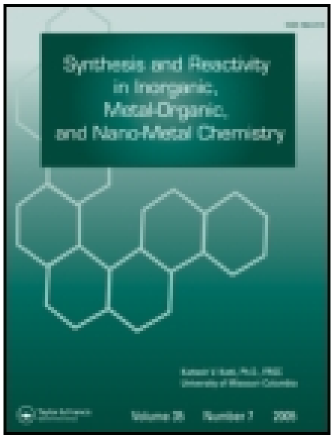
This article was downloaded by: [University of Victoria]
On: 18 November 2014, At: 23:23
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt20

Synthesis and Spectroscopic Studies of Group 6 Metal Carbonyl Complexes With a Novel Cyclotriphosphazane Ligand

Mitchell W. Denker [a] & Monte L. Helm [a]
[a] Department of Chemistry , Fort Lewis College , Durango, Colorado, USA

Published online: 15 Feb 2007.

To cite this article: Mitchell W. Denker & Monte L. Helm (2005) Synthesis and Spectroscopic Studies of Group 6 Metal Carbonyl Complexes With a Novel Cyclotriphosphazane Ligand, Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry, 35:3, 227-231, DOI: 10.1081/SIM-200052654

To link to this article: http://dx.doi.org/10.1081/SIM-200052654

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry, 35:227–231, 2005
Copyright © 2005 Taylor & Francis, Inc.
ISSN: 0094-5714 print / 1532-2440 online
DOI: 10.1081/SIM-200052654

Taylor & Francis
Taylor & Francis Group

Synthesis and Spectroscopic Studies of Group 6 Metal Carbonyl Complexes With a Novel Cyclotriphosphazane Ligand

Mitchell W. Denker and Monte L. Helm
Department of Chemistry, Fort Lewis College, Durango, Colorado, USA

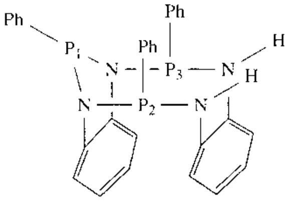
The syntheses and spectroscopic properties of Cr(0) and Mo(0) carbonyl complexes involving the novel cyclotriphosphazane $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2$ (1) are reported. The cyclotriphosphazane 1 is an interesting cyclic ligand that contains two unique types of phosphorus coordination environments as well as potential N-H reactivity. Reactions of 1 with one, two and excess molar equivalents of $M(CO)_5(THF)$ (M = Cr, Mo and W) were studied, leading to two new cyclophosphazane metal complexes $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2 \cdot 2M(CO)_5$ (M = Cr, Mo), where metal coordination is observed only to the phosphorus atoms that have their lone pair of electrons oriented exodentate to the phosphazane ring. The structures for the two new metal complexes are supported by ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectroscopy. The reaction of 1 with $W(CO)_5(THF)$ yields a mixture of ring opened and decomposition phosphazane products.

Keywords Chromium complexes; cyclophosphazane; molybdenum complexes; pentacarbonyl complexes; phosphazane

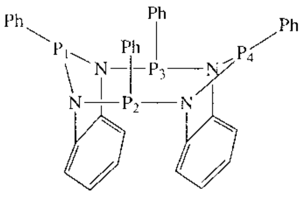
INTRODUCTION

Crown type compounds, host macrocycles containing at least two donor atoms, have found a wide use in a variety of areas (Bradshaw et al., 1996; Gokel et al., 2004; Lehn 1995; Nesterov 2000; Pederson et al., 2001). For example, they are often used to dissolve inorganic salts in organic solvents by forming coordinate covalent bonds with the metal ion in a molecular cavity. Although there are many sulfur and nitrogen analogs of the crown ethers, there are few that contain phosphorus donors (Blower et al., 1999; Baker et al., 2002; Caminade and Majoral et al., 1994; Coles et al., 1995; Diel et al., 1989; Edwards et al., 2000). Phosphorus-containing host molecules should be expected to have different properties than other main group analogs because phosphorus is a soft-base donor. Also, phosphorus has a higher barrier to pyramidal inversion, which should result in more rigid structures with well defined cavities. Examples of phosphorus-containing host molecules are known, many of which contain both phosphorus and heteroatom donor sites; however, there are few examples where the phosphorus atoms are held in fixed positions with their coordinating electrons in a protected area of reactivity.

Phosphazane compounds, compounds that contain phosphorus-nitrogen single bonds, have received recent attention for their metal coordinating properties (Balakrishna et al., 1994; Lief et al., 2004; Moser et al., 2003). For example, Krishnamurthy and co-workers have done extensive studies on the metal coordination of diphosphazane ligands with a variety of transition metals (Balakrishna et al., 1994; Mandal et al., 2003, 2003a; Raghuraman et al., 2003; Venkatakrishnan et al., 2003). Molecules that contain cavities or clefts can offer opportunities for a highly selective coordination of guest atoms or molecules, and the chemistry within these regions can be unique. Previously reported cyclophosphazanes, $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2$ (**1**) and $[C_6H_4N_2(PR)_2]_2$ (**2**), are examples of such molecules that possess structure rigidity and unique position of the phosphorus donor sites (Barendt et al., 1991a, 1991b). The cyclotetraphosphazane (**2**) incorporates an 8-member P-N ring where two phosphorus atoms, P(1) and P(4), have their lone pair electrons pointing endodentate to the phosphazane ring in a well defined cavity. This is in contrast to the P(2) and P(3) atoms that have their lone pair



1



2

Received 13 October 2004; accepted 10 November 2004.

We thank the Camille and Henry Dreyfus foundation, Research Corporation (DS0332) and Fort Lewis College for funding that supported this research.

Address correspondence to Monte L. Helm, Department of Chemistry, Fort Lewis College, Durango, CO 81301, USA. E-mail: helm_m@fortlewis.edu.

electrons oriented in an exodentate fashion to the ring. Compound **2** has been shown to selectively bind small metals, such as Ag^+, within the cavity while showing no affinity for larger metal ions such as Mo(0) (Young et al., 1995). To date, no such studies have been conducted with the cyclotriphosphazane (**1**). Previously reported structural studies of **1** have suggested the endodentate cavity is larger than the observed cavity in the cyclotetraphosphazane (**2**) (Helm et al., 1998). The cyclotriphosphazane (**1**) is also of particular interest because it not only contains phosphorus donor atom sites, but potential N-H reactivity to further derivatize the molecule or for use in other metal coordination studies (Spencer et al., 2004; Liang et al., 2004). In an attempt to elucidate the steric and electronic properties of the coordination chemistry of **1**, we conducted metal complexation studies using group 6 metal carbonyls. We now wish to report these metal coordination studies of the novel cyclotriphosphazane ligand (**1**) with $M(CO)_5(THF)$, M = Cr, Mo and W.

EXPERIMENTAL

Standard procedures for the manipulation of air-sensitive materials were employed. Unless otherwise stated, all manipulations were carried out at ambient temperature under an atmosphere of dry nitrogen gas using standard Schlenk, syringe and high vacuum-line techniques. Solvents were dried, freshly distilled under nitrogen, and degassed prior to use. All NMR spectra were recorded on a JEOL GSX-270 spectrometer (^1H NMR, 270.166 MHz; ^{13}C, 67.933 MHz; ^{31}P 109.365 MHz). The ^{31}P chemical shifts downfield from 85% H_3PO_4 (external) are reported as positive ($+\delta$). Infrared spectra were recorded with a Thermo Nicolet Avatar 360 FT-IR infrared spectrophotometer. The cyclotriphosphazane (**1**) was made according to a previously published procedure. (Helm et al., 1998)

Preparation of $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2 \cdot 2Cr(CO)_5$ (3)

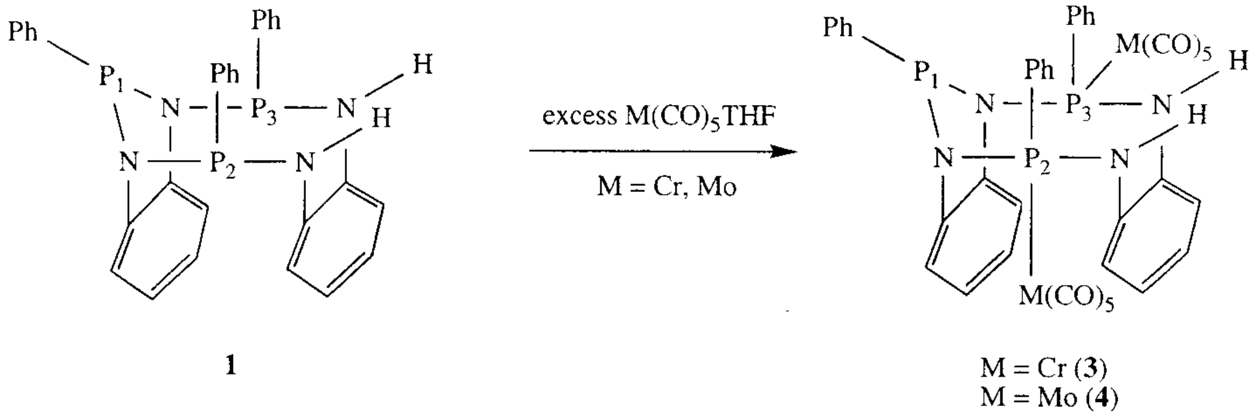
A two-fold excess of $[Cr(CO)_5THF]$ was prepared in a THF solution (46 mL) from $Cr(CO)_6$ (0.167 g, 0.76 mmol). Exactly 0.101 g (0.19 mmol) of $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2$ (**1**) in THF (5.0 mL) was added to $[Cr(CO)_5THF]$ solution and stirred for 3 h, during which the color changed from orange to yellow. After removal of the solvent, the dark yellow solid was dissolved in THF (10 mL) and filtered through a column of silica (230–400 mesh, 2 cm × 30 cm) using THF as the eluting solvent. The light yellow fractions were collected and solvents removed yielding pure **3** (0.136 g, 78% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 137.4 [d, area 2, $^2J_{PP} = 24.1$ Hz P(2,3)], 106.1 [t, area 1, P(1)]. ^1H NMR (C_6D_6): δ 7.84–7.59 [complex mult., area 4, C_6H_4], 7.45–7.39 [complex mult., area 4, C_6H_4], 6.87–6.83 [complex mult., area 15, $3C_6H_5$], 4.92 [broad s, area 2, 2NH]. IR (thf, ν_{CO}): 2068 w, 2012 vw, 1956 br. m, 1851 m cm^{-1}.

Preparation of $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2 \cdot 2Mo(CO)_5$ (4)

A two-fold excess of $[Mo(CO)_5THF]$ was prepared in a THF solution (54 mL) from $Mo(CO)_6$ (0.219 g, 0.83 mmol). Exactly 0.109 g (0.20 mmol) of $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2$ (**1**) in THF (5.0 mL) was added and the $[Mo(CO)_5THF]$ solution and stirred for 3 h, during which the color changed from light yellow to dark yellow. After removal of the solvent, the dark yellow solid was dissolved in THF (10 mL) and filtered through a column of silica (230–400 mesh, 2 cm × 30 cm) using THF as the eluting solvent. The light yellow fractions were collected and solvents removed yielding pure **4** (0.155 g, 56% yield). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 112.2 [d, area 2, $^2J_{PP} = 26.8$ Hz P(2,3)], 97.1 [t, area 1, P(1)]. ^1H NMR (C_6D_6): δ 7.96–7.79 [complex mult., area 4, C_6H_4], 7.51–7.46 [complex mult., area 4, C_6H_4], 6.91–6.84 [complex mult., area 15, $3C_6H_5$], 5.55 [broad s, area 2, 2NH]. IR (thf, ν_{CO}): 2073 w, 2032 vw, 1985 m, 1950 br. s, 1861 m cm^{-1}.

RESULTS AND DISCUSSION

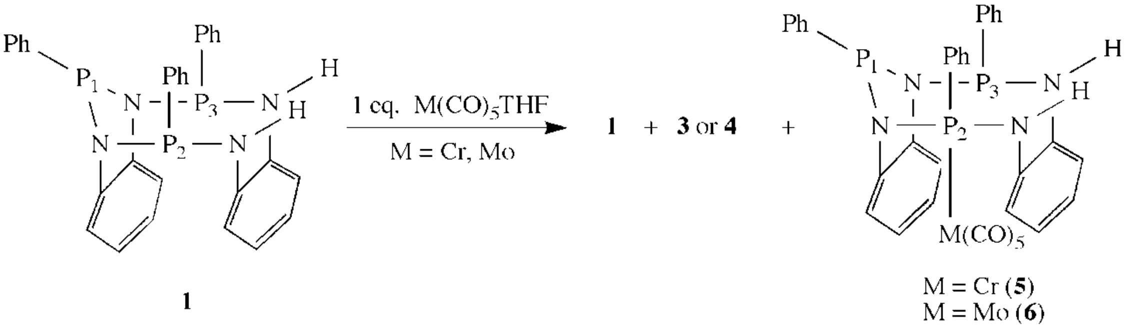
Reaction of the cyclotriphosphazane (**1**) with excess $M(CO)_5(THF)$ (M = Cr and Mo) yield the metal complexes $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2 \cdot 2Cr(CO)_5$ (**3**) and $(C_6H_4N_2)(PPh)_3C_6H_4(NH)_2 \cdot 2Mo(CO)_5$ (**4**) (Scheme 1). The presence



1

M = Cr (**3**)
M = Mo (**4**)

SCH. 1.



SCH. 2.

of **3** and **4** in their reaction mixtures can be initially identified by their distinct ^{31}P{^{1}H} NMR spectral resonances, which are sharp, well defined resonances shifted downfield from the free ligand. The reactions are carried out at room temperature and are complete in 3 h in near quantitative yield, as analyzed by ^{31}P{^{1}H} NMR spectroscopy. Separation from excess metal carbonyl and purification of the metal complexes is best accomplished by passing the solution through a column of silica.

Reaction of **1** with 1, 2 and excess equivalents of $W(CO)_5(THF)$ yield only ring opened and decomposed phosphazane products. Attempts to isolate any of the many reaction products were unsuccessful. Presumably, coordination of $W(CO)_5$ to **1** must create a steric or electronic environment that facilitates P-N bond cleavage resulting in the decomposition of the cyclotriphosphazane ligand.

Reactions of **1** with one equivalent of $M(CO)_5(THF)$ (M=Cr and Mo) yield a mixture of products including the bimetallic complexes (**3** or **4**), mono-metallic complexes (e.g., **5**, **6**) and un-reacted **1** as analyzed by ^{31}P{^{1}H} NMR spectroscopy (Scheme 2). Attempts to separate these reaction mixtures were unsuccessful. Although not isolated, compounds **5** and **6** can be identified in the reaction mixtures through their distinctive AMX ^{31}P{^{1}H} NMR splitting patterns. For example, compound **5** shows 38, 15 and 1 ppm downfield chemical shifts for P(2), P(1) and P(3) phosphorus atoms, respectively. The large downfield chemical shift for P(2) is due to direct metal coordination, whereas the smaller downfield shifts seen in P(1) and P(3) are due to inductive effects. The chemical shift assignments are also supported through $^2J_{PP}$ and $^4J_{PP}$ coupling constant data. This reaction indicates there is relatively no deactivation of the second 'side' phosphorus atom, P(2) or P(3), upon coordination of the first metal carbonyl. Somewhat surprisingly, even in the presence of excess metal carbonyl, we saw no indication of metal coordination to the center phosphorus atom, P(1), indicating this position is most likely too sterically hindered to allow for metal coordination of this type.

The ^{31}P{^{1}H} NMR spectra of the two complexes (**3** and **4**) show a simple doublet/triplet AX_2 splitting pattern with peak positions that clearly indicate formation of the metal complexes. In the case of **3**, the doublet from P(2,3) is shifted downfield 44 ppm relative to the free ligand (**1**), where the center phosphorus atom P(1) shows a 33 ppm downfield shift relative to the free ligand (Table 1). The downfield chemical shift observed for P(1) is most likely an inductive effect as a result of metal coordination to the nearby P(2) and P(3) atoms, as also observed in the mono-coordinated complexes (**5**, **6**). A similar trend in the downfield shifts are observed for **4** (Table 1). In addition to the changes in the chemical shifts, the $^2J_{PP}$ coupling constants increase to 24.1 Hz and 26.8 Hz for **3** and **4**, respectively, from 8.3 Hz as seen in the free ligand (**1**). The increase in phosphorus-phosphorus coupling constants upon metal coordination has been

TABLE 1
^{31}P{^{1}H} NMR, ^{1}H NMR and infrared data for **1**, **3** and **4**

Compound	^{31}P{^{1}H} NMR (ppm) P(1)	P(2,3)	^{1}H (ppm) N-H	IR (cm^{-1}) ν CO
1	73.2	93.4	5.88	—
3 (M = Cr)	106.1	137.4	4.92	2068 w, 2012 vw, 1956 br. m, 1851 m
4 (M = Mo)	97.1	112.2	5.55	2073 w, 2032 vw, 1985 m, 1950 br. s, 1861 m

previously observed in other phosphazane systems. (Young et al., 1994; 1995).

The ^1H and $^{13}C\{^1H\}$ NMR spectra also support formation of **3** and **4**. The ^1H NMR shows the expected aromatic peaks for the C_6H_5 and C_6H_4 rings ranging between 7.84–6.83 ppm and 7.96–6.84 ppm for **3** and **4**, respectively. The N-H peak, appears at 4.92 and 5.55 ppm for **3** and **4**, respectively, both shifted upfield from the free ligand N-H peak, which appears at 5.88 ppm (Table 1). The observed upfield chemical shift for the N-H peaks upon metal coordination may be a result of increased backbonding into a P-N antibonding orbital, thus increasing electron shielding around the hydrogen bonded to the nitrogen. The $^{13}C\{^1H\}$ NMR spectra for the two compounds are ambiguous because of phosphorus coupling and multiple overlapping peaks, but generally show a grouping of carbonyl carbon peaks and aromatic carbon peaks between 220–216 and 138–122 ppm, respectively, for **3** and 205–201 and 136–121 ppm, respectively, for **4**.

The IR spectra of the two complexes (Table 1) show multiple carbonyl stretching frequencies ranging from 2068–1851 cm^{-1} and 2073–1861 cm^{-1} for **3** and **4**, respectively, as expected for a low symmetry complex of this type.

CONCLUSIONS

The novel cyclophosphazane ligand (**1**) reacts readily with $M(CO)_5THF$, M=Cr, Mo, to form the new metal complexes **3** and **4**. This study indicates the 'side' phosphorus atoms, P(2,3), in **1** are less sterically hindered and more readily coordinate to group 6 metals than the center phosphorus atom, P(1). Future studies in our lab aim to use smaller metal ions to access the center phosphorus atom in **1** for coordination, as well as exploration of the N-H reactivity for potential cooperative coordination between the nitrogen atoms and center phosphorus atom, P(1).

REFERENCES

Baker, R. J.; Davies, P. C.; Edwards, P. G.; Farley, R. D.; Liyanage, S. S.; Murphy, D. M.; Yong, B. Early transition metal complexes of triphosphorus macrocycles. *Eur. J. Inorg. Chem.* **2002** (8), 1975–1984.

Balakrishna, M. S.; Reddy, V. S.; Krishnamurthy, S. S.; Nixon, J. F.; Burckett, J. C. T. R. Coordination chemistry of diphosphinoamine and cyclodiphosphazane ligands. *Coord. Chem. Rev.* **1994**, *129* (1–2), 1–90.

Barendt, J. M.; Bent, E. G.; Young, S. M.; Haltiwanger, R. C.; Norman, A. D. New orthocyclophane cyclotetraphosphazanes: $[C_6H_4N_2(PR)_2]_2$ (R=Ph, Me) and $[C_6H_4N_2(PPh)(PhPS)]_2$. *Inorg. Chem.* **1991a**, *30* (2), 325–331.

Barendt, J. M.; Haltiwanger, R. C.; Squier, C. A.; Norman, A. D. New classes of skeletally stabilized tri- and tetraphosphazanes. *Inorg. Chem.* **1991b**, *30* (10), 2342–2349.

Blower, P. J.; Chadwick, A. V.; Jeffery, J. C.; Mullen, G. E.D.; Powell, A. K.; Salek, S. N.; Smith, R. J.; Went, M. J. Synthesis and coordination chemistry of 1-phenyl-1-phospha-4,7-dithiacyclononane. *Inorg. Chim. Acta* **1999**, *294* (2), 170–178.

Bradshaw, J. S.; Izatt, R. M.; Bordunov, A. V.; Zhu, C. Y.; Hathaway, J. K. Crown ethers. *Comprehensive Supramolecular Chemistry*; Elsevier Science Ltd: Oxford, 1996; Vol. 1. pp. 35–95.

Caminade, A.-M.; Majoral, J. P. Synthesis of phosphorus-containing macrocycles and cryptands. *Chem. Rev.* **1994**, *94* (5), 1183–1213.

Coles, S. J.; Edwards, P. G.; Fleming, J. S.; Hursthouse, M. B. 1,5,9-Triphosphacyclododecane complexes of molybdenum and tungsten. Crystal structure of tricarbonyl[1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane]molybdenum(0). *J. Chem. Soc., Dalton Trans.* **1995** (7), 1139–1145.

Diel, B. N.; Brandt, P. F.; Haltiwanger, R. C.; Hackney, M. L. J.; Norman, A. D. Metal-templated synthesis of macrocyclic (triphosphine)molybdenum complexes. *Inorg. Chem.* **1989**, *28* (14), 2811–2816.

Edwards, P. G.; Whatton, M. L.; Haigh, R. A new nine-membered triphosphorus macrocycle. *Organometallics* **2000**, *19* (14), 2652–2654.

Gokel, G. W.; Leevy, W. M.; Weber, M. E. Crown ethers: sensors for ions and molecular scaffolds for materials and biological models. *Chem. Rev.* **2004**, *104* (5), 2723–2750.

Helm, M. L.; Noll, B. C.; Norman, A. D. New cleft-containing hetero-substituted cyclophosphazanes. *Inorg. Chem.* **1998**, *37* (18), 4478–4479.

Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinhein, 1995.

Liang, L.-C.; Lee, W.-Y.; Yin, C.-C. Nickel(II) complexes containing bidentate diarylamido phosphine ligands. *Organometallics* **2004**, *23*, 3538–3547.

Lief, G. R.; Moser, D. F.; Stahl, L.; Staples, R. J. Syntheses and crystal structures of mono- and bi-metallic zinc compounds of symmetrically- and asymmetrically-substituted bis(amino)cyclodiphosph(V)azanes. *J. Organomet. Chem.* **2004**, *689* (7), 1110–1121.

Mandal, S. K.; Krishnamurthy, S. S.; Nethaji, M. Organometallic chemistry of diphosphazanes. Part 19. Palladium-carbon s-bonded complexes bearing diphosphazane and diphosphazane monosulphide ligands. *Indian Journal of Chemistry, Section A: Inorganic, Bio-inorganic, Physical, Theoretical & Analytical Chemistry* **2003a**, *42A* (9), 2422–2426.

Mandal, S. K.; Nagana Gowda, G. A.; Krishnamurthy, S. S.; Nethaji, M. Palladium(II) allyl complexes of chiral diphosphazane ligands: ambident coordination behaviour and stereodynamic studies in solution. *J. Chem. Soc., Dalton Trans.* **2003** (5), 1016–1027.

Moser, D. F.; Grocholl, L.; Stahl, L.; Staples, R. J. Bis(tert-butylamido)- and bis(arylamido)cyclodiphosph(III)azane complexes of Ti, V, Zr and Hf: ligand substituent effects and coordination number. *J. Chem. Soc., Dalton Trans.* **2003** (7), 1402–1410.

Nesterov, S. V. Crown ethers in radiochemistry. Advances and prospects. *Russian Chemical Reviews* **2000**, *69* (9), 769–782.

Pederson, C. J.; Lehn, J. M.; Cram, D. J. Crowns and crypts: a fascinating group of multidentate macrocyclic ligands. *Resonance* **2001**, *6* (6), 71–79.

Raghuraman, K.; Krishnamurthy, S. S.; Nethaji, M. Late transition metal complexes derived from diphosphazane monosulfide ligands: X-ray crystal structures of $[Ru_3(m\text{-}CO)(CO)_7(\mu_3\text{-}S)\{Ph_2PN((S)\text{-}CHMePh)PPh_2\text{-}\kappa_2P,P\}]$ and $[Rh(CO)Cl\{Ph_2PN((S)\text{-}CHMePh)P(S)Ph_2\}\text{-}\kappa_2P,S]$

part 16. Organometallic chemistry of diphosphazanes. *J. Organomet. Chem.* **2003**, *669* (1–2), 79–86.

Spencer, L. P.; Winston, S. Tridentate amido carbene ligands in early-transition-metal coordination chemistry. *Organometallics* **2004**, *23*, 3372–3374.

Venkatakrishnan, T. S.; Nethaji, M.; Krishnamurthy, S. S. Ruthenium carbonyl cluster of diphosphazanes bearing axially chiral moieties. *Current Science* **2003**, *85* (7), 969–974.

Young, S. M.; Barendt, J. M.; Carperos, V.; Haltiwanger, R. C.; Hands, R. M.; Norman, A. D. Cleft reactivity in skeletally-stabilized cyclotetraphosphazanes. *Inorg. Chem.* **1995**, *34* (20), 5003–5012.

Young, S. M.; Tarassoli, A.; Barendt, J. M.; Squiers, C. A.; Barthelemy, F.; Schaeffer, R.; Haltiwanger, R. C.; Norman, A. D. Molecular cleft reactivity and conformational properties of skeletally stabilized triphosphazanes. *Inorg. Chem.* **1994**, *33* (13), 2748–2757.