

Simple tertiary phosphines to hexaphosphane ligands: Syntheses, transition metal chemistry and their catalytic applications

MARAVANJI S BALAKRISHNA*, SOWMYA RAO and BIMBA CHOUBEY

Department of Chemistry, Phosphorus Laboratory, Indian Institute of Technology Bombay, Mumbai 400 076, India
e-mail: krishna@chem.iitb.ac.in

Abstract. Designing efficient phosphorus-based ligands to make catalysts for homogeneous catalysis has been a great challenge for chemists. Despite a plethora of phosphorus ligands ranging from simple tertiary phosphines to polyphosphines are known, the enthusiasm to generate new ones is mainly due to the demand from industry for economical and robust catalytic system operational under normal atmospheric conditions. In this context, we have developed new synthetic methodologies for making unusual inorganic ring systems containing trivalent phosphorus centres, novel phosphorus-based multidentate and hybrid ligands and explored their rich transition metal chemistry and catalytic applications. We have also fine tuned a few existing ligand systems with donor functionalities to employ them in homogeneous catalysis. The details are summarized in this account.

Keywords. Phosphines; transition metal complexes; catalysis; carbon–carbon coupling reactions; hydrogenation reactions; multidentate ligands.

1. Introduction

The ceaseless curiosity in designing new types of phosphorus-based ligands is essentially due to their flexible coordination behaviour with both early and late transition metals and their applications in organic synthesis.¹ The undeniable fact is that they provide colossal agility in the incorporation of a range of steric and electronic attributes at phosphorus atoms that in turn facilitates the generation of appropriate metal complexes which can promote homogeneous catalysis under mild conditions with remarkable turnover numbers.²

We have designed several phosphorus-based ligands ranging from simple monodentate to tri-, tetra- or hexadentate systems and also modified a few existing ligands with donor functionalities and explored their rich transition metal chemistry³ and catalytic applications.⁴ The details of our contributions are briefly summarized.

2. 10-Membered heterocyclic diphosphanes

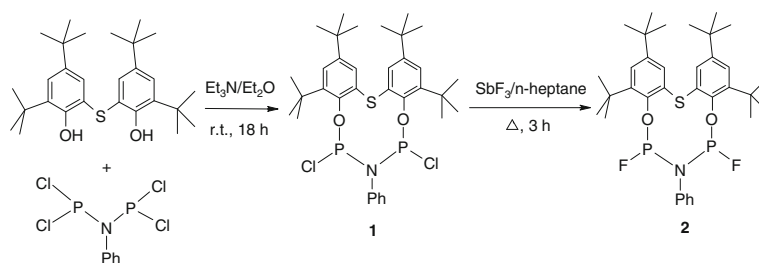
Bis(dichlorophosphino)aniline, $\text{PhN}(\text{PCl}_2)_2$ reacts with one equivalent of 2,2'-thiobis(4,6-di-*tert*-butylphenol) to afford a 10-membered heterocycle, $\text{PhN}(\text{PCl}_2)_2\{-(-\text{OC}_6\text{H}_2(\text{tBu})_2)(\mu\text{-S})(\text{tBu})_2\text{C}_6\text{H}_2\text{O}-)\}$ (**1**) in high yield (see scheme 1). The structure of the heterocycle **1** has been determined by a single-crystal X-ray

analysis. The 10-membered heterocycle **1** reacts with SbF_3 to afford the corresponding fluoro derivative **2** in good yield. The compounds **1** and **2** act as tridentate ligands with molybdenum carbonyl derivatives forming complexes of the type, $[\text{Mo}(\text{CO})_3\{\eta^3\text{-PhN}(\text{PX})_2\{-(-\text{OC}_6\text{H}_2(\text{tBu})_2)(\mu\text{-S})(\text{tBu})_2\text{C}_6\text{H}_2\text{O}-)\}\}]$ (**3**, $\text{X} = \text{Cl}$; **4**, $\text{X} = \text{F}$). A crystal structure of the fluoro derivative **4** showed the facial tricarbonyl complex comprising of a relatively strain free tetracyclic structure with molybdenum in an octahedral environment coordinated to two phosphorus and sulphur atoms.⁵ The heterocyclic diphosphane **2** readily reacts with various transition metal derivatives exhibiting η^2 and η^3 modes of coordination as shown in scheme 2.

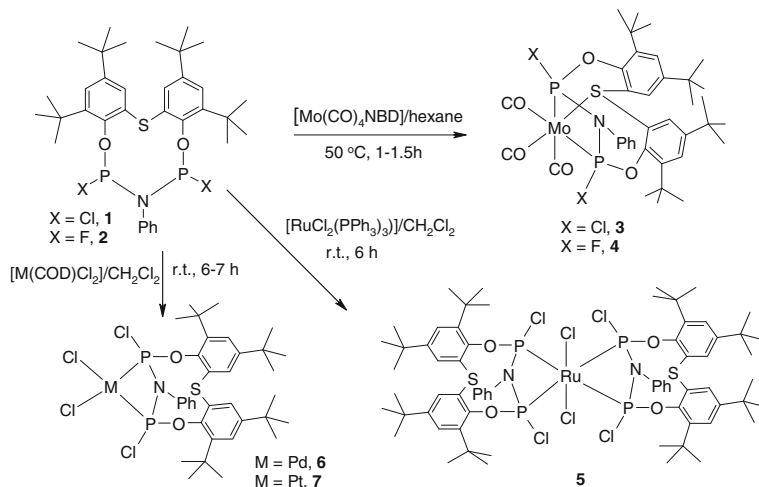
3. Transition metal derivatives of aminophosphines, $\text{Ph}_2\text{PN}(\text{H})\text{R}$ (**8**, $\text{R} = \text{Ph}$; **9**, C_6H_{11})

The reactions of aminophosphines, $\text{Ph}_2\text{PN}(\text{H})\text{R}$ (**8**, $\text{R} = \text{Ph}$; **9**, C_6H_{11}) with $\text{Pd}(\text{COD})\text{Cl}_2$ lead to the P–N bond cleavage to produce a chloro-bridged dimer, $[\text{Pd}(\text{PPh}_2\text{O})(\text{PPh}_2\text{OH})(\mu\text{-Cl})_2]$ (**10**), whereas with $\text{Pt}(\text{COD})\text{Cl}_2$, disubstituted complexes, *cis*- $[\text{PtCl}_2\{\text{PPh}_2\text{N}(\text{H})\text{R}\}_2]$ (**11**, $\text{R} = \text{Ph}$; **12**, C_6H_{11}) were obtained. The reaction of **8** or **9** with K_2PtCl_4 afforded the platinum complex, $[\text{Pt}\{\text{PPh}_2\text{O}\}_2\text{H}]_2$ (**13**), via P–N bond cleavage, as shown in scheme 3. The ^{31}P NMR spectrum of **13** shows a single resonance at 53.4 ppm with a $^1J_{\text{PtP}}$ coupling of 3958 Hz.⁶

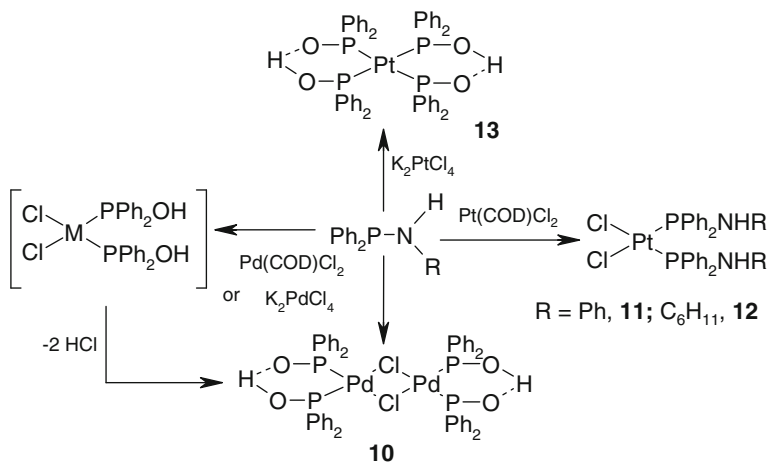
*For correspondence



Scheme 1. Preparation and fluorination of heterocyclic diphosphane **1**.



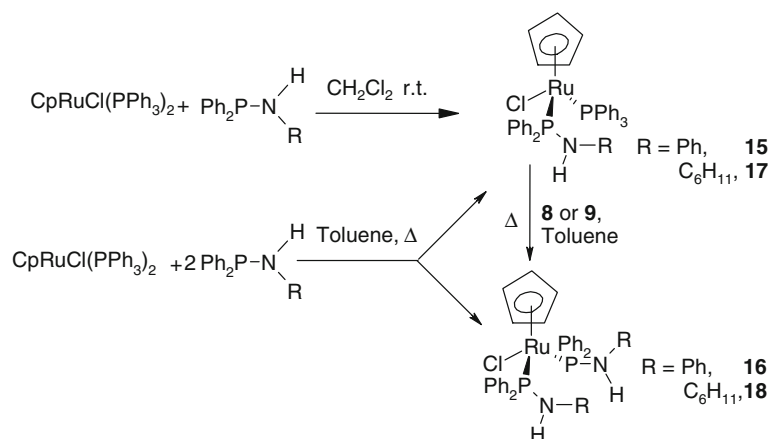
Scheme 2. Reactions of cyclodiphosphane **1**.



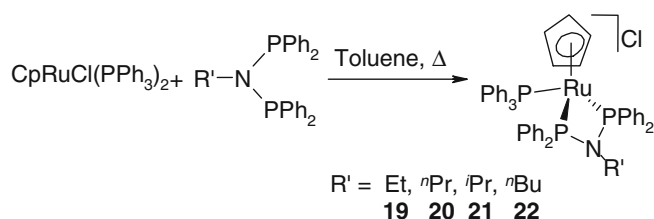
Scheme 3. Reactions of aminophosphine with Pd^{II} and Pt^{II} derivatives.

The reaction of **9** with either RuCl₂(DMSO)₄ or RuCl₂(PPh₃)₃ in 4:1 molar ratio yielded the ionic complex, [RuCl{Ph₂PN(H)C₆H₁₁}₃]Cl (**14**). The ³¹P NMR spectrum of **14** consists of a single resonance at 76.4 ppm indicating the tetrahedral nature of the molecule and the mass spectrum of the complex showed

a molecular ion peak (MS FAB: 986 [M⁺]) corresponding to the cationic species. The rare low-coordination of ruthenium in the molecule is attributed to the sterically demanding aminophosphine ligands. However, a trigonal bipyramidal geometry around the ruthenium(II) centre with two chlorides in axial positions and the three



Scheme 4. Preparation of ruthenium(II) complexes **15–18**.



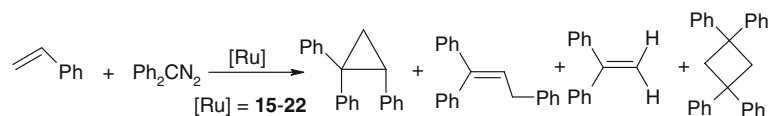
Scheme 5. Preparation of ruthenium(II) cationic complexes **19–22**.

phosphorus centres in the trigonal plane could not be ruled out as the ^{31}P NMR spectrum will show a single resonance.

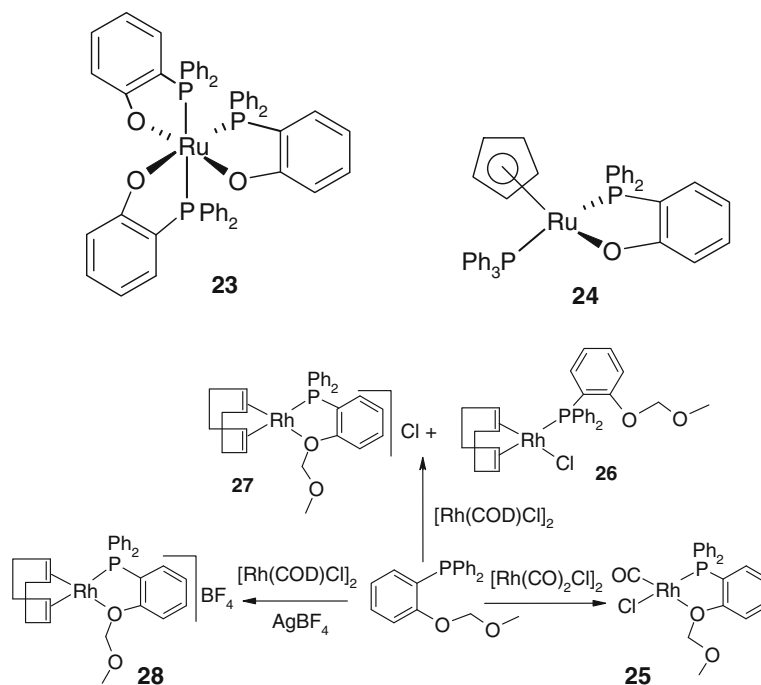
The reactions of aminophosphines, $\text{Ph}_2\text{PN(H)R}$ with $\text{CpRuCl(PPh}_3)_2$ afford monosubstituted $[\text{CpRuCl(PPh}_3)(\text{PPh}_2\text{N(H)R})]$ or disubstituted $[\text{CpRuCl(PPh}_2\text{N(H)R)}_2]$ complexes depending upon the stoichiometry and the reaction conditions. The reactions of $\text{Ph}_2\text{PN(H)R}$ ($\text{R} = \text{Ph}$, **8**; C_6H_{11} , **9**) with $[\text{CpRuCl(PPh}_3)_2]$ in dichloromethane in equimolar ratio at room temperature, gave $[\text{CpRuCl(PPh}_3)(\text{PPh}_2\text{N(H)R})]$ (**15**, $\text{R} = \text{Ph}$; **17**, C_6H_{11}) in good yield. The ^{31}P NMR spectra of complexes **15** and **17** show two doublets at 42.9, 72.4 ppm and 42.9, 77.9 ppm, respectively. The chemical shifts at high fields are due to the PPh_3 group whereas the aminophosphines appear at lower field. The $^2J_{\text{PRuP}}$ couplings are 42.4 and 48.5 Hz for complexes **15** and **17**, respectively. In contrast, the reactions of $[\text{CpRuCl(PPh}_3)_2]$ with **8** and **9** in 1:2 molar ratio in toluene at 80–90°C gave disubstituted complexes of the type, $[\text{CpRuCl(PPh}_2\text{N(H)R)}_2]$ (**16**,

$\text{R} = \text{Ph}$; **18**, C_6H_{11}) in ~75% yield containing trace amount of respective monosubstituted complexes, $[\text{CpRuCl(PPh}_3)(\text{PPh}_2\text{N(H)R})]$ (**15**, $\text{R} = \text{Ph}$, **15**; C_6H_{11} , **17**). The ^{31}P NMR spectra of complexes **16** and **18** showed single resonances at 72.6 and 81.8 ppm, respectively. The monosubstituted complexes **15** and **17** with an excess of the corresponding ligand also afforded the disubstituted complexes **16** and **18** as shown in scheme 4. The reactions of aminobis(phosphines), $\text{Ph}_2\text{PN(R)PPh}_2$ ($\text{R} = \text{Et}$, ^nPr , ^iPr , ^nBu) with equimolar quantity of $[\text{CpRuCl(PPh}_3)_2]$ yielded cationic complexes, $[\text{CpRu(PPh}_3)(\text{Ph}_2\text{PN(R)PPh}_2)]\text{Cl}$ ($\text{R} = \text{Et}$ (**19**), ^nPr (**20**), ^iPr (**21**), ^nBu (**22**)) in 50–60% yield (see scheme 5).

The half-sandwich ruthenium complexes were employed in the cyclopropanation reaction of styrene derivatives in the presence of diphenyldiazomethane. Interestingly, all complexes afforded 1,1,3,3-tetraphenyl cyclobutane along with cyclopropane derivatives with $[\text{CpRu(PPh}_2\text{N}^n\text{Bu)PPh}_2)(\text{PPh}_3)]\text{Cl}$ (**22**) showing better selectivity in the formation of 1,1,2-triphenylcyclopropane (see scheme 6). In all reactions, appreciable amounts of cyclopropanation and metathesis products, 1,2-diphenylcyclopropane and 1,1-diphenylethene, were obtained along with 1,1,3-triphenylpropene derivatives. The variable temperature ^1H NMR studies have suggested that the cyclopropanation reactions in the presence of ionic complex, $[\text{CpRu(PPh}_2\text{N(R)PPh}_2)(\text{PPh}_3)]\text{Cl}$ (**22**) proceeds via carbene intermediate, $[\text{CpRu(=CPh}_2)(\text{PPh}_2\text{N(R)PPh}_2)(\text{PPh}_3)]\text{Cl}$.⁷



Scheme 6. Cyclopropanation reactions catalysed by Ru^{II} -aminophosphine complexes.



Scheme 7. Rhodium complexes of functionalized phosphine { $\text{Ph}_2\text{PC}_6\text{H}_4(\text{OCH}_2\text{OMe}-o)$ }.

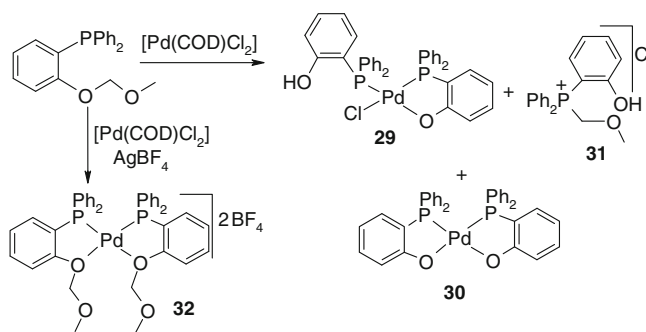
4. Phosphines with ether and alcohol functionalities

The chemistry of phosphine ethers is interesting due to the hemilabile nature of the ether oxygen which can coordinate to soft metals along with soft-phosphorus donors. Such complexes are very useful in homogeneous catalysis. Hemilabile phosphines can coordinate to the metal centre and stabilize it in lower oxidation state and enhance the chelating possibilities through ether O-centre. Further, the labile M–O coordinate bond can be readily cleaved as and when it is required during the catalytic and biological processes. In view of this, we have extensively studied⁸ the transition metal chemistry of phosphine ethers of the type $\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o$ and $\text{PhP}(\text{C}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o)_2$ and phosphinophenol, $\text{Ph}_2\text{PC}_6\text{H}_4\text{OH}-o$. The reaction of $\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o$ with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ gave trischelated octahedral ruthenium(III) complex, $[\text{Ru}(\text{Ph}_2\text{PC}_6\text{H}_4\text{O}-o)_3]$ (**23**) through metathetical elimination of three equivalents of $\text{CH}_3\text{OCH}_2\text{Cl}$, whereas the reaction with $\text{CpRu}(\text{PPh}_3)_2\text{Cl}$ resulted in the formation of $[\text{CpRu}(\text{Ph}_2\text{PC}_6\text{H}_4\text{O}-o)\text{PPh}_3]$ (**24**).

Treatment of $\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o$ with rhodium(I) derivatives resulted in the formation of complexes **25–28** with phosphine ligand exhibiting both mono- and bidentate modes of coordination involving the phosphorus centre and the phenolic oxygen as shown in scheme 7.

The reaction of $\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o$ with $[\text{PdCl}_2(\text{COD})]$ led to the isolation of two mononuclear complexes, $[\text{PdCl}(\text{Ph}_2\text{PC}_6\text{H}_4\text{O}-o)(\text{Ph}_2\text{PC}_6\text{H}_4\text{OH}-o)]$ (**29**) cocrystallized with phosphonium salt, $[\text{Ph}_2\text{P}(\text{CH}_2\text{OCH}_3)\text{C}_6\text{H}_4\text{OH}-o]\text{Cl}$ (**31**) and $[\text{Pd}(\text{Ph}_2\text{PC}_6\text{H}_4\text{O}-o)_2]$ (**30**) (see scheme 8) as confirmed by X-ray diffraction study. The former shows extensive hydrogen bonding interactions between the complex and the phosphonium salt. The reaction between $\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o$ and $[\text{PdCl}_2(\text{COD})]$ in the presence of AgBF_4 afforded cationic complex $[\text{PdCl}(\text{Ph}_2\text{PC}_6\text{H}_4\text{OCH}_2\text{OCH}_3-o)_2][\text{BF}_4]_2$ (**32**) in quantitative yield.

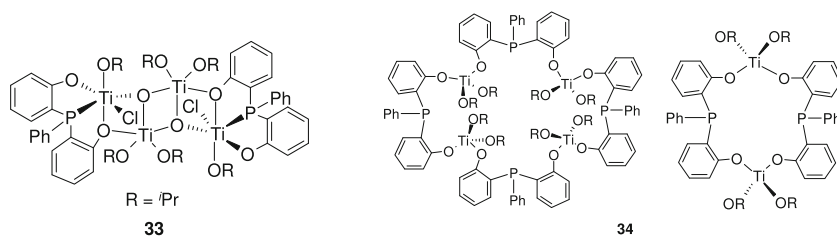
A novel tetranuclear titanium complex, $[(i\text{PrO})_2\text{-Ti}(\mu_3\text{-O})\text{TiCl}(i\text{PrO})((\text{OC}_6\text{H}_4)_2\text{PPh})_2]_2$ (**33**) containing penta- and hexacoordinated titanium centres was



Scheme 8. Palladium complexes of functionalized phosphine { $\text{Ph}_2\text{PC}_6\text{H}_4(\text{OCH}_2\text{OMe}-o)$ }.

obtained in the reaction of *bis(o-phenol)phenylphosphine* with titanium tetrachloride. The X-ray structure depicted the presence of both the bridging and the terminal isopropoxy groups.⁹ Although we anticipated a dimeric or tetrameric aryloxy complexes of the type **34** with uncoordinated phosphorus(III)

centres for possible coordination to low-valent platinum metals, the preferential binding of soft-phosphorus atoms to oxophilic titanium centres to form **33** is due to the diphenolate substituents on phosphorus centres, which bring the Ti and P atoms in close proximity to establish Ti–P bonds.



5. Large bite *bis*(phosphine) ligands

The ligating properties of bisphosphine ligands depend to a large extent on the nature of the spacer besides the phosphorus substituents. In stereogenic ligands such as binap, restricted rotations makes them ideal ligands for asymmetric synthesis. If the bulky groups can rotate freely about a pivoting group, the induced ring strain can facilitate the dissociation of one of the metal-phosphorus bonds so that a catalyst precursor may be generated.¹⁰ In such cases, the large bite angle will enhance the steric congestion around the metal centre, which favours the less sterically demanding transition state leading to selectivity in catalysis.¹¹ In view of this, several large-bite *bis*(phosphine) ligands were synthesized¹² and their transition metal chemistry and catalytic reactions were investigated.

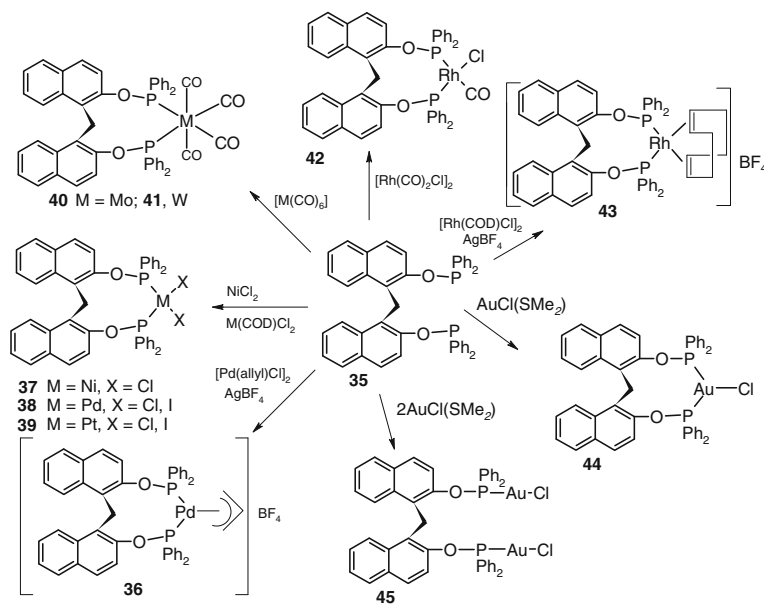
Bis(2-diphenylphosphinoxy-naphthalen-1-yl)methane (**35**) reacts with Group 6 metal carbonyls, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, anhydrous NiCl_2 , $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2/\text{AgBF}_4$ and $\text{M}(\text{COD})\text{X}_2$ to give the corresponding 10-membered chelate complexes **36–42** as shown in scheme 9. Reaction of **35** with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in the presence of AgBF_4 afforded a cationic complex, $[\text{Rh}(\text{COD})\{\text{Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O})\text{-PPh}_2\}]\text{BF}_4$ (**43**). Treatment of **35** with $\text{AuCl}(\text{SMe}_2)$ gives mononuclear chelate complex, $[(\text{AuCl})\{\text{Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O})\text{-PPh}_2\}]$ (**44**) as well as a binuclear complex, $[\text{Au}(\text{Cl})\{\mu\text{-Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O})\text{-PPh}_2\}\text{AuCl}]$ (**45**) with ligand **35** exhibiting both chelating and bridged bidentate modes of coordination respectively (see scheme 9). The mixture of $\text{Pd}(\text{OAc})_2$ and **35** effectively catalyses Suzuki cross-coupling reactions of a range of aryl halides

with aryl boronic acids in MeOH at room temperature or at 60°C, giving generally high yields even under low catalytic loads. The cationic rhodium(I) complex, $[\text{Rh}(\text{COD})\{\text{Ph}_2\text{P}(-\text{OC}_{10}\text{H}_6)(\mu\text{-CH}_2)(\text{C}_{10}\text{H}_6\text{O})\text{-PPh}_2\}]\text{BF}_4$ (**43**) catalyses the hydrogenation of styrenes to afford the corresponding alkyl benzenes at room temperature or at 70°C with excellent turnover frequencies.¹³

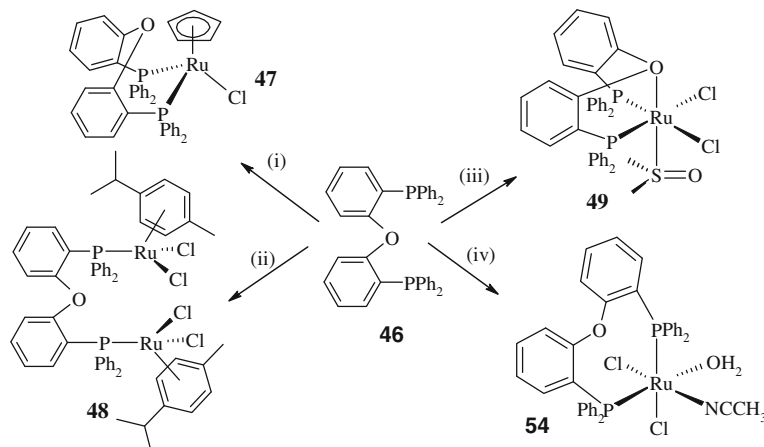
6. Diphenylether based bisphosphine and phosphino-phosphinimine ligands

The large bite *bis*(2-(diphenylphosphino)phenyl)ether (DPEphos) (**46**) with a relatively rigid diphenyl ether backbone and containing both oxygen and phosphorus donor sites¹⁴ offers different coordination modes exhibiting rich coordination and organometallic chemistry with various metal centres. van Leeuwen and coworkers¹⁵ have extensively studied the coordination chemistry and catalytic utility of DPEphos. As part of our research interest, we have investigated the ruthenium¹⁶ and copper¹⁷ chemistry DPEphos and also catalytic hydrogenation of styrene.

The half-sandwich complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{RuCl}(\text{DPEphos})]$ (**47**) and $[\{(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2\}_2(\mu\text{-DPEphos})]$ (**48**) were synthesized by the reaction of *bis*(2-(diphenylphosphino)phenyl)ether (DPEphos) (**46**) with a mixture of ruthenium trichloride trihydrate and cyclopentadiene and with $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$, respectively. Treatment of **46** with *cis*- $[\text{RuCl}_2(\text{dmsO})_4]$ afforded *fac*- $[\text{RuCl}_2(\eta^3\text{-DPEphos})(\text{dmsO})]$ (**49**). The dmsO ligand in **49** can be substituted by pyridine, 2,2'-bipyridine, 4,4'-bipyridine and PPh_3 to yield



Scheme 9. Reactions of **35** transition metal derivatives.

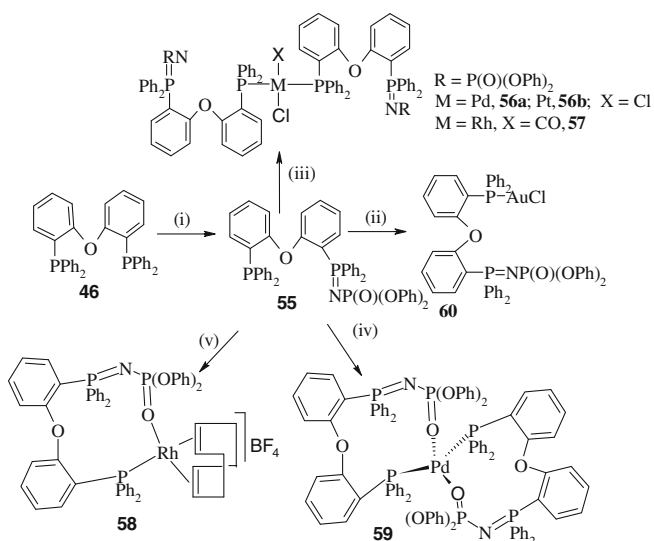


Scheme 10. Reactions of DPEphos with (i) $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ and Cp in ethanol; (ii) $[\text{RuCl}_2(p\text{-cymene})]_2$ in CH_2Cl_2 ; (iii) $\text{cis-}[\text{RuCl}_2(\text{dmsol})_4]$ in CH_2Cl_2 ; (iv) $[\text{RuCl}_2(p\text{-cymene})]_2$ in CH_3CN .

trans,cis- $[\text{RuCl}_2(\text{DPEphos})(\text{C}_5\text{H}_5\text{N})_2]$ (**50**), *cis,cis*- $[\text{RuCl}_2(\text{DPEphos})(2,2'\text{-bipyridine})]$ (**51**), *trans,cis*- $[\text{RuCl}_2(\text{DPEphos})(\mu\text{-}4,4'\text{-bipyridine})]_n$ (**52**) and *mer,trans*- $[\text{RuCl}_2(\eta^3\text{-DPEphos})(\text{PPh}_3)]$ (**53**), respectively. Refluxing $[(\eta^6\text{-}p\text{-cymene})\text{RuCl}_2]_2$ with DPEphos in moist acetonitrile leads to the elimination of the *p*-cymene group and the formation of the octahedral complex *cis,cis*- $[\text{RuCl}_2(\text{DPEphos})(\text{H}_2\text{O})(\text{CH}_3\text{CN})]$ (**54**) (see scheme 10). The catalytic activity of these complexes for the hydrogenation of styrene is studied.¹⁷

7. Iminophosphoranephosphine ether as a heterodifunctional ligand

Partially oxidized hemilabile iminophosphoranephosphane ligand **55** was synthesized by treating bis[2-(diphenylphosphanyl)phenyl]ether (**46**) with phosphoryl azide by Staudinger reaction.¹⁸ The iminophosphorane shows both monodentate and bidentate chelating coordination modes. The platinum(II), palladium(II), and rhodium(I) complexes **56a**, **56b**, and **57**, respectively, are obtained as *trans* isomers as shown



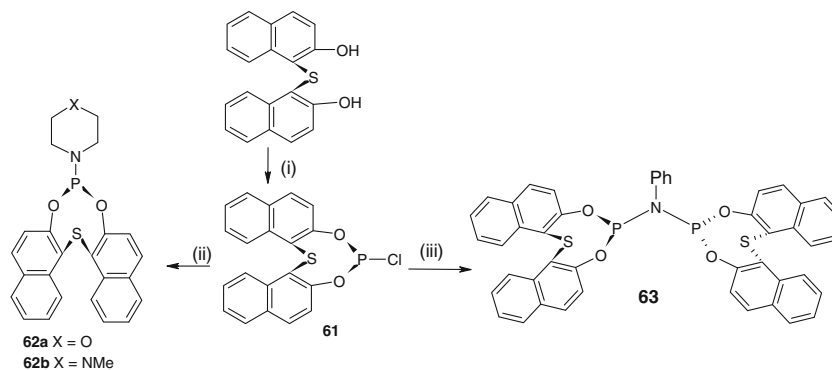
Scheme 11. Reactions of DPEphos with (i) $N_3P(O)(OPh)_2$ in CH_3CN ; (ii) $AuCl(SMe_2)$ in CH_2Cl_2 ; (iii) $M(COD)Cl_2$ or $[Rh(CO)_2Cl]_2$ in CH_2Cl_2 ; (iv) Pd_2dba_3 in C_6H_6 ; (v) $[Rh(COD)Cl]_2$, $2AgBF_4$ in CH_2Cl_2 .

in scheme 11. The reaction of 55 with $[Rh(COD)Cl]_2$ and $AgBF_4$ produced the 11-membered macrocyclic square-planar complex 58 with iminophosphorane ligand showing chelating-bidentate mode of coordination. The cationic rhodium(I) complex 58 is catalytically active for the hydrogenation of olefins with a TON of 2×10^5 and a TOF of $6 \times 10^5 \text{ h}^{-1}$. The Pd^0 complex 59, in which ligand 55 binds in a chelating fashion, was synthesized by the reaction of 55 with $[Pd_2(dba)_3]$. The Pd^0 complex 59 is catalytically active for Suzuki cross-coupling reactions of various aryl bromides and phenylboronic acid. A lower catalytic loading of 0.05 mol% of 59 allows complete conversion of several aryl bromides into biaryls.

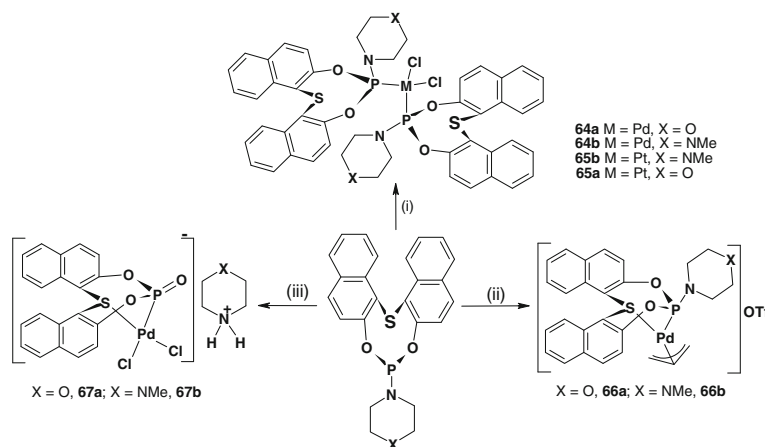
8. Mesocyclic thioetherphosphonites

The coordination chemistry and catalytic utility of ether and diphenyl ether-based ligands have been studied. However, the corresponding thioether-based bisphosphines or phosphonites are less extensive. Ligands combining phosphorus centres as well as sulphur centres are especially interesting. Both phosphorus and sulphur are excellent donor atoms for a wide range of transition metals, while the low ionization energy of sulphur and the existence of several lone pair of electrons (three in the case of a thiolate anion) offer the possibility of a rich sulphur-based chemistry of the complexes. To the best of our knowledge, there are no reports on cyclic thioether-aminophosphonite type of ligands, either in coordination chemistry or in catalysis. Holmes and co-workers have reported several eight-membered cyclic P, S compounds where sulphur shows coordinative interaction towards phosphorus.¹⁹ They have shown that the donor action provided by sulphur leads to an increase in coordination at phosphorus from tricoordinate to pseudopentacoordinate. However, there are no reports on coordination behaviour or catalytic activity of such ligands. It will be interesting to see the coordination chemistry of such ligands as sulphur shows coordinative tendency towards phosphorus. In this context, following mixed P, S mesocyclic ligands were prepared and their transition metal chemistry and catalytic reactions were investigated (scheme 12).

Mesocyclic thioether-aminophosphonite ligands, $\{-OC_{10}H_6(\mu-S)C_{10}H_6O-\}PNC_4H_8O$ (62a) and $\{-OC_{10}H_6(\mu-S)C_{10}H_6O-\}PNC_4H_8NCH_3$ (62b) are obtained by reacting $\{-OC_{10}H_6(\mu-S)C_{10}H_6O-\}PCl$ (61) with corresponding nucleophiles.²⁰ Similar reaction with aniline led to the isolation of nitrogen bridged bis(phosphonite) 63 in good yield.²¹ The ligands 62a and 62b react with $(PhCN)_2PdCl_2$ or $M(COD)Cl_2$ ($M = Pd^{II}$ or Pt^{II}) to



Scheme 12. (i) PCl_3 , Et_3N , DMAP, $-20^\circ C$, THF; (ii) morpholine or *N*-methyl piperazine, $0^\circ C$, THF; (iii) $PhNH_2$, Et_3N , DMAP, Et_2O .



Scheme 13. (i) $M(\text{COD})\text{Cl}_2$, CH_2Cl_2 , 25°C ; (ii) $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2/\text{AgOTf}$, CH_2Cl_2 , 25°C ; (iii) $(\text{PhCN})_2\text{PdCl}_2$, H_2O (trace), toluene, 90°C .

afford P-coordinated *cis*-complexes, $[\{(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O})\text{-PNC}_4\text{H}_8\text{X}\}_2\text{MCl}_2]$ (**64**, $M = \text{Pd}$; **65**, $M = \text{Pt}$) as shown in scheme 13. Compounds **62a** and **62b** on treatment with $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2$ in the presence of AgOTf produce the P, S-chelated cationic complexes, $[\{(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O})\text{-PNC}_4\text{H}_8\text{X}\}\text{Pd}(\eta^3\text{-C}_3\text{H}_5)](\text{CF}_3\text{SO}_3)$ (**66a**, $X = \text{O}$; **66b**, $X = \text{NMe}$). Treatment of **62a** and **62b** with $(\text{PhCN})_2\text{PdCl}_2$ in the presence of trace amount of H_2O afforded P, S-chelated anionic complexes, $[\{(-\text{OC}_{10}\text{H}_6(\mu\text{-S})\text{C}_{10}\text{H}_6\text{O})\text{-P(O)}\}\text{PdCl}_2](\text{H}_2\text{NC}_4\text{H}_8\text{X})$ (**67a**, $X = \text{O}$, **67b**, $X = \text{NMe}$), via P–N bond cleavage. The crystal structures of most of these compounds have been determined by X-ray diffraction studies. The compound **67a** is a rare and first example of crystallographically characterized anionic transition-metal complex containing a thioether-phosphonate ligand.^{20a} The reactions of thioether-aminophosphonites with $\text{Pt}(\text{COD})\text{Cl}_2$ gave exclusively phosphorus coordinated *cis*-complexes with high σ -donor strength. Most of these palladium complexes proved to be very active catalysts for the Suzuki–Miyaura, Heck–Mizoroki carbon–carbon cross coupling and amination reactions with excellent turnover numbers (TON up to 9.2×10^4 using complex **67a** as catalyst).²¹

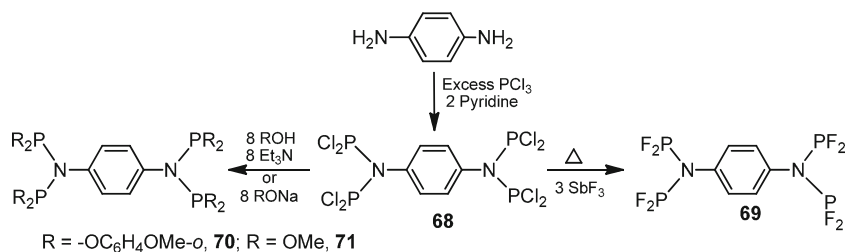
9. Tetra- and hexaphosphane ligands

The chemistry of Group 11 metal complexes in their +1 oxidation state have attracted much attention due to their catalytic applications,²² role in biochemistry²³ and photochemical areas.²⁴ Also, Group 11 metals serve as versatile connecting nodes for the synthesis of supramolecular architectures through the use of

dynamic coordination chemistry and weak $d^{10}\text{-}d^{10}$ metallophilic interactions²⁵ involving rigid *N*-donor ligands, such as 4,4'-bipyridine, 4,4'-dibenzonitrile, pyrazine which can offer multi-dimensional, metal–organic materials with diverse properties. 4,4'-Bipyridine has served as an effective bridging group and hundreds of interesting supramolecular architectures have been reported.²⁶ Instances of the use of rigid linear phosphines, analogous to 4,4'-bipyridine, in the synthesis of polynuclear complexes are less extensive.²⁷ In this context, we have designed novel tetraphosphane ligands of the type $\{(X_2\text{P})_2\text{NC}_6\text{H}_4\text{N}(\text{PX}_2)_2\}$ and explored their rich transition metal chemistry and catalytic applications. These tetraphosphanes can be compared to two 4,4'-bipyridine units fused sideways containing both electronically and sterically tunable phosphorus donor centres. A few important reactions of these ligands with transition metals are described.

The reaction of *p*-phenylenediamine with excess of PCl_3 in the presence of pyridine affords $(\text{Cl}_2\text{P})_2\text{NC}_6\text{H}_4\text{N}(\text{PCl}_2)_2$ (**68**) in good yield. Fluorination of **68** with SbF_3 produces $(\text{F}_2\text{P})_2\text{NC}_6\text{H}_4\text{N}(\text{PF}_2)_2$ (**69**) in moderate yield.²⁸ The aminotetra(phosphonites), *p*- $\text{C}_6\text{H}_4[\text{N}\{\text{P}(\text{OC}_6\text{H}_4\text{OMe-}o)_2\}_2]_2$ (**70**) and *p*- $\text{C}_6\text{H}_4[\text{N}\{\text{P}(\text{OMe})_2\}_2]_2$ (**71**) have been prepared by reacting **68** with appropriate amount of 2-(methoxy)-phenol or methanol, respectively, in the presence of triethylamine (see scheme 14).

Interestingly, the compounds of the type **68–71** can adopt several conformations depending upon the orientation of the P–N–P skeleton with respect to the phenylene ring. Three major idealized possibilities are: (i) both phenylene and P–N–P skeletons can be coplanar; (ii) the phenylene ring can be perpendicular to the P–N–P skeletons; (iii) the phenylene and one of the



Scheme 14. Preparation of octachlorotetraphosphane and its derivatives.

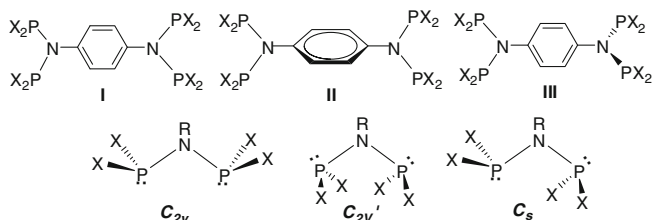


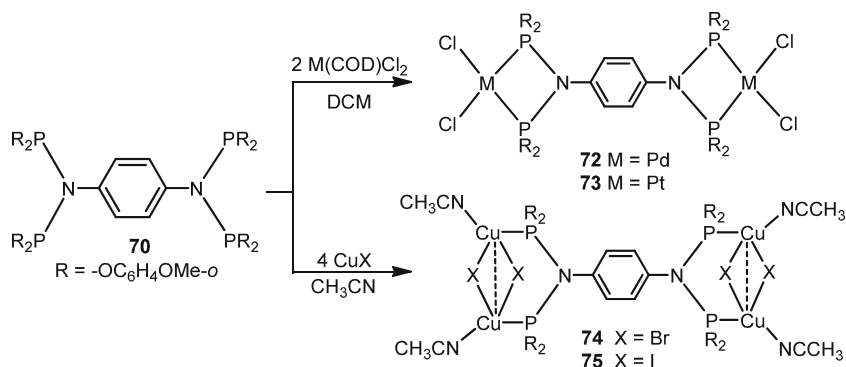
Chart 1. Possible conformations of tetraphosphane derivatives.

P–N–P skeletons can be in one plane and orthogonal to the other P–N–P skeleton. Further, the P–N–P moieties in each conformation can adopt C_{2v} , C_{2v}' or C_s conformations depending on the mutual orientation of phosphorus lone pairs with respect to the phosphorus-substituents as shown in chart 1, so there is a total of 18 possible conformations.

Reactions of **70** with $[\text{M}(\text{COD})\text{Cl}_2]$ ($\text{M} = \text{Pd}$ or Pt) resulted in the formation of chelate complexes, $[\text{M}_2\text{Cl}_4\text{-}p\text{-C}_6\text{H}_4\{\text{N}\{\text{P}(\text{OC}_6\text{H}_4\text{OMe-}o)_2\}_2\}_2]$ (**72**, $\text{M} = \text{Pd}$; **73**, $\text{M} = \text{Pt}$). The reactions of **70** with four equivalents of CuX ($\text{X} = \text{Br}$ and I) produce the tetranuclear complexes, $[\text{Cu}_4(\mu_2\text{-X})_4(\text{NCCH}_3)_4\text{-}p\text{-C}_6\text{H}_4\{\text{N}\{\text{P}(\text{OC}_6\text{H}_4\text{OMe-}o)_2\}_2\}_2]$ (**74**, $\text{X} = \text{Br}$; **75**, $\text{X} = \text{I}$) in quantitative yield as shown in scheme 15. The

molecular structures of many of these compounds are confirmed by single crystal X-ray diffraction studies.²⁹ The weak intermolecular $\text{P} \cdots \text{P}$ interactions observed in **68** leads to the formation of a 2-D sheet like structure (figure 1) which is also examined by DFT calculations. The palladium(II) complex **72** is an efficient catalyst for the coupling of several activated and deactivated aryl bromides and chlorides with phenylboronic acid and also for the one-pot multiple carbon–carbon couplings at room temperature.

The reactions of **70** with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in 1:2 and 1:1 molar ratio gave chelate complexes, $[\text{Rh}_4(\text{COD})_2\text{-}(\mu\text{-Cl})_4\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]$ (**76**) and $[\text{Rh}_2(\mu\text{-Cl})_2\text{-}\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]_n$ (**77**), whereas similar reaction of **71** with $[\text{Rh}(\text{COD})\text{Cl}]_2$ in dichloromethane–acetonitrile mixture gave a dinuclear complex, $[\text{Rh}_2\text{Cl}_2(\text{CH}_3\text{CN})_2\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]$ (**78**). The reaction of **77** or **78** with CO afforded a dinuclear carbonyl derivative, $[\text{Rh}_2\text{Cl}_2(\text{CO})_2\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]$ (**79**) (see scheme 16). Treatment of **78** with two equivalents of pyrazine or 4,4'-bipyridine produced one-dimensional coordination polymers, $[\text{Rh}_2\text{Cl}_2\text{-}(\text{C}_4\text{H}_4\text{N}_2)\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]_n$ (**80**) (figure 2) and $[\text{Rh}_2\text{Cl}_2(\text{C}_{10}\text{H}_8\text{N}_2)\{\text{R}_2\text{PN}(\text{C}_6\text{H}_4)\text{NPR}_2\}]_n$ (**81**), in quantitative yield.³⁰ These polymers have the metals in conjugation with aromatic π -systems through P–N–P skeletons with P–N bonds showing multiple bond



Scheme 15. Palladium, platinum and copper complexes of **70**.

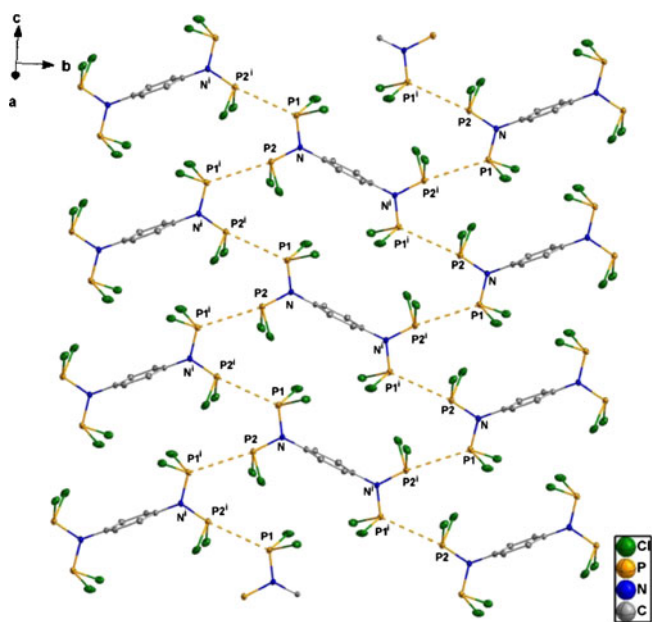
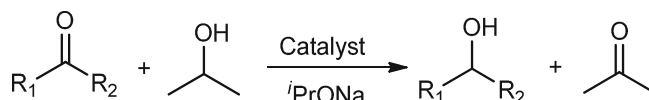


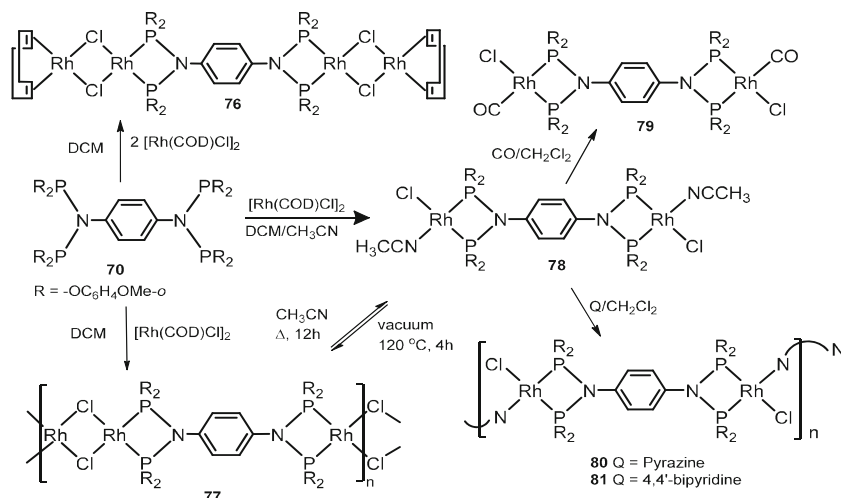
Figure 1. Octachlorotetraphosphane (**68**) showing intermolecular P...P interactions.



Scheme 17. Transfer hydrogenation reaction of ketones using rhodium(I)-tetraphosphane complexes **76–81**.

character evinced by X-ray structure determination. By choosing appropriate redox-active metals and substituents at the P-centres it is possible to design efficient conducting polymers.

The catalytic activity of rhodium(I) complexes **76–81** and some ruthenium(II) complexes³¹ have been investigated in transfer hydrogenation reactions (see scheme 17). Among them, the tetra metallic complex **76** appeared to be the most active precursor for the reduction of acetophenone (8 h, TON = 199 h⁻¹) and further it was used for the reduction of ketones other than acetophenone. The reduction performed with benzophenone yielded 80% of diphenylmethanol after 24 h with



Scheme 16. Reactions of tetraphosphane **70** with rhodium derivatives.

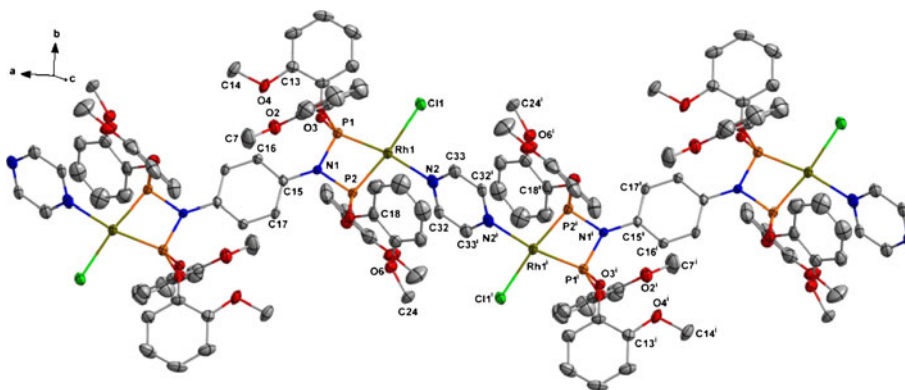
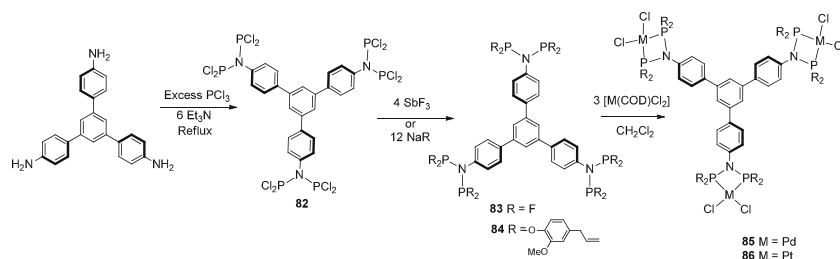


Figure 2. Molecular structure of one-dimensional Rh^I zigzag coordination polymer [Rh₂Cl₂(C₄H₄N₂){R₂PN(C₆H₄)NPR₂}]_n (**80**).



Scheme 18. Preparation and derivatization of dodecachlorohexaphosphane **82**.

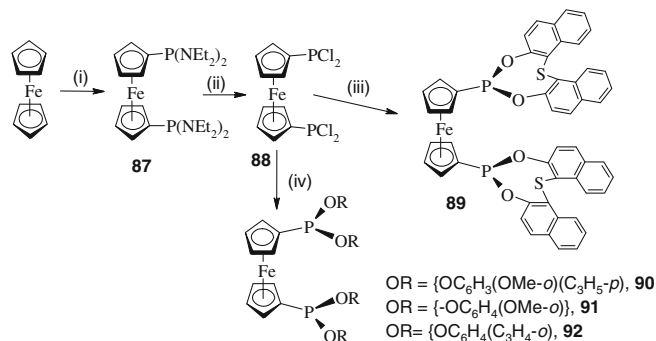
complex **76**. The complex **76** also showed good activity in the transfer hydrogenation of six-membered cyclic ketones such as α -tetralone and cyclohexanone but at different rates. Further, the reduction of 4-bromo acetophenone tends to proceed at significantly lower rate with low yield because of the higher mesomeric effect caused by bromide substitution.

10. Hexaphosphanes and metallocene-based bisphosphanes

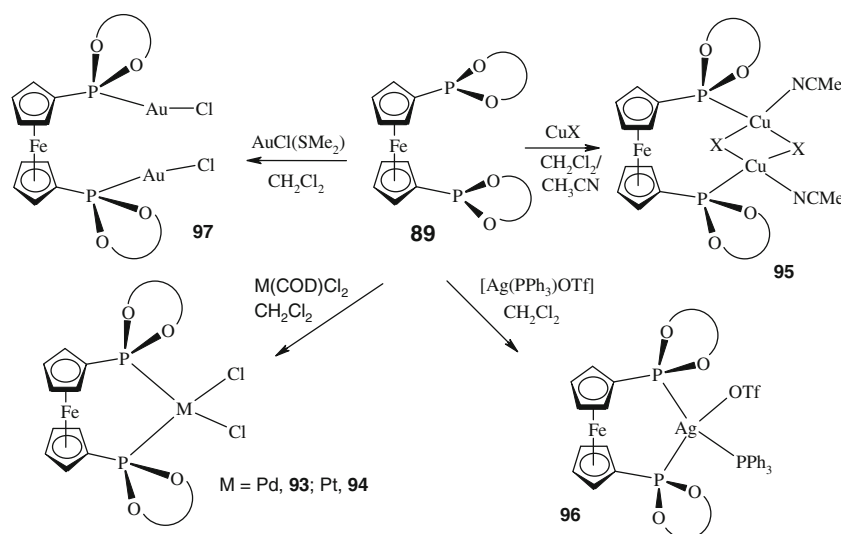
The reaction of 1,3,5-*tris*(4'-aminophenyl)benzene with phosphorus trichloride in the presence of three equivalents of pyridine afforded the novel dodecachlorohexaphosphane, 1,3,5- $C_6H_3[p-C_6H_4N(PCl_2)_2]_3$ (**82**) as a pale yellow crystalline solid in 20% yield. The yield has been further improved by carrying out the reaction in the presence of a strong base like triethylamine with a catalytic amount of *N,N*-dimethyl-4-aminopyridine (see scheme 18). The compound **82** readily decomposes on exposure to air and moisture. The fluorination of **82** with antimony trifluoride yielded the fluoro analogue, 1,3,5- $C_6H_3[p-C_6H_4N(PF_2)_2]_3$ (**83**) in good yield. The ^{31}P NMR spectrum of **82** consists of a single peak at 153.7 ppm, whereas **83** shows the A portion of an $AA'X_2X'_2$ multiplet centred at 130.4 ppm with $|^1J_{PF}|$, $|^3J_{PF}|$ and $|^2J_{PP}|$ couplings of 1246, 124 and 372 Hz, respectively. The single crystal X-ray diffraction analysis of **82** showed the distorted pyramidal geometry about the phosphorus centres and a planar environment around the nitrogen centres with the sum of the angles around nitrogen almost 360° in all cases. Further the bridging phenylene rings are almost perpendicular to the plane of the P–N–P skeletons. The reaction of **82** with 12 equivalents of 4-allyl-2-methoxyphenol in the presence of triethylamine afforded hexaphosphonite, 1,3,5- $C_6H_3[p-C_6H_4N\{P(OR)_2\}_2]_3$ [$R = -C_6H_3OMe(C_3H_5)$] (**84**) in quantitative yield. Compounds **82–84** are potential hexadentate ligands and are expected to behave as simple aminobisphosphine units mimicking their coordination behaviour. In a preliminary

study, the ligand **84** has been used for the preparation of platinum group metal complexes. Treatment of **84** with three equivalents of $[M(COD)Cl_2]$ ($M = Pd$ or Pt) in dichloromethane afforded the chelate complexes, 1,3,5- $C_6H_3[p-C_6H_4N\{P(OR)_2\}_2(MCl_2)]_3$ [$R = -C_6H_3OMe(C_3H_5)$] (**85**, $M = Pd$; **86**, $M = Pt$) in good yield. The ^{31}P NMR spectra of complexes **85** and **86** show single resonances at 63.2 and 57.9 ppm, respectively, which are considerably shielded compared to the free ligand. The platinum complex exhibits a large $^1J_{PtP}$ coupling of 5913 Hz, which is consistent with the proposed *cis* geometry around the platinum centre.³²

Ferrocenyl–phosphine ligands are versatile and are able to form complexes with transition metals in a variety of coordination geometries and oxidation states, which have proven to be efficient catalysts in homogeneous catalysis. Several ferrocenyl–phosphines have been extensively studied and have shown good catalytic activity in organic synthesis. In contrast, ferrocenyl–phosphonites or –phosphite derivatives are less extensive although, due to their easy preparation methods, can be an attractive alternative to ferrocenyl–phosphines. In view of this, we have made several bisphosphonites, phosphites and aminophosphines based on ferrocenyl framework and explored their transition metal chemistry and catalytic applications. Few of these ligands and their transition metal chemistry



Scheme 19. (i) 1. n -BuLi, TMEDA; 2. CIP(Net₂)₂; (ii) HCl(g), Et₂O, -78°C ; (iii) Diol, Et₃N, Et₂O; (iv) ROH, Et₃N, Et₂O, -20°C .



Scheme 20. Metal complexes of Ferrocenyl-phosphonite **89**.

is described. The synthetic method adopted for the preparation of various ferrocenyl-phosphanes is given in scheme 19.

The chloro-precursor **88** readily undergoes nucleophilic substitution at phosphorus centres to form bis-phosphonites of the type **89–92** in good to moderate yields. Ferrocenyl-phosphonite ligand **89** readily react with platinum and Group 11 metals to form interesting metal complexes (see scheme 20). The palladium complexes show good catalytic activity towards Suzuki–Miyaura cross coupling reactions.^{33–35}

11. Summary

Several phosphorus based ligands ranging from simple tertiary phosphines to hexaphosphane ligands have been synthesized and their transition metal chemistry and catalytic applications have been investigated. The synthetic flexibility, easy synthetic methodology with readily accessible nucleophilic sites and the presence of three soft donor centres make the heterocyclicdiphosphanes (**1**- and **2**) a valuable ligand system. Aminophosphines and aminobis(phosphines) form interesting ruthenium(II) complexes and they catalyse cyclopropanation reactions. Formation of 1,1,3,3-tetraphenyl cyclobutane was observed for the first time in the cyclopropanation reactions.

Phosphinoethers show both monodentate and bidentate coordination modes involving P(III) and ether oxygen centres. These ligands also generate metal-phenoxide bonds through metathetical elimination of methoxymethylchloride on treatment with platinum metal halide-derivatives. The reaction of *bis(o*-phenol)phenylphosphine with TiCl_4 in toluene and

isopropanol yielded a novel heptacyclic tetranuclear titanium complex containing four different types of oxygen binding along with formal titanium–phosphorus bonds. Large-bite *bis*(phosphonite) **35** with $\text{Pd}(\text{OAc})_2$ catalyses Suzuki–Miyaura C–C coupling reactions, whereas the rhodium complex **43** catalyses the hydrogenation of various styrenes with excellent turnover numbers. *Bis*(diphenylphosphino)phenylether **46** and its partially oxidized iminophosphorane–phosphane derivative **55** form interesting complexes with various transition metals and the palladium(0) and rhodium(I) complexes of later show excellent catalytic activity towards Suzuki–Miyaura C–C coupling reactions and hydrogenation of styrenes and acetylenes, respectively. The mesocyclic thioether–aminophosphonites due to their flexible framework display rich coordination chemistry, especially, the anionic palladium complex **67** promotes Suzuki–Miyaura, Mizoroki–Heck coupling reactions as well as amination reactions with very high catalytic activity (TON up to 1.5×10^6). Octachlorotetraphosphane **68** shows intermolecular P···P interactions whose estimated strength is around -5 to -10 kJ mol^{-1} . Tetraphosphane derivatives form simple binuclear to tetranuclear and polynuclear metal complexes and 1D-, 2D- and 3D-coordination polymers with Group 11 metals. Tetraphosphanes in combination with pyridyl ligands could serve as efficient tectons for the generation of interesting conglomerates which might find useful applications. For the first time an efficient one-pot synthesis of a novel dodecachlorohexaphosphane is achieved in our laboratory and its preliminary reactions have been carried out. These polydentate phosphorus ligands on aromatic framework are best suited to generate polynuclear complexes with metals in close proximity to understand their

mutual cooperativity, in case, such metal complexes are found suitable for homogeneous catalysis.

Acknowledgements

The majority of the work described here has been performed by my past graduate students; Drs. S Priya, R Panda, P P George, B Punji and C Ganesamoorthy. I am thankful to them for their synthetic skills and dedication. I am indebted to Prof. Joel T Mague, Tulane University, New Orleans, for X-ray structure determination. Our work was supported by the Department of Science and Technology (DST), the Council of Scientific and Industrial Research (CSIR), New Delhi, and we are grateful for their continued support.

References

- (a) *Applied homogeneous catalysis with organometallic compounds* 2002 2nd Edition, B Cornils, W A Herrmann (eds) (Weinheim: Wiley-VCH); (b) Miyaura N and Suzuki A 1995 *Chem. Rev.* **95** 2457; (c) Suzuki A 1998 In: *Metal catalysed cross coupling reactions*, F Diederich, P J Stang (eds) (Weinheim: Wiley-VCH) p. 49 and references therein
- (a) Balakrishna M S, Reddy V S, Krishnamurthy S S, Nixon J F and St Laurent B C T R 1994 *Coord. Chem. Rev.* **129** 1; (b) van der Vlugt J I, Sablong R, Mills A M, Kooijman H, Spek A L, Meetsma A and Vogt D 2003 *Dalton Trans.* 4690; (c) Punji B, Mague J T and Balakrishna M S 2006 *J. Organomet. Chem.* **691** 4265; (d) Smith R C and Protasiewicz J D 2004 *Organometallics* **23** 4215
- (a) Chandrasekaran P, Mague J T, Venkateswaran R and Balakrishna M S 2007 *Eur. J. Inorg. Chem.* 4988; (b) Chandrasekaran P, Mague J T and Balakrishna M S 2005 *Inorg. Chem.* **44** 7925; (c) Suresh D, Balakrishna M S and Mague J T 2008 *Dalton Trans.* 3272; (d) Balakrishna M S, Venkateswaran R and Mague J T 2009 *Inorg. Chem.* **48** 1398; (e) Chandrasekaran P, Mague J T and Balakrishna M S 2009 *Dalton Trans.* 5478; (f) Suresh D, Balakrishna M S, Rathinasamy K, Panda D and Mobin S M 2008 *Dalton Trans.* 2812; (g) Balakrishna M S 2010 *J. Organomet. Chem.* **695** 925; (h) Balakrishna M S, Suresh D, Rai A, Mague J T and Panda D 2010 *Inorg. Chem.* **49** 8790
- (a) Ganesamoorthy C, Balakrishna M S, Mague J T and Tuononen H M 2008 *Inorg. Chem.* **47** 7035; (b) Punji B, Mague J T and Balakrishna M S 2007 *Inorg. Chem.* **46** 10268; (c) Punji B, Mague J T and Balakrishna M S 2006 *J. Organomet. Chem.* **691** 4265; (d) Priya S, Mague J T and Balakrishna M S 2001 *Inorg. Chem. Commun.* **4** 437; (e) Balakrishna M S, Panda R, Smith Jr D C, Klamann A and Nolan S P 2000 *J. Organomet. Chem.* **599** 159; (f) Punji B, Mague J T and Balakrishna M S 2006 *J. Mol. Cat. A Chem.* **259** 78; (g) Venkateswaran R, Mague J T and Balakrishna M S 2007 *Inorg. Chem.* **46** 809; (h) Ganesamoorthy C, Balakrishna M S, George P P and Mague J T 2007 *Inorg. Chem.* **46** 848; (i) Kaboudin B and Balakrishna M S 2007 *Synth. Commun.* **31** 2773; (j) Mohanty S and Balakrishna M S 2010 *J. Chem. Sci.* **122** 137
- Balakrishna M S, Panda R and Mague J T 2001 *Inorg. Chem.* **40** 5620
- (a) Priya S, Balakrishna M S and Mague J T 2003 *J. Organomet. Chem.* **679** 116; (b) Priya S, Balakrishna M S, Mague J T and Mobin S M 2003 *Inorg. Chem.* **42** 1272
- Priya S, Balakrishna M S, Mobin S M and McDonald R 2003 *J. Organomet. Chem.* **688** 227
- Priya S, Balakrishna M S and Mague J T 2004 *J. Organomet. Chem.* **689** 3335
- Priya S, Balakrishna M S and Mague J T 2004 *Chem. Lett.* **33** 308
- (a) Guo R, Lough A J, Morris R H and Song D 2004 *Organometallics* **23** 5524; (b) Kesanli B and Lin W 2004 *Chem. Commun.* 2284; (c) Hölscher M, Franciò G and Leitner W 2004 *Organometallics* **23** 5606; (d) Wiles J A, Daley C J A, Hamilton R J, Leong C G and Bergens S H 2004 *Organometallics* **23** 4564
- Carbó J J, Maseras F, Bo C and van Leeuwen P W N M 2001 *J. Am. Chem. Soc.* **123** 7630
- (a) Balakrishna M S, Panda R and Mague J T 2002 *J. Chem. Soc. Dalton Trans.* **40** 4617; (b) Balakrishna M S, Priya S and Panda R 2003 *Phosphorus, Sulfur, Silicon* **178** 1391
- Punji B, Mague J T and Balakrishna M S 2006 *Dalton Trans.* 1322
- Kamer P C J, van Leeuwen P W N M and Reek J N H 2001 *Acc. Chem. Res.* **34** 895
- (a) Kranenburg M, van der Burgt Y E, Kamer P C J, van Leeuwen P W N M, Goubitz K and Fraanje J 1995 *Organometallics* **14** 3081; (b) Zuideveld M A, Swennenhuis B H G, Boele M D K, Guari Y, van Strijdonck G P F, Reek J N H, Kamer P C J, Goubitz K, Fraanje J, Lutz M, Spek A L and van Leeuwen P W N M 2002 *J. Chem. Soc. Dalton Trans.* 2308
- Venkateswaran R, Mague J T and Balakrishna M S 2007 *Inorg. Chem.* **46** 809
- Venkateswaran R, Balakrishna M S, Mobin S M and Tuononen H M 2007 *Inorg. Chem.* **46** 6535
- Venkateswaran R, Balakrishna M S and Mobin S M 2007 *Eur. J. Inorg. Chem.* 1930
- (a) Sherlock D J, Chandrasekaran A, Day R O and Holmes R R, 1997 *J. Am. Chem. Soc.* **119** 1317; (b) Sherlock D J, Chandrasekaran A, Day R O and Holmes R R 1997 *Inorg. Chem.* **36** 5082
- (a) Punji B, Mague J T and Balakrishna M S 2006 *Inorg. Chem.* **45** 9454; (b) Punji B, Mague J T and Balakrishna M S 2007 *Eur. J. Inorg. Chem.* 720
- Punji B, Mague J T and Balakrishna M S 2007 *Inorg. Chem.* **46** 11316
- (a) Gorin D J and Toste F D 2007 *Nature* **446** 395; (b) Jimenez-Nunez E and Echavarren A M 2007 *Chem. Commun.* 333; (c) Hashmi A S K and Hutchings G J 2006 *Angew. Chem. Int. Ed.* **45** 7896
- (a) Marzano C, Pellei M, Alidori S, Brossa A, Lobbia G G, Tisato F and Santini C 2006 *J. Inorg. Biochem.* **100** 299; (b) Pellei M, Lobbia G G, Santini C, Spagna R, Camalli M, Fedeli D and Falcioni G 2004 *Dalton Trans.* 2822

24. (a) Harkins S B and Peters J C 2005 *J. Am. Chem. Soc.* **127** 2030; (b) Araki H, Tsuge K, Sasaki Y, Ishizaka S and Kitamura N 2005 *Inorg. Chem.* **44** 9667; (c) Cuttell D G, Kuang S-M, Fanwick P E, McMillin D R and Walton R A 2002 *J. Am. Chem. Soc.* **124** 6
25. (a) Schmidbaur H 1995 *Chem. Soc. Rev.* **24** 391; (b) Gimeno M C and Laguna A 1997 *Chem. Rev.* **97** 511; (c) Puddephatt R J 2001 *Coord. Chem. Rev.* **216-217** 313; (d) Schmidbaur H 2001 *Nature* **413** 31; (e) Hunks W J, Jennings M C and Puddephatt R J 2002 *Inorg. Chem.* **41** 4590
26. (a) Blake A J, Champness N R, Hubberstey P, Li W-S, Withersby M A and Schroder M 1999 *Coord. Chem. Rev.* **183** 117; (b) Matsumoto K, Harada Y, Yamada N, Kurata H, Kawase T and Oda M 2006 *Cryst. Growth Des.* **6** 1083; (c) Reger D L, Watson R P and Smith M D 2006 *Inorg. Chem.* **45** 10077
27. (a) Irwin M J, Vittal J J and Puddephatt R J 1997 *Organometallics* **16** 3541; (b) Catalano V J, Malitz M A, Horner S J and Vasquez J 2003 *Inorg. Chem.* **42** 2141; (c) Lin R, Yip J H K, Zhang K, Koh L L, Wong K-Y and Ho K P 2004 *J. Am. Chem. Soc.* **126** 15852
28. Ganesamoorthy C, Balakrishna M S, Mague J T and Tuononen H M 2008 *Inorg. Chem.* **47** 7035
29. Ganesamoorthy C, Balakrishna M S and Mague J T 2009 *Inorg. Chem.* **48** 3768
30. Ganesamoorthy C, Balakrishna M S and Mague J T 2009 *Dalton Trans.* 1984
31. Ganesamoorthy C, Balakrishna M S and Mague J T 2009 *J. Organomet. Chem.* **694** 3390
32. Sowmya R, Ganesamoorthy C, Mobin S M and Balakrishna M S 2011 *Dalton Trans.* **40** 5841
33. Punji B, Mague J T and Balakrishna M S 2007 *Inorg. Chem.* **46** 10268
34. Balakrishna M S and Mague J T 2007 *Organometallics* **26** 4677
35. Sowmya R, Balakrishna M S and Mague J T 2012 (Unpublished results)