5] Roesky et al. have synthesized several heterometallacyclophosphazenes by using acyclic phosphazene ligands, which have depicted rather interesting features both in view of their structure and utility.^[6-8] Phosphazene derivatives are well known as potential precursors in the field of ceramic and inorganic polymer chemistry.^[1,2,8,9] Phosphazene unit, $N=PR_2$, is isoelectronic to the siloxane group, $O = SiR_2$, that have a broad range of applications as fluids, greases, resins, elastomers and emulsions.^[10] Since, the cyclic titanaisiloxanes might act as precursor for high-temperature polymer, the thermal degradation of polytitanodimethylsiloxanes has been explored in detail.^[10] Literature survey revealed that transition metals as well as main group elements have been incorporated into the P-N ring system. which resulted the formation of numerous interesting phosphazene derivatives.^[11] We have also investigated the phosphazene chemistry during the past few years and incorporated several elements into the P-N ring skeleton.[12-17] It is observed that there is paucity of work on the chemistry of titanium(IV) cyclophosphazenes. Titanium(IV) compounds are known to possess significant antiproliferative effects toward some tumors and leukemia.^[18,19] The interest in the compounds of titanium is due to their activity as catalysts in the polymerization of olefins i.e., its pre-eminence in the Ziegler-Natta catalyst.^[20,21] In view of the above and knowing that TiCl₄,

 $TiCl_2(OPr^i)_2TiCl_2(OPr^i)_2$, and $OCH_2CH_2OTi(OPr^i)_2$ are good synthones for preparing titanium(IV) complexes, it was thought worthy to incorporate titanium into the P–N–P ring system. So, we report herein on the synthesis and characterization of the cyclotitanaphosphazenes corresponding to $[{N(PPh_2NR)_2}_nTiCl_{4-n}], [{N(PPh_2NR)_2}_nTiCl_{2-n}(OPr^i)_2]$ and $[{N(PPh_2NR)_2}_nTiOGO(OPr^i)_{2-n}].$

EXPERIMENTAL

Materials and Methods

Standard Schlenk techniques, N₂ atmosphere and vacuum line were used to carry out all manipulations. All solvents



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Dedicated to Professor Dr. Herbert W. Roesky on his 70th birthday.

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were distilled over sodium metal and degassed before use. The bis-silulated phosphazene ligand (A), $[HN(PPh_2NSiMe_3)_2]$ and bis-phenylated phosphazene ligand (**B**), $[HN(PPhNPh)_2]$ were prepared by literature method.^[15,22] High purity TiCl₄ was procured commercially (Aldrich) and used as received. TiCl₂(OPrⁱ)₂ and OCH₂CH₂OTi(OPrⁱ)₂ were prepared in the laboratory. Dichlorodiisopropoxytitanium(IV), TiCl₂(OPr¹)₂, was prepared by 1:2 molar reaction of titaniumtetrachloride with isoprapanol. Cycloethylenedioxydiisopropoxytitanium(IV), OCH₂CH₂OTi(OPrⁱ)₂, was synthesized by the reaction of $TiCl_2(OPr^i)_2$ with ethylene glycol in 1:1 molar ratio in the presence of triethylamine. Elemental analyses (C, H and N) were carried out in the Micro-analytical lab at Regional Research laboratory, Jammu. Titanium was estimated gravimetrically as TiO₂. Chlorine was estimated by Volhard's method whereas isopropoxy group was determined by potassium dichromate oxidation method. Molecular weights were determined cryoscopically in freezing benzene. IR spectra were recorded in KBr mulls in the range $4000-200 \text{ cm}^{-1}$ on a Perkin-Elmer 377 spectrophotometer. The ¹H, ¹³C, and ³¹P 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 ³¹P NMR.

Synthesis of $[{N(PPh_2NR)_2}_n TiCl_{4-n}]$ (R = Ph or SiMe₃, n = 1 or 2)

A weighed amount (1.70 g, 3.04 mmol) of bis-silylated phosphazene ligand, [HN(PPh₂NSiMe₃)₂], was dissolved in toluene $(\sim 30 \text{ ml})$ in a round bottom flask and then 0.58 g (3.05 mmol) of TiCl₄ solution in toluene (\sim 30 ml) alongwith equimolar amount of triethylamine was added to it dropwise under icecooled conditions. The contents were stirred at ice-cooled temperature for ~ 2 hours and subsequently at room temperature for \sim 2 hours, during this time the color of the reaction mixture was turned from pale yellow to reddish. The precipitates of triethylamine hydrochloride, Et₃NHCl, were filtered off by using alkoxy funnel fitted with a G-4 sintered disc and the excess of solvent was removed from the filtrate under reduced pressure which yielded the compound $[N(PPh_2NSiMe_3)_2TiCl_3]$ (1) as a reddish solid in 93% yield. All other analogous compounds (2-4) were prepared by a similar method and their synthetic and analytical data are given in Table 1.

Synthesis of $[{N(PPh_2NR)_2}_nTiCl_{2-n}(OPr^i)_2]$ (R = Ph or SiMe₃, n = 1 or 2)

A toluene solution (\sim 30 ml) of TiCl₂(OPr¹)₂ (0.50 g, 2.11 mmol) alongwith equimolar amount of triethylamine, Et₃N, (0.26 ml, 2.11 mmol) was added dropwise with stirring to a toluene solution (\sim 30 ml) of 1.18 g (2.11 mmol) of bis-silylated phosphazene ligand, [HN(PPh₂NSiMe₃)₂], at room temperature. The contents were stirred for 2 hours at room temperature and then refluxed for 3 hours. The color of the contents was changed from light yellow to pale yellow and precipitation of triethylamine hydrochloride, Et_3NHCl , took place. The precipitates of triethylamine hydrochloride were filtered off by using an alkoxy funnel fitted with a G-4 sintered disc and the excess of solvent was removed from the filtrate under reduced pressure, which yielded the compound $[N(PPh_2NSiMe_3)_2-$ TiCl(OPrⁱ)₂] (5) as yellow solid in 95% yield. All other analogous compounds (6–8) were prepared by a similar method, and their synthetic and analytical data are given in Table 1.

Synthesis of $[{N(PPh_2NR)_2}_n TiOGO(OPr^i)_{2-n}](R = Ph or SiMe_3, n = 1 or 2)$

A weighed amount of $OCH_2CH_2OTi(OPr^i)_2$ (0.41 g, 1.82 mmol) in 30 ml toluene was added dropwise to a toluene solution (~30 ml) of 1.02 g (1.82 mmol) of bis-silylated phosphazene ligand, [HN(PPh₂NSiMe₃)₂], at room temperature. The contents of the reaction mixture were first stirred at the same temperature for 1 hour and subsequently refluxed for 6 hours under ratio head, the color of the contents was changed to pale yellow. The isopropanol, formed during the course of reaction, was removed azeotropically at the rate of one drop per minute. The excess of solvent was removed under reduced pressure and dried finally for 2 hours *in vacuo*, which yielded the compound [N(PPh₂NSiMe₃)₂TiOGO(OPrⁱ)₂] (**9**) as yellow solid in 93% yield. All other analogous compounds (**10–12**) were prepared by a similar method, and their synthetic and analytical data are given in Table 1.

RESULTS AND DISCUSSION

Acyclic bis-silylated phosphazene (**A**), [HN(PPh₂NSiMe₃)₂], and bis-phenylated phosphazene (**B**), [HN(PPh₂NPh)₂], ligands are the new members of a fundamentally important class of nitrogen containing chelating ligands and known to form M-N bond with several transition as well as non-transition atoms. The acyclic bis-silylated phosphazene (**A**) and bis-phenylated phosphazene (**B**) ligands were reacted with titanium tetrachloride, TiCl₄, in 1:1 and 2:1 molar in presence of equimolar amount of triethylamine under anhydrous and inert conditions, which resulted the formation of compounds corresponding to [{N(PPh₂ NR)₂}_nTiCl_{4-n}] (R = Ph or SiMe₃, n = 1 or 2) (**1**–**4**) as reddish solid. These reactions were appeared to be quite facile as indicated by immediate precipitation of triethylamine hydrochloride, Et₃NHCl, in both 1:1 and 1:2 molar reactions (Scheme 1).

The yellow-colored solid compounds corresponding to formula $[{N(PPh_2NR)_2}_nTiCl_{2-n}(OPr^i)_2]$ (R = Ph or SiMe₃, n = 1 or 2) (**5**–**8**) have been isolated by the reaction of acyclic bis-phenylated phosphazene, $[HN(PPh_2NPh)_2]$, and bis-silylated phosphazene, $[HN(PPh_2NSiMe_3)_2]$, ligands with dichlorodiisopropoxytitanium(IV), $TiCl_2(OPr^i)_2$, in 1:1 and 2:1 molar ratio in toluene and also in the presence of equimolar amount of triethylamine (Scheme 1). These reactions were appeared to be rather sluggish, compared to the reactions with TiCl₄, as required refluxing for 4–6 hours.

5	Reactants		Molar		Vield ^a	MW found	Analysis (%) found (calcd.)				
no.	TiX ₄	gm (mmol)	(Ref.)	Product (Physical state)	$(m.p.)^b$	(calcd.)	Ti	Cl	С	Н	Ν
1	1.70 (3.041)	TiCl ₄ 0.58 (3.05)	1:1	[N(PPh ₂ NSiMe ₃) ₂ TiCl ₃] (Reddish solid)	93 (101)	711.1 (711.3)	6.76 (6.72)	14.94 (14.91)	50.59 (50.53)	5.43 (5.33)	5.72 (5.89)
2	1.17 (2.091)	TiCl ₄ 0.20 (1.05)	2:1	[{N(PPh ₂ NSiMe ₃) ₂ } ₂ TiCl ₂] (Reddish solid)	94 (98)	1240.9 (1234.8)	3.89 (3.87)	58.90 (5.47)	5.76 (58.30)	6.73(6.15)	6.49 (6.80)
3	1.73 (3.05)	TiCl ₄ 0.58 (3.05)	1:1	[N(PPh ₂ NPh) ₂ TiCl ₃] (Reddish solid)	92 (117)	730.5 (719.3)	6.34 (6.65)	14.67 (14.66)	59.68 (59.96)	4.26 (4.16)	6.02 (5.83)
4	1.18 (2.09)	$TiCl_4 0.20$ (1.05)	2:1	[{N(PPh ₂ NPh) ₂ } ₂ TiCl ₂] (Reddish solid)	95 (82)	1240.3 (1250.8)	3.73 (3.82)	5.87 (5.67)	69.73 (69.07)	4.31 (4.79)	6.83 (6.74)
5	1.18 (2.07)	$TiCl_2(OPr^i)_2$ 0.18 (1.04)	1:1 (4 h)	[N(PPh ₂ NSiMe ₃) ₂ TiCl(OPr ⁱ) ₂] (yellow solid)	95 (88)	760.3 (759.3)	6.45 (6.30)	4.69 (4.67)	56.38 (56.88)	6.39 (6.84)	5.09 (5.53)
6	0.68 (1.21)	$TiCl_2(OPr^i)_2$ 0.14 (0.60)	2:1 (6 h)	[{N(PPh ₂ NSiMe ₃) ₂ } ₂ Ti(OPr ⁱ) ₂] (yellow solid)	96 (94)	1290.5 (1281.8)	3.79	—	61.83 (61.78)	7.12 (7.02)	6.85 (6.55)
7	0.96 (1.69)	$\frac{\text{TiCl}_2(\text{OPr}^{i})_2}{0.40}$	1:1 (4 h)	[N(PPh ₂ NPh) ₂ TiCl(OPr ⁱ) ₂] (yellow solid)	95 (97)	780.4 (767.3)	6.24 (6.23)	4.63 (4.62)	65.47 (65.67)	5.47 (5.73)	5.51 (5.47)
8	1.53 (2.69)	$TiCl_2(OPr^i)_2$ 0.31 (1.30)	2:1 (4 h)	[N(PPh ₂ NPh) ₂ Ti(OPr ⁱ) ₂] (yellow solid)	92 (89)	730.2 (724.8)	3.69 (3.68)	—	71.93 (72.11)	5.59 (5.57)	6.57 (6.47)
9	1.02 (1.82)	$ \begin{array}{r} \overline{OGOTi(OPr^{i})_{2}} \\ 0.41 \\ (1.82) \end{array} $	1:1 (6 h)	$[N(PPh_2NSiMe_3)_2 TiogO(OPr^i)]$ (yellow solid)	93 (107)		6.73 (6.60)	—	56.72 (56.84)	6.21 (6.36)	5.31 (5.60)
10	1.08 (1.93)	OGOT i(OPr ⁱ) ₂ 0.21 (0.87)	2:1 (6 h)	[{N(PPh ₂ NSiMe ₃) ₂ } ₂ TiOGO] (yellow solid)	94 (120)	740.2 (732.8)	3.87 (3.91)	_	59.93 (60.10)	6.56 (6.46)	6.59 (6.78)
11	0.90 (1.58)	$\overrightarrow{OGOTi(OPr^{i})_{2}}$ 0.34 (1.58)	1:1 (6 h)	$[N(PPh_2NP)_2TiOGO(OPr^i)]$ (yellow solid)	95 (123)	—	_	6.54 (6.61)	65.71 (65.87)	5.58 (5.48)	5.59 (5.62)
12	1.65 (2.91)	OGOTi(OPr ⁱ) ₂ 0.32 (1.41)	2:1 (6 h)	$[{N(PPh_2NPh)_2}_2TiOGO] (yellow solid)$	93 (132)	1240.3 (1239)	3.89 (3.86)	_	73.96 (74.64)	5.12 (5.10)	6.71 (6.69)

 TABLE 1

 Synthetic and analytical data of cyclometallaphosphazene complexes of titanium(IV)

where $G = CH_2CH_2$, X = Cl, $Cl_2(OPr^i)_2$ or $OGO(OPr^i)$.

^{*a*}In % age.

^bIn [°]C.

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$$[HN(PPh_{2})_{2}NR] \xrightarrow{\text{TiCl}_{4}, \text{ Et}_{3}N} [\{N(PPh_{2}NR)_{2}\}_{n}\text{TiCl}_{4-n}]$$

$$[HN(PPh_{2})_{2}NR] \xrightarrow{\text{TiCl}_{2}(OPr^{i})_{2}} [\{N(PPh_{2}NR)_{2}\}_{n}\text{TiCl}_{2-n}(OPr^{i})_{2}]$$

$$\xrightarrow{\text{-nEt}_{3}NHCl} [\{N(PPh_{2}NR)_{2}\}_{n}\text{TiOGO}(OPr^{i})_{2-n}]$$

SCH. 1. Reactions of $[HN(PPh_2NR)_2]$ with TiCl₄, TiCl₂(OPrⁱ)₂ and \Box OCH₂CH₂OTi(OPrⁱ)₂ (R = Ph or SiMe₃, G = CH₂CH₂ and n = 1 or 2).

The pale yellow-colored solid compounds $[{N(PPh_2NR)_2}_n TiOGO(OPr^i)_2](9-12)$ were obtained when the acylic phosphazene ligands (A) or (B) were reacted with cycloethylenedioxydiisopropoxytitanium(IV), $OCH_2CH_2OTi(OPr^i)_2$ in 1:1 and 2:1 molar ratio in toluene. These reactions got completed on refluxing for longer time and simultaneous azeotropic removal of isopropanol.

These compounds were obtained with sufficient purity; however, the compounds (1-8) were further purified by washing with dried diethylether while the compounds (9-12)were washed with dried *n*-hexane. These heterometallacyclophosphazenes appeared to be moisture sensitive but can be stored for long without any aging phenomenon under dried atmosphere. Molecular weight determinations of these compounds have indicated the monomeric nature. The elemental analyses of these complexes, particularly C, H, N, Ti, Cl, and determination of isopropoxy were found to be consistent with their molecular compositions.

IR Spectra

The tentative assignments for important bands have been made on the basis of literature reports.^[7,8,11-14] The ring formation in these complexes is responsible for the appearance of some new bands, which are absent in the spectra of the parent ligands. The absorptions for $\nu(P-N)$ bands were found in the region 1284-1026 cm⁻¹, which is in agreement to the symmetric nature of $\nu(P-N-P)$ ring system. The disappearance of a strong band for ν (NH) at 3345 cm⁻¹ and the appearance of new bands in the region $520-513 \text{ cm}^{-1}$ are suggestive of formation of a Ti-N bond. The sharp bands of medium intensity in the region $360-340 \text{ cm}^{-1}$ have been assigned to $\nu(\text{Ti}-\text{Cl})$ in compounds (1-4) and the strong bands for $\nu(P = N)$ were found in the region $1497-1437 \text{ cm}^{-1}$ with a slight shift of $60-40 \text{ cm}^{-1}$ toward the lower frequency region. A strong band was also observed in the region $680-620 \text{ cm}^{-1}$, which is attributed to the Ti-O bond (5-12). The relevant IR data of these complexes are given in Table 2.

¹H NMR Spectra

In the ¹H NMR spectra of these complexes, the peak for the NH proton in the range $\delta 4.5-5.0$ ppm (present in the parent phosphazene ligands) was found absent, which indicates deprotonation of the ligand as a consequence of complexation to the titanium atom. The phenyl protons due to PPh₂ and NPh groups in the complexes with the bis-phenylated ligand, [HN(PPh₂NPh)₂], were found as two multiplets in the region $\delta 6.30-8.40$ ppm and the phenyl protons due to PPh₂ in the complexes with the bis-silylated phosphazene ligand,

S. no.	Compound	$\nu(P = N)$	ν (P-N-P) (Ring-vibrations)	ν(Ti-O)	ν(Ti-N)	v(Ti-Cl)
1	[N(PPh ₂ NSiMe ₃) ₂ TiCl ₃]	1437, vs	1219-1026	_	513, s	350, m
2	$[{N(PPh_2NSiMe_3)_2}_2TiCl_2]$	1437, vs	1260-1026		513, s	360, m
3	$[N(PPh_2NPh)_2TiCl_3]$	1497, vs	1284-1120		518, s	360, m
4	$[{N(PPh_2NPh)_2}_2TiCl_2]$	1490, vs	1280-1115		520, vs	340, m
5	[N(PPh ₂ NSiMe ₃) ₂ TiCl(OPr ⁱ) ₂]	1436, vs	1203-1026	620, s	515, vs	330, m
6	$[{N(PPh_2NSiMe_3)_2}_2Ti(OPr^i)_2]$	1436, vs	1203-1026	693, s	514, s	_
7	$[N(PPh_2NPh)_2TiCl(OPr^i)_2]$	1430, vs	1210-1120	685, s	515, vs	330, m
8	$[\{N(PPh_2NPh)_2\}_2Ti(OPr^i)_2]$	1497, vs	1261-1119	692, s	519, vs	
9	$[N(PPh_2NSiMe_3)_2TiOCH_2CH_2O(OPr^i)]$	1440, vs	1260-1110	680, vs	510, vs	
10	$[{N(PPh_2NSiMe_3)_2}_2TiOCH_2CH_2O]$	1420, vs	1230-1115	640, vs	520, vs	—
11	$[N(PPh_2NPh)_2TiOCH_2CH_2O(OPr^i)]$	1430, vs	1240-1090	630, s	515, vs	_
12	$[{N(PPh_2NPh)_2}_2TiOCH_2CH_2O]$	1420, vs	1200-1105	620, vs	510, vs	_

 TABLE 2

 IR data (cm⁻¹) of cyclometallaphosphazene complexes of titanium(IV)

Where vs = very strong, s = strong and m = medium.

[HN(PPh₂NSiMe₃)₂], were found as a single multiplet in the region $\delta 6.10-8.40$ ppm. The chemical shift of the methyl protons of SiMe₃ was observed around $\delta 0.12$ ppm, showing no appreciable change in position compared to the parent phosphazene moiety. The presence of isopropoxy group in the complexes (**5**-**9** and **11**) was confirmed by the appearance of the chemical shift for the methyl protons of the isopropoxy

group as well as OCH group. The chemical shift for the methyl protons was found as doublet in the region $\delta 0.75$ –1.60 ppm, while a quartet was observed for OCH group in the region $\delta 3.60$ –5.00 ppm. The chemical shift for OCH₂ group of glycoxy moiety was observed in the region $\delta 4.60$ –5.25 ppm. The ¹H NMR spectral data of these compounds are summarized in Table 3.

S. no.	Compound	¹ H chemical shift	³¹ P chemical shift
1	[N(PPh ₂ NSiMe ₃) ₂ TiCl ₃]	0.12, s, 18H (SiMe ₃)	15.04, s
		6.10-8.40, m, 20H (PPh ₂)	
2	$[{N(PPh_2NSiMe_3)_2}_2TiCl_2]$	0.10, s, 36H (SiMe ₃)	16.40, s
		6.30-8.40, m, 40H (PPh ₂)	
3	[N(PPh ₂ NPh) ₂ TiCl ₃]	6.50–6.90, m, 10H (NPh)	14.37, s
		7.55-8.40, m, 20H (PPh ₂)	
4	$[{N(PPh_2NPh)_2}_2TiCl_2]$	6.30–6.80, m, 20H (NPh)	15.34, s
		7.35-8.20, m, 40H (PPh ₂)	
5	$[N(PPh_2NSiMe_3)_2TiCl(OPr^i)_2]$	0.12, s, 18H (SiMe ₃)	16.19, s
		0.90–1.40, d, 12H (CH ₃)	
		4.60–5.00, m, 2H (OCH)	
		6.50-8.25, m, 40H (PPh ₂)	
6	$[{N(PPh_2NSiMe_3)_2}_2Ti(OPr^i)_2]$	0.13, s, 36H (SiMe ₃)	15.17, s
		0.90–1.40, d, 12H (CH ₃)	
		4.60–5.00, m, 2H (OCH)	
		6.50–8.25, m, 40H (PPh ₂)	
7	$[N(PPh_2NPh)_2TiCl(OPr^i)_2]$	0.75–1.60, d, 12H (CH ₃)	14.08, s
		3.60–4.20, m, 2H (OCH)	,
		6.20–6.95, m, 20H (NPh)	
		7.40–8.30, m, 40H (PPh ₂)	
8	$[{N(PPh_2NPh)_2}_2Ti(OPr^i)_2]$	0.75–1.60, d, 12H (CH ₃)	15.06, s
		3.60–4.20, m, 2H (OCH)	,
		6.20–6.95, m, 20H (NPh)	
		7.40–8.30, m, 40H (PPh ₂)	
9	[N(PPh ₂ NSiMe ₃) ₂ TiOCH ₂ CH ₂ O(OPr ⁱ)]	0.12, s, 36H (SiMe ₃)	19.89, s
		0.85–1.80, d, 12H (CH ₃)	
		3.65–4.30, m, 2H (–OCH)	
		4.60–5.25, t, 4H (OCH ₂)	
		6.50–8.30, m, 40H (PPh ₂)	
10	[{N(PPh ₂ NSiMe ₃) ₂ } ₂ TiOCH ₂ CH ₂ O]	0.12, s, 36H (SiMe ₃)	19.63, s
		4.60–5.25, t, 4H (OCH ₂)	
		6.50-8.30, m, 40H (PPh ₂)	
11	[N(PPh ₂ NPh) ₂ TiOCH ₂ CH ₂ O(OPr ⁱ)]	0.75-1.60, d, 12H (CH ₃)	14.03, s
		3.60–4.20, m, 2H (OCH)	
		4.60–5.25, t, 4H (OCH ₂)	
		6.50–8.30, m, 40H (PPh ₂)	
12	$[{N(PPh_2NPh)_2}_{2TiOCH_2CH_2O}]$	4.60-5.25, t, 4H (OCH ₂)	15.41, s
		6.50-8.30, m; 40H (PPh ₂)	- · , -

TABLE 3 ¹H and ³¹P NMR spectral data of cyclometallaphosphazene complexes of titanium(IV) in CDCl₃ in δ ppm

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

S. no	Compound	CH ₃	Ph	CH ₃	OCH		
1	[N(PPh ₂ NSiMe ₃) ₂ TiCl ₃]	3.5, s	120–139, m				
2	$[{N(PPh_2NSiMe_3)_2}_2TiCl_2]$	3.6, s	123–138, m				
3	[N(PPh ₂ NPh) ₂ TiCl ₃]	3.9, s	120–140, m				
4	$[{N(PPh_2NPh)_2}_2TiCl_2]$	3.8, s	122–138, m				
5	[N(PPh ₂ NSiMe ₃) ₂ TiCl(OPr ⁱ) ₂]	3.8, s	120–140, m	25.5, s	45.5, m		
6	$[{N(PPh_2NSiMe_3)_2}_2Ti(OPr^i)_2]$	3.7, s	122–140, m	22.5, s	44.5, m		
7	$[N(PPh_2NPh)_2TiCl(OPr^i)_2]$	3.5, s	120–140, m	26.5, s	45.7, m		
8	$[\{N(PPh_2NPh)_2\}_2Ti(OPr^i)_2]$	3.9, s	120–138, m	27.9, s	44.5, m		
9	[N(PPh ₂ NSiMe ₃) ₂ TiOCH ₂ CH ₂ O(OPr ⁱ)]	3.7, s	120–139, m	24.5, s	44.7, m		
10	$[\{N(PPh_2NSiMe_3)_2\}_2TiOCH_2CH_2O]$	3.6, s	120–140, m	26.5, s	45.5, m		
11	[N(PPh ₂ NPh) ₂ TiOCH ₂ CH ₂ O(OPr ⁱ)]	3.8, s	120–140, m	23.5, s	44.5, m		
12	$[{N(PPh_2NPh)_2}_2TiOCH_2CH_2O]$	3.8, s	120–138, m	27.9, s	45.7, m		

TABLE 4 ¹³C NMR spectral data of cvclometallaphosphazene complexes of titanium(IV) in δ ppm

Where s = singlet and m = multiplet.

¹³C NMR Spectra

The ¹³C NMR spectra of these complexes do not show any appreciable change in their chemical shift from the corresponding values of the parent acyclic phosphazene ligands. The chemical shift of the methyl carbons of the trimethylsilyl group was observed at $\delta 3.8-3.9$ ppm. The phenyl carbons occur as a multiplet in the region $\delta 120-140$ ppm. The chemical shift for the methyl carbons of the isoprpoxy group was observed at $\delta 25-30$ ppm and for the OCH₂ group was observed in the region $\delta 60-70$ ppm. The appearance of the chemical shift due to methyl carbon and the carbon of OCH₂ group authenticate the insertion of titanium atom into the phosphazene ring (Table 4).



FIG. 1. Trigonal bipyramidal geometry of the complexes $[N(PPh_2NR')_2-TiCl_3]$ (X and Y = Cl) and $[N(PPh_2NR)_2TiCl(OPr^i)_2]$ (X = OPrⁱ, Y = Cl) (where R = Ph or SiMe₃).



FIG. 2. Octahedral geometry of the complexes $[{N(PPh_2NR)_2}_2TiCl_2]$ (X = Cl) and $[{N(PPh_2NR)_2}_2Ti(OPr^i)_2]$ (X = OPrⁱ) (where R = Ph or SiMe_3).

³¹P NMR Spectra

In the ³¹P NMR spectra, only 1 singlet was observed in each complex with a downfield shift of δ 4–8 ppm compared to the parent acyclic bis-phenylated phosphazene ligand, [HN(PPh₂NPh)₂], and bis-silylated phosphazene ligand, [HN(PPh₂NSiMe₃)₂]. The chemical shift in these compounds occurs at δ 15–16 ppm. This downfield shift may be attributed to the bidentate linkage of the phosphazene ligand. Further, the



FIG. 3. Trigonal bipyramidal geometry of the complexes $[N(PPh_2NR)_2 \cap T_iOCH_2CH_2O(OPr^i)]$ (G = CH₂CH₂, R = Ph or SiMe₃).



FIG. 4. Octahedral geometry of the complexes $[{N(PPh_2NR)_2}_2 TiOCH_2CH_2O]$ (where $G = CH_2CH_2$, R = Ph or SiMe₃).

occurrence of a singlet may be due to the equivalent nature of the phosphorus nuclei in the molecule and also symmetric nature of species. The ³¹P NMR spectra of these complexes are summarized in Table 3.

Structural Features

Our efforts to get suitable crystals for the single-crystal X-ray analysis were not successful. Therefore, it is not possible to predict the precise structure of these complexes. However, on the basis of elemental analyses, molecular weight determinations and spectroscopic studies like IR and NMR (IR, ¹H, ¹³C, and ³¹P) and in conjunction with the literature reports, $[^{7,8,11-14,23-25]}$ a trigonal bipyramidal geometry around the titanium in the 5 coordination in the complexes [N(PPh₂NR)₂TiCl₃] (**1** and **3**) [N(PPh₂NR)₂TiCl₂(OPrⁱ)₂] (**5** and **7**), and [N(PPh₂NR)₂TiOCH₂CH₂O(OPrⁱ)] (**9** and **11**) may plausibly be assigned whereas an octahedral geometry around the titanium in six coordination for the complexes type [{N(PPh₂NR)₂TiCl₂] (**2** and **4**), [{N(PPh₂NR)₂]₂TiOCH₂CH₂O] (**10**

and 12) may be proposed in which the phosphazene moiety bonded with titanium in bidentate manner (Figures 1-4).

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