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Cyclodiphosphazane appended with thioether functionality: Synthesis, transition metal chemistry and catalytic application in Suzuki–Miyaura cross-coupling reactions

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Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday.

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ABSTRACT

The coordination chemistry of thioether functionalized cyclodiphosphazane ligand, *cis*-{^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$ (**1**) is described. The reactions of **1** with [Pd (COD)Cl$_2$] in 1:1, 1:2 and 2:1 M ratios afforded *cis*-[PdCl$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**2**), *cis*-[{PdCl$_2$}$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**3**) and *trans*-[PdCl$_2${(^{t}BuNP(OCH$_2$CH$_2$SCH$_3$))$_2$}$_2$] (**4**), respectively. Treatment of **1** with [Pd(PEt$_3$)Cl$_2$]$_2$ or [PdCl(η^3-C$_3$H$_5$)]$_2$ in appropriate molar ratios produce the mono- and binuclear complexes [PdCl$_2$(PEt$_3${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**5**) and [{PdCl(η^3-C$_3$H$_5$)}$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**6**) in good yield. The reaction of **1** with [{Ru(*p*-cymene)Cl$_2$}$_2$] afforded the mononuclear cationic complex, [{(*p*-cymene)RuCl{^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$]Cl (**7**), whereas the reactions of [Rh(COD)Cl]$_2$, [Pt(COD)Cl$_2$] and [Au(SMe$_2$)Cl] with **1** yielded the corresponding P-coordinated neutral complexes, [RhCl(COD){^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**8**) *cis*-[PtCl$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**9**), respectively. The binuclear palladium(II) complex **3** was found to be an effective catalyst for the Suzuki–Miyaura cross-coupling reactions.

1. Introduction

In recent years there has been a resurgence in the use of hybrid ligands containing both hard (N, O) and soft donor (P, S) centers. These hemi labile or difunctional ligands form weak metal–oxygen [1], metal–sulfur [2], or metal–nitrogen bonds [3], while phosphorus atoms, with both σ-donor and π-acceptor ability, can strongly coordinate to the low-valent platinum metal centers. The hard centers in these hemi-labile ligands may behave as donor-solvent molecules and provide coordinative saturation to the metal center, and due to the chelate effect these complexes are found to be much more stable than the simple solvent adducts. Such systems would be ideal for homogeneous catalysis [4] as the more labile donor centers can readily dissociate during the oxidative addition to provide one or more vacant coordination sites, thus facilitating the catalytic process under very mild conditions.

Cyclodiphosphazanes are the major class of P–N compounds having alternate phosphorus and nitrogen atoms in their four-membered cyclic skeletons [5]. Recently we have explored the transition metal chemistry of cyclodiphosphazanes appended with donor functionalities [6]. Slight variations in the phosphorus substituents have brought significant changes in their coordination properties to yield complexes with novel structural features [7]. As a part of our continued interest in studying coordination behavior, catalytic [8] and biological applications [9] and also for the interest of others [10] in cyclodiphosphazane ligand systems, we report in this paper some transition metal complexes and catalytic application of cyclodiphosphazane appended with thioether functionalities.

2. Results and discussion

2.1. Reactions with palladium(II) derivatives

The thioether functionalized cyclodiphosphazane, *cis*-{^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$ (**1**) was prepared by the reported procedure and characterized with multinuclear NMR techniques [7c]. The reactions of cyclodiphosphazane **1** with [Pd(COD)Cl$_2$] differ significantly from other cyclodiphosphazanes and is highly dependent on the stoichiometry of the reactants used.

The reaction of **1** with one equivalent of [Pd(COD)Cl$_2$] in dichloromethane afforded the mono-chelated complex *cis*-[PdCl$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**2**) in 88% yield. Similar reaction of **1** with two equivalents of [Pd(COD)Cl$_2$] yielded a bis-chelated binuclear complex, *cis*-[{PdCl$_2$}$_2${^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$] (**3**) as shown in Scheme 1. Changing the ligand to metal ratio from 1:2 to 2:1 re-

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sulted in the formation of a mixture of both *cis*-complex (**2**) and *trans*-[{$PdCl_2$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$}$_2$] (**4**) in 4:1 ratio as evinced from the ^{31}P NMR data. However, the *trans*-complex **4** was synthesized exclusively in 68% yield by reacting two equivalents of **1** with *trans*-[$Pd(SMe_2)_2Cl_2$] under similar reaction conditions. The binuclear complex **3** was precipitated within 10 min from the reaction mixture and is insoluble in almost all organic solvents except in methanol and dimethyl sulphoxide, whereas the mononuclear complexes **2** and **4** are highly soluble in all organic polar solvents. The ^{31}P NMR spectrum of complex **2** shows two sharp singlets at 104.6 and 76.9 ppm, for the uncoordinated and coordinated phosphorus centers, respectively, while the binuclear complex **3** shows a sharp singlet at 104.6 ppm. The signals at 2.37 and 2.16 ppm for the SCH_3 protons in the ^{1}H NMR spectrum of **2** confirm that one of the SMe groups is coordinated to the metal center. The EI mass spectrum of **2** shows molecular ion peak at 528.9 which corresponds to the M–Cl fragment. The ^{31}P NMR spectrum of **4** shows a singlet at 129.6 ppm for the uncoordinated phosphorus centers while the palladium bound phosphorus centers appear at 83.2 ppm and no $^2J_{PP}$ coupling was observed. The phosphorus-31 NMR spectrum of ligand **1** shows a single resonance at 134.1 ppm [7c].

Addition of $[Pd(PEt_3)Cl_2]_2$ in dichloromethane to **1** in 1:2 M ratio afforded the mononuclear complex [$PdCl_2(PEt_3)$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$] (**5**) with cyclodiphosphazane showing monodentate coordination *via* one of the phosphorus which occupies the *cis* position with respect to PEt_3 (Scheme 2). The ^{31}P NMR spectrum of **5** consists of three resonances; the uncoordinated phosphorus appears as a doublet at 131.2 ppm ($^2J_{PNP}$ = 3.8 Hz), while PEt_3 appears as a doublet centered at 24 ppm ($^2J_{PP}$ = 12.3 Hz) and are coupled to the coordinated phosphorus, which appears as a doublet of doublets centered at 84.3 ppm. Treatment of $[PdCl(\eta^3\text{-}C_3H_5)]_2$ with **1** in equimolar ratio gave a binuclear complex [{$PdCl(\eta^3\text{-}C_3H_5)$}$_2$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$] (**6**) as yellow crystalline solid. The ^{31}P NMR spectrum of complex **6** shows a sharp singlet at 121.1 ppm with the coordination shift of 13 ppm. The ^{1}H NMR and analytical data of complexes **2–6** are consistent with the proposed structures. Further, the molecular structure of **2** is confirmed by single crystal X-ray diffraction study.

2.2. Reactions with Ru^{II}, Rh^{I}, Pt^{II} and Au^{I} derivatives

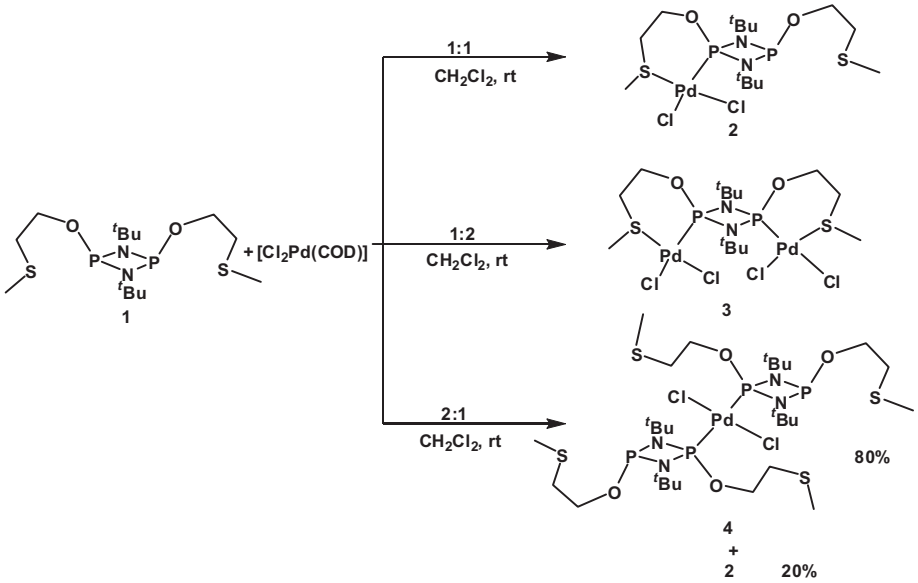
The reaction of $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ with **1** in a 1:2 ratio at room temperature afforded a cationic P,S-chelated mononuclear complex, [$(\eta^6\text{-}p$-cymene)RuCl\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$]Cl (**7**) as a red crystalline solid. The ^{31}P NMR spectrum of **7** shows two doublets centered at 116.8 and 108.5 ppm, respectively, for the uncoordinated and coordinated phosphorus centers with a $^2J_{PP}$ coupling of 60 Hz. The ^{1}H NMR spectrum of **7** shows two singlets at 2.19 and 2.01 ppm for the metal bound and free SCH_3 protons, respectively. The EI mass spectrum of **7** shows molecular ion peak at 657.3 corresponding to the cationic moiety. Treatment of $[RhCl(COD)]_2$ with **1** in 1:2 M ratio resulted in the formation of a mononuclear complex [RhCl(COD)\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$ (**8**) at room temperature. The complex **8** shows a singlet at 133.6 ppm for the uncoordinated phosphorus center and a doublet centered at 102.9 ppm for the rhodium bound phosphorus center, respectively, in its phosphorus-31 NMR spectrum with a $^1J_{RhP}$ coupling of 221 Hz. Slow addition of $[Pt(COD)Cl_2]$ to hemi-labile ligand **1** in 1:1 M ratio produced a mononuclear complex *cis*-[$PtCl_2$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$] (**9**) as shown in Scheme 3.

The reaction of **1** with $[Au(SMe_2)Cl]$ in 1:2 M ratio afforded a P-coordinated binuclear complex [$(ClAu)_2$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$] (**10**). The complex **10** is sensitive to light which on exposure to sunlight turns pink. The ^{31}P NMR spectrum of **9** shows two singlets at 106.2 ppm and 49.3 ppm, respectively, for the uncoordinated and coordinated phosphorus centers whereas the complex **10** shows a single resonance at 100.3 ppm. The complex **9** shows platinum satellites with a $^1J_{PtP}$ coupling of 4750 Hz. The ^{1}H NMR and analytical data of complexes **7–10** are consistent with the proposed structures.

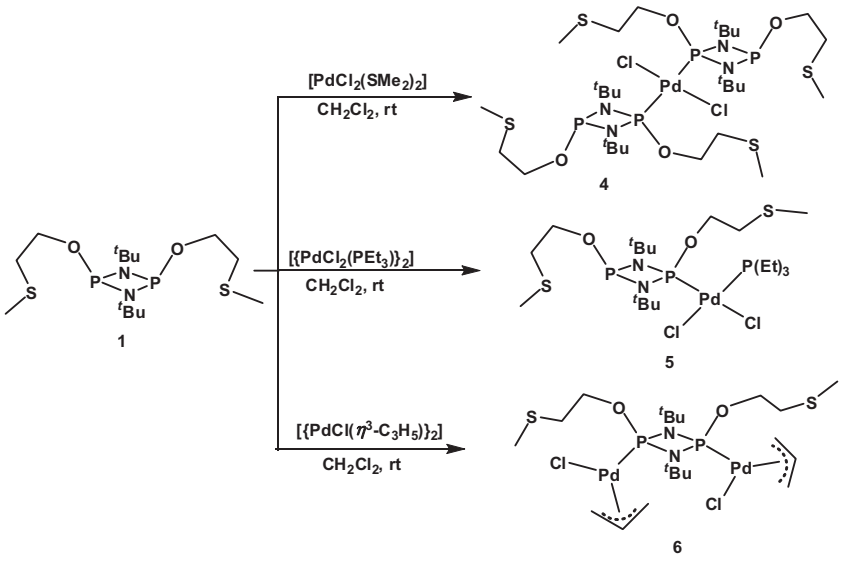
3. Crystal and molecular structure of 2

The perspective view of the molecular structure of complex *cis*-[$PdCl_2$\{^{t}BuNP($OCH_2CH_2SCH_3$)\}$_2$] (**2**) is shown in Fig. 1. The details of structural determination are given in Table 1 while the selected bond lengths and bond angles are given as figure caption.

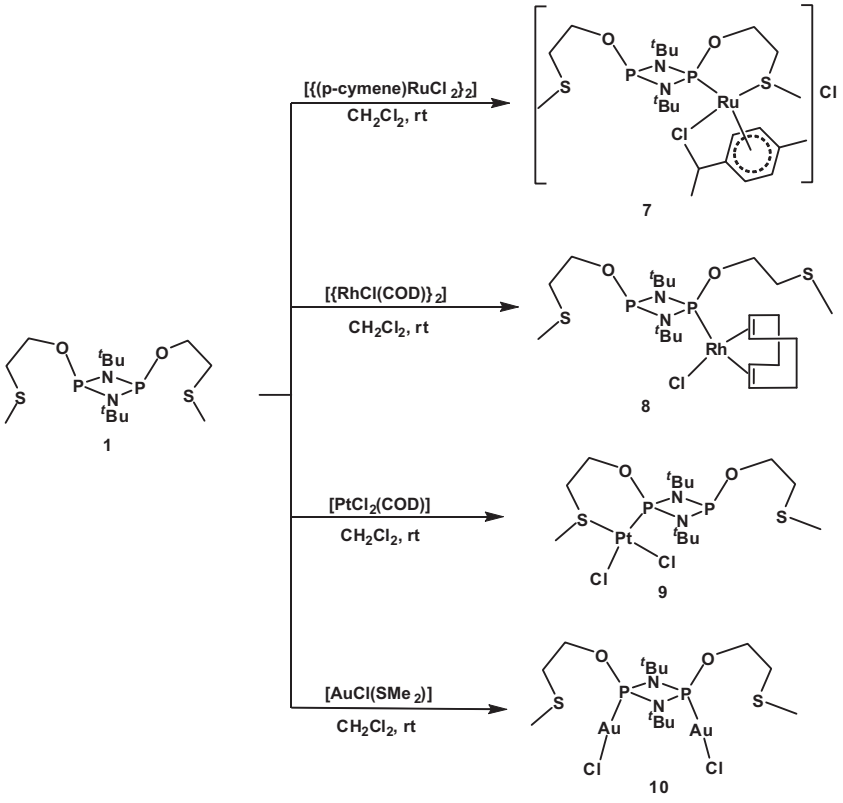
The yellow crystals suitable for X-ray diffraction study were obtained by slow evaporation of dichloromethane/petroleum ether



Scheme 1.



Scheme 2.



Scheme 3.

mixture of **2** at room temperature. The cyclodiphosphazane adopts a chelating mode of coordination to the palladium metal *via* the phosphorus and sulfur atoms in a *cis* fashion to make a twisted six-membered chelate ring with palladium atom in a distorted square planar environment along with two chloride ligands which are in a mutually cis-disposition. The *trans*-Cl1–Pd–S1 and *trans*-Cl2–Pd–P1 bond angles are respectively, 172.95(1)° and 86.78(1)°, while the *cis* angles around the palladium center vary from 82.53(1)° (S1–Pd–Cl2) to 98.66(1)° (S1–Pd–P1) clearly indicating the distortion in the square planar geometry. The P2N2 ring is in a slightly puckered conformation with angles around nitrogen is ~357°. The Pd–P1 and Pd–S1 bond lengths are 2.2226(4) Å and 2.2920(4) Å, respectively, which are comparable to the same in analogous P and S chelated complex, [{^{t}BuSC$_6$H$_4$CH$_2$Ph$_2$P-*o*}PdCl$_2$] (Pd–P, 2.2247(9) Å; Pd–S 2.2979(9) Å [11]). The Pd–Cl1 (2.3160(4) Å) bond distance is shorter than the Pd–Cl2 (2.3650(4) Å) and is expected due to the more *trans* influence of phosphorus atom compared to the sulfur atom.

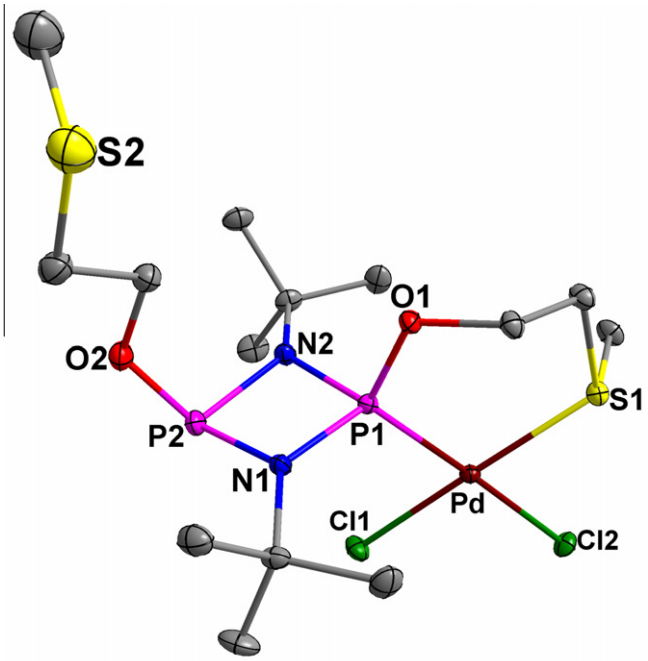


Fig. 1. The molecular structure of **2**. All hydrogen atoms were omitted for clarity. Thermal ellipsoids are drawn at 50% probability level. Selected bond lengths (Å): Pd–Cl1, 2.3160(4); Pd–Cl2, 2.3650(4); Pd–S1, 2.2920(4); Pd–P1, 2.2226(4); P1–O1, 1.5969(12); P2–O2, 1.6166(13); P1–N1, 1.6652(14); P1–N2, 1.6555(15); P2–N1, 1.7307(15); P2–N2, 1.7374(14). Selected bond angles (°): Cl1–Pd–Cl2, 92.14(1); Cl1–Pd–S1, 172.95(1); Cl1–Pd–P1, 86.78(1); Cl2–Pd–S1, 82.53(1); Cl2–Pd–P1, 178.26(2); S1–Pd–P1, 98.66(1); Pd–P1–N1, 120.54(5); Pd–P1–N2, 119.40(5).

Table 1
Crystallographic information for complex **2**.

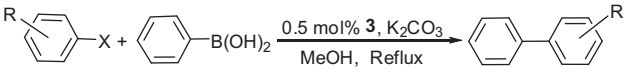
Formula	$C_{14}H_{32}Cl_2N_2O_2P_2PdS_2$
Formula weight	563.78
Crystal system	monoclinic
space group	$P2_1/c$ (no. 14)
a (Å)	17.9290(10)
b (Å)	10.4706(7)
c (Å)	12.1842(8)
α (°)	90
β (°)	98.0560(10)
γ (°)	90
V (Å^3)	2264.7(2)
Z	4
ρ_{calc} (g cm^{-3})	1.654
μ (Mo Kα) (mm^{-1})	1.393
F(0 0 0)	1152
Crystal size (mm)	0.11 × 0.14 × 0.15
T (K)	100
2θ Range (°)	2.3, 28.3
Total number of reflections	39,035
Number of independent reflections	5612 [R_{int} = 0.036]
R_1[a]	0.0222
wR_2[b]	0.0552
Goodness-of-fit (GOF) F^2	1.061

[a] $R = F_o - F_c/F_o$.

[b] $wR_2 = \left\{ \left[w\left(F_o^2 - F_c^2\right) / w\left(F_o^2\right)^2 \right] \right\}^{1/2}$ $w = 1/^2\left(F_o^2\right) + (xP)^2$ where $P = \left(F_o^2 + 2F_c^2\right)/3$.

4. Suzuki cross-coupling reaction catalyzed by 3

The palladium-catalyzed cross-coupling reaction is known with a variety of transmetallating agents. However, the Suzuki–Miyaura cross-coupling reaction for the C-C bond formation is the most attractive and practical protocol because of its tolerance for a wide range of functional groups [12].



(1)

The binuclear palladium complex **3** was examined in the Suzuki cross coupling reaction of arylboronic acid with the aryl bromides. The electronically activated and deactivated aryl bromides and the sterically hindered aryl bromides were coupled with phenylboronic acid using 0.5 mol% of **3** at 60 °C in the presence of K_2CO_3 as base in methanol medium (Eq. (1)). The results are summarized in Table 2. It is evident from the Fig. 2 that the coupled biaryls were obtained in more than 50% yield within 30 min for all the aryl bromide substrates when coupled with the phenylboronic acid under the given reaction conditions.

The cross-coupling reactions of "easy-to-couple" substrate 4-bromoacetophenone and the electron poor 4-bromobenzonitrile with the phenylboronic acid proceed efficiently within 30 min to afford the coupled product in 100% and 99% yield, respectively (Table 2, entries 1, 2). The 3-bromobenzaldehyde was coupled with phenylboronic acid to yield 93% conversion to the coupled products (Table 2, entry 3) in the presence of 0.5 mol% of **3** while 3-bromobenzaldehyde required slightly longer time (1.5 h) to give the expected biaryl product (Table 2, entry 4). The electronically neutral bromobenzene and the electron rich 4-bromoanisole were coupled with phenylboronic acid to produce coupled products in 91% and 86%, respectively. The 2-bromo-6-methoxynaphthalene and the sterically hindered 1-bromo-2,4-dimethoxybenzene took longer time to afford good conversion of the coupled products. The use of heterocyclic derivative 2-bromothiophene afforded 100% of the coupled product within 3 h whereas the 2-bromorpyridine produced 85% of coupled product only after 13 h (Table 2, entry 10). The classical mercury test was carried out to prove the homogeneous nature of the catalysis [13]. Addition of a drop of mercury to the reaction mixture did not affect the conversion rate of the reaction which suggests that the catalysis is homogeneous in nature, since heterogeneous catalysis would form an amalgam, thereby poisoning it.

5. Conclusions

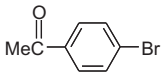
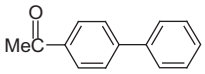
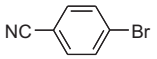
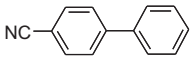
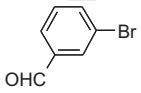
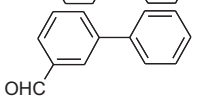
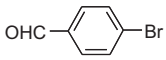
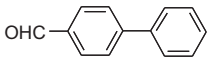
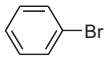
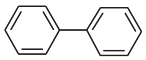
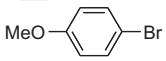
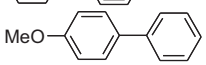
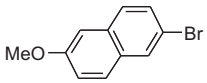
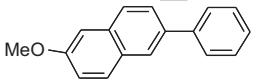
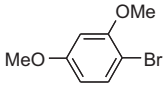
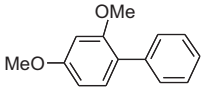
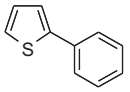
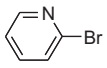
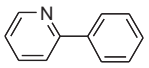
The hemi-labile cyclodiphosphazane *cis*-{^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$ exhibits versatile coordination behavior with various transition metals. The reactions of hemi-labile ligand with palladium derivatives lead to the isolation of both the *cis*-, *trans*-isomers of mono as well as binuclear complexes. The reactions with Rh^{II}, Au^{I} derivatives afforded the P-coordinated neutral complexes while the reaction with Ru^{II} gave the chelated (P,S) mononuclear cationic complex. The bischelated binuclear palladium(II) complex was found to be an active catalyst for the Suzuki cross-coupling reactions. Further utilization of these classes of ligands in various other catalytic reactions is under active investigation in our laboratory.

6. Experimental section

6.1. General procedures

All experimental manipulations were carried out under a dry nitrogen or argon atmosphere, using standard Schlenk techniques unless otherwise stated. Solvents were dried and distilled prior to use by conventional methods. The precursors *cis*-{^{t}BuNP(OCH$_2$CH$_2$SCH$_3$)}$_2$ (**1**) [7c], [M(COD)Cl$_2$] (M = Pd, Pt [14]) [Pd(SMe$_2$)$_2$Cl$_2$] [15], [Pd(PEt$_3$)Cl$_2$]$_2$ [16], [PdCl(η^3-C$_3$H$_5$)]$_2$ [17],

Table 2
Suzuki cross-coupling of aryl halides with boronic acids catalyzed by **3**.[a]

Entry	Aryl halide	Product	Conv. (%)[b]	Final time	Conv.
1			100	30	100
2			99	30	99
3			93	1 h	93
4			68	1.5 h	85
5			83	4 h	91
6			75	2 h	86
7			89	5 h	97
8			49	18 h	65
9			93	3 h	100
10			48	13 h	85

[a] Aryl bromide (1 mmol); phenylboronic acid (1.5 mmol); catalyst **3** (0.5 mol%); K_2CO_3 (2 mmol); methanol (5 mL) at 60 °C.
[b] Conversion after 30 min.

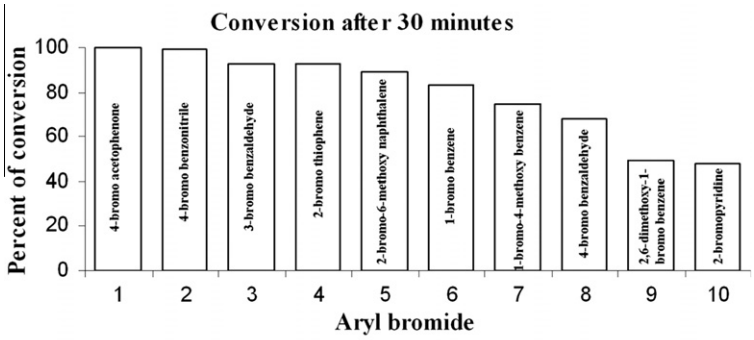


Fig. 2. Graphical representation of the conversion of the coupled product for various aryl halides after 30 min.

[Ru(η^6-*p*-cymene)Cl_2]$_2$ [18], [Rh(COD)Cl]$_2$ [19] and [Au(SMe_2)Cl] [20] were prepared according to the published procedures.

6.2. Spectroscopy

The ^{1}H and ^{31}P NMR (δ in ppm) spectra were obtained on a Varian VXR 400 spectrometer operating at frequencies of 400 and 162 MHz, respectively. The tetramethylsilane and 85% H_3PO_4 were used as an internal and external standards for ^{1}H and ^{31}P{^{1}H} NMR, respectively. Positive shifts lie downfield of the standard in all the cases. Microanalyses were carried out on a Carlo Erba Model 1106 elemental analyzer. Electro-spray ionization (EI) mass spectrometry experiments were carried out by using Waters Q-Tof micro-YA-105. Melting points of all compounds were determined on Veego melting point apparatus and were uncorrected. GC analyses were performed on a Perkin–Elmer Clarus 500 GC fitted with FID detector and packed column.

6.2.1. Synthesis of *cis*-[$PdCl_2${^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**2**)

A dichloromethane solution (4 mL) of [Pd(COD)Cl_2] (0.038 g, 0.133 mmol) was added dropwise to *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.051 g, 0.132 mmol) also in dichloromethane (5 mL) at room temperature. The clear solution was stirred for 6 h at room temperature. The reaction mixture was then concentrated to 5 mL; added 2 mL of petroleum ether and kept at room temperature for a day to afford **2** as yellow crystalline solid. Yield: 88% (0.065 g). Mp: 230–232 °C (dec). *Anal.* Calc. for $C_{14}H_{32}N_2P_2O_2S_2PdCl_2$: C, 29.82; H, 5.72; N, 4.96; S, 11.37. Found: C, 29.77; H, 5.66; N, 4.88; S, 11.27%. ^{1}H

NMR (400 MHz, $CDCl_3$): 4.45 (d, J_{HH} = 14.8 Hz OCH_2, 2H), 4.02 (t, 7 Hz, OCH_2, 2H), 2.82 (s, SCH_2, 2H), 2.71 (s, SCH_2, 2H), 2.37 (s, SCH_3, 3H), 2.16 (s, SCH_3, 3H), 1.53 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 104.6 (s), 76.9 (s, Pd–P).

*6.2.2. Synthesis of cis-[{$PdCl_2$}$_2${^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**3**)*

To a solution of *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.035 g, 0.091 mmol) in dichloromethane (10 mL) was added dropwise [Pd(COD)Cl_2] (0.052 g, 0.181 mmol) in the same solvent (5 mL) and the reaction mixture was stirred well at room temperature for 8 h. The yellow precipitate formed was filtered and dried under vacuum to give analytically pure product of **3**. Yield: 78% (0.053 g). Mp: 192–194 °C (dec). *Anal.* Calc. for $C_{14}H_{32}N_2P_2O_2S_2Pd_2Cl_4$: C, 22.68; H, 4.35; N, 3.78; S, 8.65. Found: C, 22.60; H, 4.48; N, 3.83; S, 8.75%. ^1H NMR (400 MHz, DMSO-d_6): 4.52 (s, OCH_2, 4H), 2.86 (s, SCH_2, 4H), 2.79 (S, SCH_3, 4H), 1.59 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, DMSO-d_6): 104.6 (s).

*6.2.3. Synthesis of trans-[$PdCl_2${(^{t}BuNP($OCH_2CH_2SCH_3$))$_2$}$_2$] (**4**)*

To a stirred solution of *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.048 g, 0.124 mmol) in dichloromethane (5 mL) was added dropwise a solution of [Pd(SMe_2)$_2Cl_2$] (0.019 g, 0.062 mmol) also in of dichloromethane (5 mL) and the clear yellow solution was stirred at room temperature for 4 h. The solution was concentrated and layered with petroleum ether and stored −25 °C for two days to afford **4** as yellow crystalline compound. Yield: 68% (0.040 g). Mp: 140–144 °C (dec). *Anal.* Calc. for $C_{28}H_{64}N_4P_4O_4S_4PdCl_2$: C, 35.38; H, 6.79; N, 5.89; S, 13.49. Found: C, 35.37; H, 6.75; N, 5.81; S, 13.34%. ^1H NMR (400 MHz, $CDCl_3$): 4.22 (t, J_{HH} = 3.6 Hz, OCH_2, 4H), 3.98 (t, J_{HH} = 6.8 Hz, OCH_2, 4H), 2.72 (s, SCH_2, 8H), 2.08 (s, SCH_3, 6H), 2.07 (s, SCH_3, 6H), 1.43 (s, ^tBu, 36H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 129.6 (s), 83.2(s, Pd–P).

*6.2.4. Synthesis of cis-[$PdCl_2$(PEt_3){^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**5**)*

A dichloromethane solution (5 mL) of [Pd(PEt_3)Cl_2]$_2$ (0.028 g, 0.048 mmol) was added dropwise to *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.037 g, 0.096 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 8 h and then concentrated to 5 mL. The solution was layered with 2 mL of diethyl ether and placed at −25 °C for 18 h to afford **5** as yellow crystalline solid. Yield: 65% (0.043 g). Mp: 166–168 °C (dec). *Anal.* Calc. for $C_{20}H_{47}N_2P_3O_2S_2PdCl_2$: C, 35.22; H, 6.95; N, 4.11; S, 9.40. Found: C, 35.35; H, 6.83; N, 4.20; S, 9.47%. ^1H NMR (400 MHz, $CDCl_3$): 4.23 (t, J_{HH} = 7.6 Hz, OCH_2, 2H), 4.06 (t, J_{HH} = 7.2 Hz, OCH_2, 2H), 2.74 (m, SCH_2, 4H), 2.16 (s, SCH_3, 3H), 2.14 (s, SCH_3, 3H), 2.09 (q, J_{HH} = 10.8 Hz, P-CH_2, 6H) 1.43 (s, ^tBu, 18H), 0.94 (t, J_{HH} = 7.6 Hz, P-CH_3, 9H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 131.2 (d), 84.3 (dd), 24.0 (d, $^2J_{PNP}$ = 3.8 Hz, $^2J_{PPdP}$ = 12.3 Hz).

*6.2.5. Synthesis of cis-[{PdCl(η^3-C_3H_5){^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**6**)*

A solution of [PdCl(η^3-C_3H_5)]$_2$ (0.024 g, 0.066 mmol) in dichloromethane (5 mL) was added dropwise to a solution of *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.025 g, 0.066 mmol) in the same solvent (8 mL) at room temperature and the reaction mixture was stirred for 4 h. The pale yellow colored solution was concentrated and layered with petroleum ether to obtain **6** as yellow crystalline solid. Yield: 82% (0.041 g). Mp: 120–122 °C (dec). *Anal.* Calc. for $C_{20}H_{42}N_2P_2O_2S_2Pd_2Cl_2$: C, 31.92; H, 5.62; N, 3.72; S, 8.52. Found: C, 31.97; H, 5.61; N, 3.78; S, 8.47%. ^1H NMR (400 MHz, $CDCl_3$): 5.68 (br s, CH_2, 6H), 4.71 (br s, CH, 4H), 4.28 (m, OCH_2, 4H), 2.82 (br s SCH_2, 4H), 2.13 (s, SCH_3, 6H), 1.53 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 121.1 (s).

*6.2.6. Synthesis of cis-[RuCl(η^6-p-cymene){^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$]Cl (**7**)*

A dichloromethane (5 mL) solution of [Ru(η^6-*p*-cymene)Cl_2]$_2$ (0.050 g, 0.81 mmol) was added dropwise to *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.063 g, 0.163 mmol) in dichloromethane (5 mL) at room temperature. The reaction mixture was stirred for 6 h. The clear red colored solution obtained was concentrated to 4 mL; layered with 2 mL of petroleum ether and kept at room temperature for two days to afford **7** as red crystalline compound. Yield: 91% (0.102 g). Mp: 172–174 °C (dec). *Anal.* Calc. for $C_{24}H_{46}N_2P_2O_2S_2RuCl_2$: C, 41.61; H, 6.69; N, 4.04; S, 9.25. Found: C, 41.55; H, 6.75; N, 4.15; S, 9.29%. ^1H NMR (400 MHz, $CDCl_3$): 5.15 (d, J_{HH} = 6.4 Hz, *Cymene phenyl*, 2H), 4.95 (d, J_{HH} = 6.4, Hz, *Cymene phenyl*, 2H), 4.73 (t, J_{HH} = 6.4 Hz, OCH_2, 2H), 4.69 (t, J_{HH} = 6.4 Hz, OCH_2, 2H), 3.02 (t, J_{HH} = 6 Hz, SCH_2, 2H), 2.76 (septet, *CH*, 1H), 2.58 (t, J_{HH} = 6 Hz, SCH_2, 2H), 2.25 (s, SCH_3, 3H), 2.19 (s, SCH_3, 3H), 2.01 (s, CH_3, 3H), 1.61 (s, ^tBu, 18H), 1.33 (d, J_{HH} = 7.2 Hz, CH_3, 6H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 116.8 (d), 108.5(d), $^2J_{PP}$ = 60 Hz. MS (EI): *m*/*z* 657.3 (M–Cl).

*6.2.7. Synthesis of cis-[RhCl(COD){^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**8**)*

A dichloromethane (5 mL) solution of [Rh(COD)Cl]$_2$ (0.044 g, 0.089 mmol) was added dropwise to a well-stirred solution of *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.069 g, 0.178 mmol) in the same solvent (5 mL) at room temperature and the stirring was continued for 6 h. The yellow colored solution was concentrated to 4 mL and layered with 2 mL of petroleum ether and stored at −25 °C to afford **8** as yellow crystalline compound. Yield: 65% (0.073 g). Mp: 146–148 °C (dec). *Anal.* Calc. for $C_{22}H_{44}N_2P_2O_2S_2RhCl$: C, 41.74; H, 7.01; N, 4.42; S, 10.13. Found: C, 41.77; H, 7.11; N, 4.56; S, 10.07%. ^1H NMR (400 MHz, $CDCl_3$): 5.40 (d, J_{HH} = 3.8 Hz, *CH*, 4H), 4.45 (m, OCH_2, 4H), 2.44 (d, J_{HH} = 4.2 Hz, CH_2, 8H), 2.82 (m, SCH_2, 4H), 2.07 (s, SCH_3, 3H), 2.06 (s, SCH_3, 3H), 1.55 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 133.6 (s), 102.9 (d, J_{RhP} = 221 Hz, Rh-P).

*6.2.8. Synthesis of cis-[$PtCl_2${^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**9**)*

This was synthesized by a procedure similar to that of **2**, using *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.022 g, 0.057 mmol) and [Pt(COD)Cl_2] (0.021 g, 0.057 mmol). Yield: 76% (0.028 g). Mp: 210–212 °C (dec). *Anal.* Calc. for $C_{14}H_{32}N_2P_2O_2S_2PtCl_2$: C, 25.77; H, 4.94; N, 4.29; S, 9.82. Found: C, 25.86; H, 4.96; N, 4.25; S, 9.77%. ^1H NMR (400 MHz, $CDCl_3$): 4.55 (d, J_{HH} = 14.8 Hz OCH_2, 2H), 4.15 (t, J_{HH} = 8.2 Hz, OCH_2, 2H), 2.85 (s, SCH_2, 2H), 2.78 (s, SCH_2, 2H), 2.38 (s, SCH_3, 3H), 2.12 (s, SCH_3, 3H), 1.45 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 106.2 (s), 49.30 (s, Pt–P), $^1J_{PtP}$ = 4750 Hz.

*6.2.9. Synthesis of cis-[($AuCl$)$_2${^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$] (**10**)*

To a solution of *cis*-{^{t}BuNP($OCH_2CH_2SCH_3$)}$_2$ (0.053 g, 0.138 mmol) in 4 mL of dichloromethane added a solution of [Au(SMe_2)Cl] (0.020 g, 0.069 mmol) in dichloromethane (8 mL) at room temperature. The reaction mixture was stirred under dark for 4 h. The clear solution was concentrated and layered with petroleum ether to get **10** as colorless compound. Yield: 86% (0.051 g). Mp: 230–232 °C (dec). *Anal.* Calc. for $C_{14}H_{32}N_2P_2O_2$-$S_2Au_2Cl_2$: C, 19.75; H, 3.79; N, 3.29; S, 7.53. Found: C, 19.82; H, 3.76; N, 3.68; S, 7.41%. ^1H NMR (400 MHz, $CDCl_3$): 4.12 (br s, OCH_2, 4H), 2.79 (br s, SCH_2, 4H), 2.12 (S, SCH_3, 6H), 1.54 (s, ^tBu, 18H). $^{31}P\{^1H\}$ NMR (161.8 MHz, $CDCl_3$): 100.3 (s).

6.2.10. Typical procedure for Suzuki–Miyaura cross-coupling reactions

In a two-necked round-bottom flask under an atmosphere of nitrogen was placed the appropriate amount of catalyst solution, and 5 mL of methanol was added to it. The correct amount of catalyst was added as a methanol solution made up by multiple vol-

umetric dilutions of stock solutions. After stirring for 5 min, aryl bromide (0.5 mmol), phenylboronic acid (0.75 mmol), and K_2CO_3 (0.138 g, 1 mmol) were introduced into the reaction flask. The mixture was heated at 60 °C for the required time under an atmosphere of nitrogen (the course of reaction was monitored by GC analysis), following which the solvent was removed under reduced pressure. The residue was diluted with H_2O (8 mL) and Et_2O (8 mL) followed by extraction twice (2 × 6 mL) with Et_2O. The combined organic fractions were dried ($MgSO_4$), stripped of the solvent under vacuum, and the residue redissolved in 5 mL of dichloromethane. An aliquot was taken with a syringe and subjected to GC analysis. Yields were calculated versus aryl bromides or dodecane as an internal standard.

5.12. X-ray crystallography

A crystal of compound **2** suitable for X-ray crystal analysis was mounted in a Cryoloop™ with a drop of paratone oil and placed in the cold nitrogen stream of the Kryoflex™ attachment of the Bruker APEX CCD diffractometer. Full spheres of data were collected using three sets of 400 scans in ω (0.5° per scan) at $\varphi = 0$, 90 and 180° plus two sets of 800 scans in φ (0.45° per scan) at $\omega = -30$ and 210° all under the control of the APEX2 [21] software packages.

The raw data were reduced to F^2 values using the SAINT software [22] and global refinements of unit cell parameters using 5228 reflections chosen from the full data sets were performed. Multiple measurements of equivalent reflections provided the basis for empirical absorption corrections as well as corrections for any crystal deterioration during the data collection (SADABS [23]). The structure was solved by direct method, and refined by full-matrix least-squares procedures using the SHELXTL program package [24]. Hydrogen atoms were placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms. Pertinent crystallographic data and other experimental details are summarized in Tables 1.

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Appendix A. Supplementary material

CCDC 796786 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.02.006.

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