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Cyclodiphosphazanes with Hemilabile Ponytails: Synthesis, Transition Metal Chemistry (Ru(II), Rh(I), Pd(II), Pt(II)), and Crystal and Molecular Structures of Mononuclear (Pd(II), Rh(I)) and Bi- and Tetranuclear Rhodium(I) Complexes

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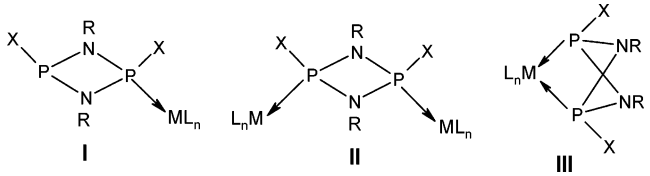
Cyclodiphosphazanes having hemilabile ponytails such as *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**), *cis*-[^{t}BuNP(OCH$_2$CH$_2$OMe)]$_2$ (**3**), *cis*-[^{t}BuNP(OCH$_2$CH$_2$SMe)]$_2$ (**4**), and *cis*-[^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)]$_2$ (**5**) were synthesized by reacting *cis*-[^{t}BuNPCl]$_2$ (**1**) with corresponding nucleophiles. The reaction of **2** with [M(COD)Cl$_2$] afforded *cis*-[MCl$_2$(**2**)$_2$] derivatives (M = Pd (**6**), Pt (**7**)), whereas, with [Pd(NCPh)$_2$Cl$_2$], *trans*-[MCl$_2$(**2**)$_2$] (**8**) was obtained. The reaction of **2** with [Pd(PEt$_3$)Cl$_2$]$_2$, [{Ru(η^6-*p*-cymene)Cl$_2$}$_2$, and [M(COD)Cl]$_2$ (M = Rh, Ir) afforded mononuclear complexes of Pd(II) (**9**), Ru(II) (**11**), Rh(I) (**12**), and Ir(I) (**13**) irrespective of the stoichiometry of the reactants and the reaction condition. In the above complexes the cyclodiphosphazane acts as a monodentate ligand. The reaction of **2** with [PdCl(η^3-C$_3$H$_5$)]$_2$ afforded binuclear complex [(PdCl(η^3-C$_3$H$_5$))$_2${(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP}] (**10**). The reaction of ligand **3** with [Rh(CO)$_2$Cl]$_2$ in 1:1 ratio in CH$_3$CN under reflux condition afforded tetranuclear rhodium(I) metallamacrocycle (**14**), whereas the ligands **4** and **5** afforded bischelated binuclear complexes **15** and **16**, respectively. The crystal structures of **8**, **9**, **12**, **14**, and **16** are reported.

Introduction

The main group and transition metal chemistry of dianionic bis(amido)cyclodiphosphazanes, *cis*-[^{t}BuNP(^{t}BuN$^-$)]$_2$, and their chalcogenide derivatives, *cis*-[^{t}BuNP(E)(^{t}BuN$^-$)]$_2$ (E = O, S, Se), has been studied extensively by Chivers,[1] Stahl,[2] and others.[3] In contrast, the coordination chemistry of neutral cyclodiphosphazanes is less extensive[4] despite their ability to show monodentate (**I**; Chart 1) and bridged bidentate (**II**) modes of coordination. Krishnamurthy et al. have reported some homo- and heterobinuclear complexes of group 6 and 8 metals with cyclodiphosphazanes showing both mono- and bridged bidentate modes of coordination.[5] A nickel complex

Chart 1. Possible Coordination Modes of Cyclodiphosphazanes



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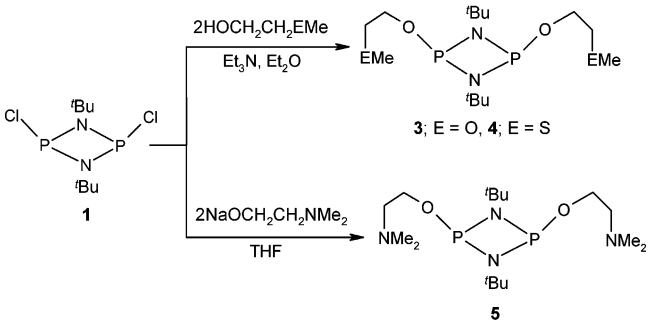
Scheme 1

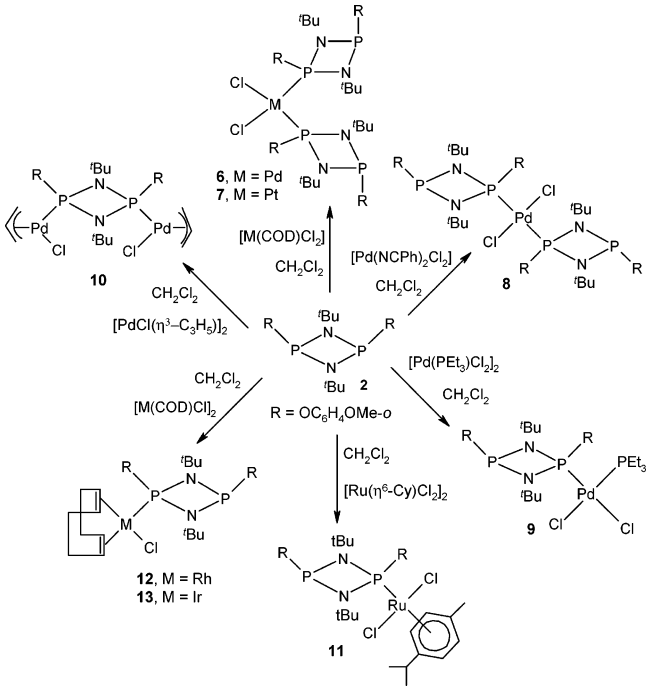


containing chelating cyclodiphosphazanes was reported without appropriate phosphorus-31 NMR data or structural support.[5c] In an effort to utilize the rigid cyclodiphosphazanes as heterodifunctional and bi- or tetradentate ligands, we incorporated pendant hemilabile functionalities on phosphorus centers so that they can show a variety of coordinating modes. As a part of our interest[6] and the interest of others[7] in transition metal chemistry of cyclic and acyclic phosphorus based ligands, we describe here the preparation and transition metal chemistry of cyclodiphosphazanes containing pendant hemilabile ponytails. The crystal and molecular structures of mononuclear (palladium(II), rhodium(I)) and bi- and tetranuclear rhodium(I) complexes are also reported.

Results and Discussion

Ligand Synthesis. The reactions of *cis*-[^{t}BuNPCl]$_2$ (**1**) with 2 equiv of 2-(methoxy)phenol or 2-substituted ethanols, ECH$_2$CH$_2$OH (E = OMe, SMe), in the presence of triethylamine afford the corresponding hemilabile cyclodiphosphazane derivatives *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**)[8] and *cis*-[^{t}BuNP(OCH$_2$CH$_2$EMe)]$_2$ (**3**; E = OMe, **4**; SMe) in quantitative yield. The corresponding amine-functionalized derivative, *cis*-[^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)]$_2$ (**5**), was prepared by reacting *cis*-[^{t}BuNPCl]$_2$ (**1**) with the sodium salt of 2-(dimethylamino)ethanol in THF (Scheme 1). Compound **2** is a white crystalline solid whereas **3**−**5** are oily liquids which were purified by vacuum distillation. The ^{31}P NMR spectra of **2**−**5** exhibit single resonances at 145.6, 133.8, 134.1, and 133.7 ppm, respectively. Interestingly, all these compounds exist in cis-conformation as indicated by phosphorus-31 chemical shifts.[9] Further, the structure and compositions of compounds **2**−**5** were confirmed by analytical data and ^{1}H NMR spectroscopy and mass spectrometry.

Scheme 2



Palladium and Platinum Derivatives. The reactions of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**) with [M(COD)Cl$_2$] (M = Pd or Pt) are independent of stoichiometry and the reaction conditions and afford exclusively cis complexes, **6** and **7**, with the ligand exhibiting monodentate coordination. In contrast, the reaction of 2 equiv of **2** with [Pd(NCPh)$_2$Cl$_2$] in dichloromethane affords a mononuclear *trans*-palladium(II) derivative **8** as shown in Scheme 2. The ^{31}P NMR spectrum of complex **6** exhibits two doublets centered at 67.9 and 121.2 ppm, respectively, for coordinated and free phosphorus centers with a $^2J_{PP}$ coupling of 53 Hz. Similarly, the phosphorus-31 chemical shift due to the coordinated phosphorus of **7** appears at 40.4 ppm whereas the uncoordinated phosphorus resonates at 126.1 ppm. The $^2J_{PP}$ coupling is 7.3 Hz. The platinum-bound phosphorus center exhibits platinum-195 satellites with a large $^1J_{PtP}$ coupling of 4861 Hz, which is consistent with the proposed cis geometry[10] for **7**. The *trans*-palladium(II) complex **8** exhibits two single resonances at 128.3 and 84.6 ppm, respectively, for uncoordinated and coordinated phosphorus centers, and no $^2J_{PP}$ coupling was observed. Treatment of *cis*-[^{t}BuNP(OC$_6$H$_4$-OMe-*o*)]$_2$ (**2**) with palladium(II) dimer [Pd(PEt$_3$)Cl$_2$]$_2$ in an equimolar ratio also affords a mononuclear complex **9** containing monodentate cyclodiphosphazane and PEt$_3$ ligands in mutually cis dispositions. The ^{31}P NMR spectrum of complex **9** consists of three resonances; uncoordinated phosphorus of cyclodiphosphazane and PEt$_3$ appear as doublets at 127.2 ($^2J_{PP}$ = 3.9 Hz) and 35. 8 ppm ($^2J_{PP}$ =

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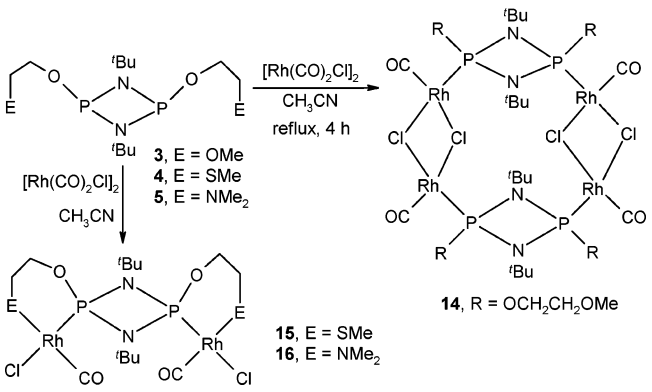
Scheme 3



16.8 Hz), respectively, and are coupled to the coordinated phosphorus, which appears as a doublet of doublets centered at 85.7 ppm. Further structural evidences come from ^{1}H NMR and mass spectral data, elemental analysis, and single-crystal X-ray diffraction studies in the case of complexes **8** and **9**. The 1:1 reaction between **2** and $[PdCl(\eta^3\text{-}C_3H_5)]_2$ in dichloromethane affords a dinuclear palladium(II) complex, $[(PdCl(\eta^3\text{-}C_3H_5))_2\{(^t\text{BuNP}(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}]$ **(10),** with cyclodiphosphazane acting as a bridging ligand. The ^{31}P NMR spectrum of **10** shows a sharp singlet at 121.1 ppm indicating the symmetrical coordination of cyclodiphosphazane.

The mononuclear Ru(II) complex **11** was prepared by reacting 2 equiv of *cis*-$[^t\text{BuNP}(OC_6H_4OMe\text{-}o)]_2$ (**2**) with $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ in dichloromethane. Even with an excess of metal reagent, only the mononuclear product was obtained. In the ^{31}P NMR spectrum of **11**, the uncoordinated phosphorus appears as a doublet centered at 133.5 ppm whereas the chemical shift due to the coordinated phosphorus appears at 109.6 ppm. The $^2J_{PP}$ coupling is 8.7 Hz.

Rhodium Derivatives. The reactions of *cis*-$[^t\text{BuNP}(OC_6H_4OMe\text{-}o)]_2$ (**2**) with $[M(COD)Cl]_2$ (M = Rh, Ir) in 1:1 molar ratio affords neutral mononuclear complexes **12** and **13** with cyclodiphosphazane showing monodentate coordination as indicated by ^{31}P NMR data. The ^{31}P NMR spectrum of **12** shows a doublet at 102.8 ppm for the coordinated phosphorus center ($^1J_{RhP}$ = 229 Hz), whereas the resonance due to the uncoordinated phosphorus appears as a singlet at 131.7 ppm. Similarly, the iridium complex **13** also shows singlets for coordinated and uncoordinated phosphorus centers at 133.0 and 88.5 ppm, respectively.

The reactions of cyclodiphosphazane derivatives with $[Rh(CO)_2Cl]_2$ afford a variety of products, depending upon the stoichiometry of the reactants, reaction conditions, and also the nature of the donor functionalities present in the pendant groups. The tetranuclear complex **14** containing two $[Rh(\mu\text{-}Cl)]_2$ units and two bridging cyclodiphosphazanes was obtained when the $[Rh(CO)_2Cl]_2$ and the ligand **3** were taken in 1:1 molar ratios. Interestingly, the reaction of **4** and **5** with 1 equiv of $[Rh(CO)_2Cl]_2$ in acetonitrile under reflux conditions afforded the dinuclear bischelated Rh(I) complexes **15** and **16**, respectively, as shown in Scheme 3. The ^{31}P NMR spectra of complexes **14**−**16** show multiplets with chemical shifts in the range of 115−124 ppm. The $^2J_{PP}$

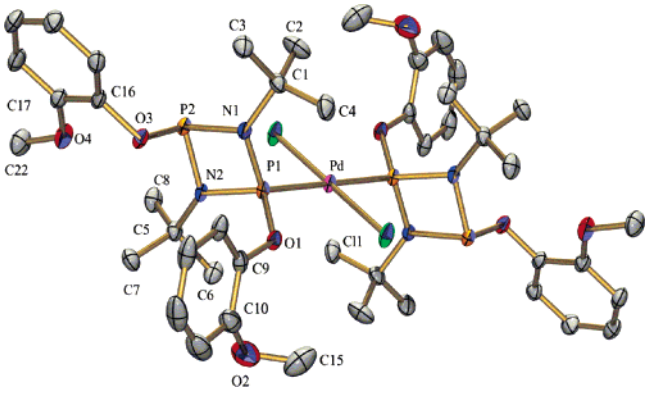


Figure 1. Molecular structure of **8**. For clarity, solvent and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): P(1)−Pd, 2.299(1); Pd−Cl(1), 2.293(1); P(1)−N(1), 1.671(2); P(1)−N(2), 1.664(2); P(2)−N(1), 1.733(2); P(2)−N(2), 1.719(2). Selected bond angles (deg): Cl(1)−Pd−P(1), 94.20(2); Cl(1)−Pd−P(1_a), 85.80(2); Cl(1_a)−Pd−P(1), 85.80(2); Cl(1_a)−Pd−P(1_a), 94.20(2); Cl(1)−Pd-Cl(1_a), 180.00; P(1)−Pd−P(1_a), 180.00; P(1)−N(1)−P(2), 95.83(9); P(1)−N(2)−P(2), 96.64(10).

couplings are in the range 42−47 Hz.[11] In ^{1}H NMR spectra of bischelated Rh(I) complexes **15** and **16**, the chemical shifts due to SMe and NMe_2 are downfield shifted considerably as compared to the same in the free ligands, which confirms the coordination of SMe and NMe_2 to the metal centers. In contrast, in the ^{1}H NMR spectrum of **14**, the chemical shift due to OMe appeared almost at same position as in the free ligand **3** which indicates the absence of OMe coordination to Rh(I) center.[12] The IR spectra of complexes **14**−**16** show two absorptions in the range 1993−2034 cm^{-1}, which is clearly consistent with the cis-related CO/phosphine structures proposed for these complexes.[10] The structures of compounds **14** and **16** were further confirmed by low-temperature single-crystal X-ray diffraction studies.

Crystal and Molecular Structures of Complexes 8, 9, 12, 14, and 16. Perspective views of the molecular structures of compounds **8**, **9**, **12**, **14**, and **16** with atom numbering schemes are shown in Figures 1−5, respectively. The crystallographic data and the details of the structure determination are given in Table 1, while selected bond length and bond angles appear below the corresponding figures.

Single crystals of *trans*-$[PdCl_2\{(^t\text{BuNP}(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}_2]$ (**8**) were grown from the 1:1 mixture of dichloromethane and diethyl ether solution at −30 °C. The asymmetric unit contains half a molecule of the metal complex and one molecule of dichloromethane. The palladium occupies the center of the square planar geometry, and the corners are occupied by two chlorines and two phosphorus centers from cyclodiphosphazane. The P(1)−Pd-P(1_a) and Cl(1)−Pd-Cl(1_a) bond angles are perfectly linear. The Cl(1)−Pd−P(1) bond angle is 94.20(2)°. The Pd−P(1) bond length (2.299(1) Å) in *trans*-Pd(II) derivative **8** is longer as compared to the Pd−P(1) bond length (2.232(1) Å) in complex **9**; this is due to the greater trans influence of phosphine ligands in the latter as compared with chloride.

(11) The ^{31}P NMR spectra of **14**−**16** are best interpreted as "A" part of an XAA"X" nuclear spin system with $J_{XX'} = 0$.
(12) Priya, S.; Balakrishna, M. S.; Mague, J. T. *J. Organomet. Chem.* **2004**, *689*, 3335.

Table 1. Crystallographic Information for Compounds **8**, **9**, **12**, **14**, and **16**

param	**8**·$2CH_2Cl_2$	**9**	**12**	**14**	**16**·CH_3CN
formula	$C_{44}H_{64}Cl_2N_4O_8P_4Pd$·$2CH_2Cl_2$	$C_{28}H_{47}Cl_2N_2O_4P_3Pd$	$C_{30}H_{44}ClN_2O_4P_2Rh$	$C_{32}H_{64}Cl_4N_4O_{12}P_4Rh_4$	$C_{18}H_{38}Cl_2N_4O_4P_2Rh_2$·$CH_3CN$
fw	1248.04	745.89	696.97	1374.19	754.24
cryst system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group (No.)	$P2_1/n$ (14)	$Pca2_1$ (29)	$P2_1/c$	$P2_1/n$ (14)	$P2_1/c$ (14)
a, Å	10.1978(9)	22.008(3)	10.7960(10)	9.3390(9)	14.0780(10)
b, Å	19.0612(2)	9.4530(10)	28.138(2)	18.286(2)	12.7090(10)
c, Å	15.4490(10)	16.257(2)	11.649(5)	14.9160(10)	18.035(2)
α, deg	90	90	90	90	90
β, deg	107.1080(10)	90	115.860(10)	99.7530(10)	109.8820(10)
γ, deg	90	90	90	90	90
V, Å^3	2870.1(3)	3382.1(7)	3184.4(14)	2510.4(4)	3034.4(5)
Z	2	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.444	1.465	1.454	1.818	1.651
μ(Mo Kα), cm^{-1}	0.765	0.883	0.757	1.688	1.403
F(000)	1288	1544	1448	1376	1528
cryst size (mm^3)	0.13 × 0.14 × 0.15	0.11 × 0.22 × 0.28	0.13 × 0.16 × 0.18	0.08 × 0.08 × 0.21	0.14 × 0.20 × 0.21
T (K)	100	293	100	100	100
2*θ* range, deg	1.7−28.3	1.9−28.3	1.5−28.3	1.8−27.7	1.5−27.8
tot. no. reflcns	25 110	28 984	47 078	21 656	26 237
no. of indepdt reflcns	6845 (R_{int} = 0.021)	8108 (R_{int} = 0.028)	47 176 (R_{int} = 0.000)	5749 (R_{int} = 0.026)	7018 (R_{int} = 0.028)
R_1[a]	0.0371	0.0228	0.0484	0.0320	0.0273
wR_2[b]	0.0979	0.0523	0.1068	0.0839	0.0650
GOF (F^2)	1.05	1.03	0.90	1.10	1.05

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = \{[\Sigma w(F_o^2 - F_c^2)/\Sigma w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (xP)^2]$, where $P = (F_o^2 + 2F_c^2)/3$.

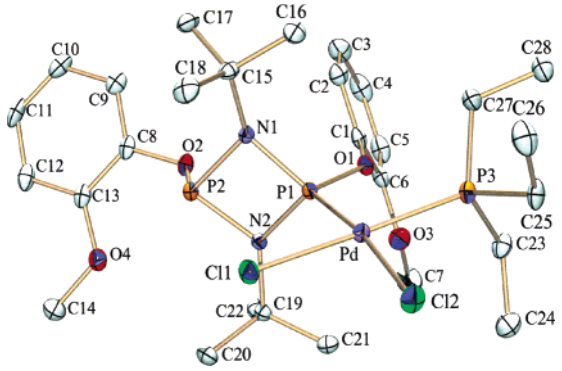


Figure 2. Molecular structure of **9**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): P(1)−Pd, 2.232(1); P(3)−Pd, 2.289(1); Pd−Cl(1), 2.359(1); Pd−Cl(2), 2.345(1); P(1)−O(1), 1.606(1); P(2)−O(2), 1.657(1); P(1)−N(1), 1.667(2); P(1)−N(2), 1.664(2); P(2)−N(1), 1.729(2); P(2)−N(2), 1.718(2). Selected bond angles (deg): P(1)−Pd−P(3), 95.71(2); Cl(1)−Pd−Cl(2), 89.55(2); Cl(1)−Pd−P(1), 85.53(2); Cl(2)−Pd−P(3), 89.52(2); P(1)−N(1)−P(2), 96.22(8); P(1)−N(2)−P(2), 96.78(9).

The two (P_2N_2) rings are arranged in opposite orientations, whereas, in a similar structurally characterized Rh(I) complex, *trans*-[RhCl(CO){(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-*κP*}$_2$], they are arranged in a parallel manner.[8]

In the molecular structure of **9**, palladium center is coordinated through two different phosphorus centers and two chlorine atoms in a square planar fashion with cis angles varying from 95.71(2)° (P(1)−Pd−P(3)) to 85.53(2)° (Cl(1)−Pd−P(1)). The two phosphorus centers are arranged in cis conformation. The P(1)−Pd (2.2325(6) Å) bond is slightly shorter than Pd−P(3) (2.2892(6) Å) bond, which is due to the stronger *π*-acceptor nature of the cyclodiphosphazane ligand **2** as compared to PEt_3. The P(1)−O(1)−C(1) (129.78(12)°) bond angle is shorter than P(2)−O(2)−C(8) (117.79(12)°), which indicates that the two *exo* cyclic phenyl substitutions are in different orientations. The (P_2N_2) ring is in a slightly puckered conformation with angles around nitrogen is ∼355°.

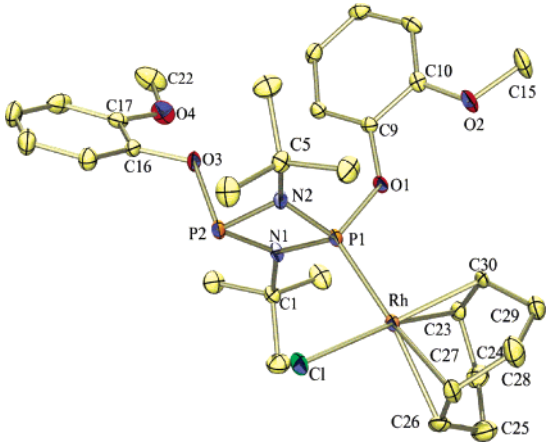


Figure 3. Molecular structure of **12**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Rh−P(1), 2.244(1); Rh−Cl, 2.361(1); Rh−C(23), 2.109(2); Rh−C(26), 2.235(2); Rh−C(27), 2.213(2); Rh−C(30), 2.133(2); P(1)−N(1), 1.693(2); P(1)−N(2), 1.673(2); P(2)−N(1), 1.719(2); P(2)−N(2), 1.708(2). Selected bond angles (deg): P(1)−Rh−Cl, 87.82(2); P(1)−Rh−C(23), 93.00(5); Cl−Rh−C(26), 91.62(6); C(23)−Rh−C(26), 81.32(7); P(1)−N(1)−P(2), 96.30(6); P(1)−N(2)−P(2), 97.46(8).

The molecular structure of **12** is shown in Figure 3. The rhodim(I) center in **12** occupies the center of distorted square planar geometry. The square planar corners were occupied by phosphorus, chloride, and 1,5-cyclooctadiene. The Rh−P(1) and Rh−Cl bond distance are 2.2438(11) and 2.3608(11) Å, respectively, and are in good agreement with the literature values for similar rhodium(I) complexes.[13] The P(1)−Rh-Cl bond angle is 87.82(2)°.

Single crystals of **14** were grown from the slow diffusion of hexane into a dichloromethane solution at room temperature. The molecular structure of tetranuclear Rh(I) complex **14** consists of two [Rh(*μ*-Cl)(CO)]$_2$ units bridged by two cyclodiphosphazanes via P(III) centers to give a tetranuclear

(13) St. Laurent, J. C. T. R. B.; Hitchcock, P. B.; Nixon, J. F. *J. Organomet. Chem.* **1983**, *249*, 243.

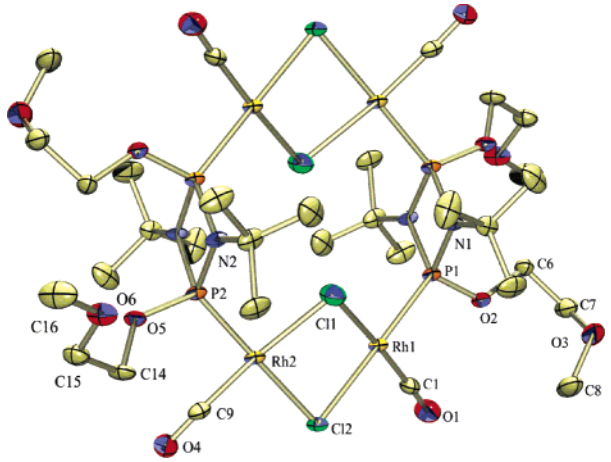


Figure 4. Molecular structure of **14**. For clarity, all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): Rh(1)−P(1), 2.191(1); Rh(2)−P(2), 2.198(1); Rh(1)−Cl(1), 2.368(1); Rh(1)−Cl(2), 2.423(1); Rh(2)−Cl(1), 2.354(1); Rh(2)−Cl(2), 2.429(1); Rh(1)−C(1), 1.823(3); Rh(2)−C(9), 1.805(4); P(1)−N(1), 1.689(3); P(2)−N(2), 1.692(3); Rh(1)···Rh(2), 3.454. Selected bond angles (deg): P(1)−Rh(1)−Cl(1), 94.44(3); P(1)−Rh(1)−C(1), 88.63(11); Cl(1)−Rh(1)−Cl(2), 84.16(3); Cl(1)−Rh(2)−P(2), 94.98(3); P(2)−Rh(2)−C(9), 90.42(10); Rh(1)−Cl(1)−Rh(2), 94.00(4); Rh(1)−Cl(2)−Rh(2), 90.77(3); P(1)−N(1)−P(2_a), 96.77(14); P(1_a)−N(2)−P(2), 96.58(14).

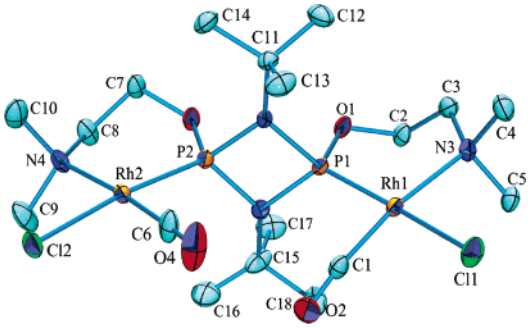
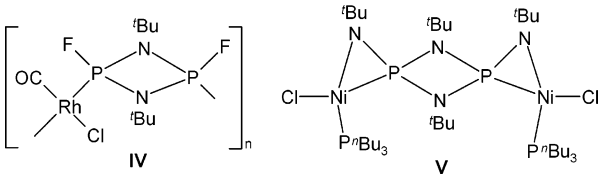


Figure 5. Molecular structure of **16**. For clarity, solvent and all hydrogen atoms have been omitted. Thermal ellipsoids are drawn at 50% probability. Selected bond distances (Å): P(1)−Rh(1), 2.178(1); P(2)−Rh(2), 2.194-(1); Rh(1)−N(3), 2.181(2); Rh(2)−N(4), 2.193(4); Rh(1)−Cl(1), 2.409(1); Rh(2)−Cl(2), 2.403(1); Rh(1)−C(1), 1.816(3); Rh(2)−C(6), 1.809(3); P(1)−N(1), 1.690(2); P(1)−N(2), 1.695(2); P(2)−N(1), 1.691(2); P(2)−N(2), 1.693(2). Selected bond angles (deg): P(1)−Rh(1)−N(3), 96.21(6); P(2)−Rh(2)−N(4), 95.75(12); P(1)−Rh(1)−C(1), 88.90(8); P(2)−Rh(2)−C(6), 90.54(9); Cl(1)−Rh(1)−N(3), 89.72(6); Cl(2)−Rh(2)−N(4), 89.40(12); P(1)−N(1)−P(2), 97.14(10); P(1)−N(2)−P(2), 96.85(11); Cl(1)−Rh(1)−P(1), 171.56(2); Cl(2)−Rh(2)−P(2), 173.66(2).

macrocycle. This is a rare example of cyclodiphosphazanes stabilizing $[Rh_2(\mu\text{-}Cl)_2]$ units to form a centrosymmetric tetranuclear rhodium(I) macrocycle. The Rh−P distances are (Rh(1)−P(1), 2.191(1) Å; Rh(2)−P(2), 2.198 (1) Å) shorter than that found in the structure of $[Rh(\mu\text{-}Cl)(PPh_3)_2]_2$ (2.213 (2) Å).[14] Two planar P_2N_2 rings are almost orthogonal to the slightly inward-puckered two $[Rh_2(\mu\text{-}Cl)_2]$ rings. The structural features are similar to those of dimolybdenum complex $[Mo(CO)_4\{PhNP(OC_6H_4Me\text{-}o)\}_2]_2$.[5a] In both the complexes, the ligands adopt cis-orientation with no significant differences in the P−N bond distances and the P−N−P bond angles. The distances Rh(1)−Cl(1) (2.368(1) Å) and Rh(1)−Cl(2) (2.423(1) Å) differ significantly. This difference can most likely be attributed to a greater trans-influence of the phosphorus ligand as compared to the carbonyl ligand. The Rh(1)−Cl(1)−Rh(2) and Rh(1)−Cl(2)−Rh(2) bond angles are 94.0 and 90.7°, respectively. These differences arise due to the presence of shorter and longer Rh−Cl bonds in complex **14**. The Rh(1)−Rh(2) distance of 3.365 Å indicates the absence of metal−metal-bonding interaction.

(14) Curtis, M. D.; Butler, W. M.; Greene, J. *Inorg. Chem.* **1978**, *17*, 2928.

Chart 2



Previously, Nixon and co-workers[15] have reported an insoluble complex of the type $[RhCl(CO)\{\mu\text{-}(^t\text{BuNPF})_2\}]_n$ (**IV**; Chart 2), whereas Stahl and co-workers[16] have reported a 16-electron anionic dinickel(II) cyclodiphosphazane complex, **V**, containing two three-membered metallacycles. In both the complexes, the cyclodiphosphazanes act as four-electron donor bridging ligands. Krishnamurthy and co-workers have reported the crystal structures of dimolybdenum and mixed molybdenum−tungsten complexes with cyclodiphosphazane $[\{PhNP(OC_6H_4Me\text{-}p)\}_2]$ exhibiting a bridged bidentate mode of coordination.[5a,b] Interestingly, the ligand $[\{PhNP(OC_6H_4Me\text{-}p)\}_2]$ exists in a trans form in the solid state but undergoes isomerization during complexation and exhibits both cis and trans conformations in the complexes probably governed by the steric attributes at the metal centers. Surprisingly, the ligands in the present investigation exist in cis form and no isomerization was observed during complexation. Complex **16** is the first example of a cyclodiphosphazane performing as an eight-electron donor tetradentate ligand to form two chelate rings with rhodium(I) centers in slightly distorted square planar environments. The CO and the phosphorus center of cyclodiphosphazane are arranged cis to each other with P(1)−Rh(1)−C(1) and P(2)−Rh(2)−C(6) bond angles of 88.90(8) and 90.54(9)°, respectively. The P_2N_2 ring is orthogonal to two chelate rings. The Rh(1)−P(1) bond distance of 2.178(1) Å is slightly shorter than Rh(2)−P(2) of 2.194(1) Å. Surprisingly, there are not much differences in other bond distances such as Rh−N, Rh−CO, and Rh−Cl. The P(1)−Rh(1)−N(3) and P(2)−Rh-(2)−N(4) bond angles are 95.75(12) and 96.21(6)°, respectively. In both the complexes **14** and **16** the P_2N_2 rings are planar with bond angles around nitrogen summing to ∼360°. The supramolecular structures of all the complexes are dominated by intra- and intermolecular C−H···Cl, C−H···π, and C−H···O interactions.

Conclusion

The cyclodiphosphazanes containing hemilabile ponytails exhibit versatile coordination properties. The exclusive formation of either cis or trans Pd(II) complexes was achieved by using appropriate metal reagents. The reactions

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with Rh(I), Ir(I), Pd(II), and Ru(II) metal dimers selectively afforded the corresponding mononuclear complexes, in which cyclodiphosphazane acts as a monodentate ligand. On the other hand, the treatment with $[PdCl(\eta^3\text{-}C_3H_5)]_2$ resulted in the formation of a dinuclear complex. The cyclodiphosphazane having ether functionality was found to preferably form the tetranuclear rhodium(I) metallacycle, whereas cyclodiphosphazanes containing thioether and amine functionality gives the bichelated dinuclear rhodium(I) complexes. The latter complexes are the first examples of cyclodiphosphazanes performing as eight-electron donor tetradentate ligands. Further research in the utilization of these novel ligands to build polymetallic complexes and clusters of high nuclearity is in progress.

Experimental Section

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedure and distilled prior to use.[17] The compounds *cis*-[^{t}BuNPCl]$_2$ (**1**),[18] *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**),[8] [M(COD)Cl$_2$] (M = Pd, Pt),[19] [Pd(NCPh)$_2$Cl$_2$],[20] [Pd(PEt$_3$)Cl$_2$]$_2$,[21] $[PdCl(\eta^3\text{-}C_3H_5)]_2$,[22] [Ru($\eta^6$-*p*-cymene)Cl$_2$]$_2$,[23] [Rh(COD)Cl]$_2$,[24] [Ir(COD)Cl]$_2$,[25] and [Rh(CO)$_2$Cl]$_2$[26] were prepared according to the published preocedures. 2-(Methoxy)ethanol (SD Fine chemicals) and 2-(dimethylamino)ethanol (Lancaster) were purified prior to use by conventional methods. 2-(Methylthio)ethanol was purchased from Lancaster and used as received. The ^{1}H and ^{31}P{^{1}H} NMR (δ in ppm) spectra were recorded using a Varian spectrometer operating at the appropriate frequencies using TMS and 85% H_3PO_4 as internal and external references, respectively. Positive shifts lie downfield in all the cases. IR spectra were recorded on a Nicolet Impact 400 FT-IR instrument in KBr disks. Microanalyses were performed on a Carlo Erba model 1112 elemental analyzer. Mass spectrometry experiments were carried out using a Waters Q-Tofmicro-YA-105. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of *cis*-[^{t}BuNP(OCH$_2$CH$_2$OMe)]$_2$ (3). A mixture of 2-(methoxy)ethanol (1.7 g, 1.8 mL, 22.86 mmol) and triethylamine (2.2 g, 3.1 mL, 22.86 mmol) in 30 mL of diethyl ether was added dropwise over 30 min to a well-stirred diethyl ether (120 mL) solution of *cis*-[^{t}BuNPCl]$_2$ (**1**) (3.14 g, 11.43 mmol) at 0 °C. The reaction mixture was then stirred at room temperature for 24 h. Et_3NHCl was filtered off, and the solvent was removed at reduced pressure to get a colorless liquid, which was further purified by vacuum distillation at 190 °C (0.4 Torr) to give the product **3**. Yield: 84% (3.4 g, 9.59 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.01 (m, *CH$_2$OP*, 4H), 3.53 (t, O*CH$_2$*, $^1J_{HH}$ = 5 Hz, 4H), 3.37 (s, *OMe*, 6H), 1.29 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$,): δ 133.8 (s). Anal. Calcd for $C_{14}H_{32}N_2P_2O_4$: C, 47.45; H, 9.10; N, 7.90. Found: C, 46.97; H, 9.42; N, 7.52. MS (EI): 355.10 (*m*/*z* + 1).

Synthesis of *cis*-[^{t}BuNP(OCH$_2$CH$_2$SMe)]$_2$ (4). A mixture of 2-(methylthio)ethanol (2.32 g, 2.2 mL, 24.12 mmol) and Et_3N (2.4 g 3.4 mL, 12.06 mmol) in 20 mL of diethyl ether was added dropwise over 30 min to a well-stirred diethyl ether solution (80 mL) of *cis*-[^{t}BuNPCl]$_2$ (**1**) (3.3 g, 12.06 mmol) at 0 °C. The reaction mixture was stirred for 24 h at room temperature. The amine hydrochloride was filtered off, and the solvent was removed at reduced pressure to get a colorless liquid of **4**, which was purified by vacuum distillation at 220 °C (0.4 Torr). Yield: 79% (3.6 g, 9.31 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): 4.04 (m, *CH$_2$OP*, 4H), 2.69 (t, *SCH$_2$*, $^1J_{HH}$ = 7.3 Hz, 4H), 2.16 (s, *SMe*, 6H), 1.30 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 134.1 (s). Anal. Calcd for $C_{14}H_{32}N_2P_2O_2S_2$: C, 43.50; H, 8.34; N, 7.24; S, 16.59. Found: C, 43.38; H, 8.57; N, 7.52; S, 17.01. MS (EI): 387.05 (*m*/*z* + 1).

Synthesis of *cis*-[^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)]$_2$ (5). A mixture of 2-(dimethylamino)ethanol (1.6 g, 1.9 mL, 18.87 mmol) and sodium (0.43 g, 18.87 mmol) was taken in 30 mL of THF in a two-necked flask attached with reflux condenser and a dropping funnel. The reaction mixture was refluxed for 6 h and then allowed to cool to room temperature. The THF (60 mL) solution of *cis*-[^{t}BuNPCl]$_2$ (2.59 g, 9.4 mmol) was transferred to the dropping funnel through a cannula, and this was added dropwise to the reaction mixture at 0 °C. The reaction mixture was further stirred for 12 h at room temperature and then filtered through a frit. The solvent was removed under reduced pressure to get an oily liquid, which was distilled at 154 °C (0.3 Torr) to get **5** as a colorless liquid. Yield: 82% (2.93 g, 7.70 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.96 (m, *CH$_2$OP*, 4H), 2.51 (t, *NCH$_2$*, $^1J_{HH}$ = 3.6 Hz, 4H), 2.27 (s, *NMe$_2$*, 12H), 1.29 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 133.7 (s). Anal. Calcd for $C_{16}H_{38}N_4P_2O_2$: C, 50.51; H, 10.06; N, 14.72. Found: C, 50.86; H, 10.43; N, 15.14. MS (EI): 380.31 (*m*/*z* + 1).

Synthesis of *cis*-[PdCl$_2${(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κ*P*}$_2$] (6). A solution of [Pd(COD)Cl$_2$] (21 mg, 0.076 mmol) in 10 mL of CH_2Cl_2 was added dropwise to a solution of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (69 mg, 0.153 mmol) in CH_2Cl_2 (7 mL) at room temperature. The reaction mixture was stirred for 5 h to give a clear yellow solution, which was concentrated to 5 mL, diluted with 3 mL of Et_2O, and then cooled to −30 °C for 1 day to get an analytically pure yellow crystalline product (**6**). Yield: 80% (65 mg, 0.06 mmol). Mp: 203−205 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.03−6.85 (m, *Ph*, 16H), 3.88 (s, *OMe*, 6H), 3.82 (s, *OMe*, 6H), 1.54 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 121.2 (d), 67.9 (d, $^2J_{PP}$ = 53 Hz). Anal. Calcd for $C_{44}H_{64}N_4P_4O_8PdCl_2$: C, 49.01; H, 5.98; N, 5.19. Found: C, 48.75; H, 6.02; N, 5.28. MS (EI): 1043.38 (*m*/*z* − Cl).

Synthesis of *cis*-[PtCl$_2${(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κ*P*}$_2$] (7). A dichloromethane solution (10 mL) of [Pt(COD)Cl$_2$] (30 mg, 0.088 mmol) was added to *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (79 mg, 0.176 mmol) in 10 mL of CH_2Cl_2 at 25 °C. The resultant clear solution was stirred for 6 h. Then the solution was concentrated to 5 mL, diluted with 5 mL of Et_2O, and stored at −30 °C for 1 day to afford an analytically pure white crystalline product (**7**). Yield: 77% (79 mg, 0.067 mmol). Mp: 182−184 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14−6.86 (m, *Ph*, 16H), 3.84 (s, *OMe*, 6H), 3.85 (s, *OMe*, 6H), 1.49 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 126.1 (d), 40.3 (d, $^2J_{PP}$ = 7.3 Hz, $^1J_{PtP}$ = 4861 Hz). Anal. Calcd for $C_{44}H_{64}N_4P_4O_8PtCl_2$: C, 45.28; H, 5.52; N, 4.80. Found: C, 45.17; H, 5.76; N, 4.57.

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Synthesis of *trans*-[PdCl$_2$\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}$_2$] (8). A dichloromethane solution (7 mL) of [Pd(NCPh)$_2$Cl$_2$] (26 mg, 0.07 mmol) was added dropwise to a 5 mL of a dichloromethane solution of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (63 mg, 0.14 mmol) at room temperature. The reaction mixture was stirred for 4 h and then concentrated to 7 mL, diluted with 2 mL of Et$_2$O, and placed at −30 °C for 2 days to afford yellow crystals. Yield: 82% (68 mg, 0.057 mmol). Mp: 210−212 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.02−6.83 (m, *Ph*, 16H), 3.88 (s, *OMe*, 6H,), 3.82 (s, OMe, 6H), 1.54 (s, ^{t}*Bu*, 36H). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 128.3 (s), 84.6 (br s). Anal. Calcd for C$_{44}$H$_{64}$O$_8$P$_4$N$_4$PdCl$_2$: C, 49.01; H, 5.98; N, 5.19. Found: C, 49.03; H, 5.97; N, 5.22.

Synthesis of *cis*-[PdCl$_2$(PEt$_3$)\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}] (9). A red colored solution of [Pd(PEt$_3$)Cl$_2$]$_2$ (31 mg, 0.052 mmol) in 5 mL of CH$_2$Cl$_2$ was added dropwise to a CH$_2$Cl$_2$ solution (7 mL) of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (49 mg, 0.11 mmol) at room temperature. The reaction mixture was stirred for 6 h. The clear pale yellow solution obtained was concentrated to 3 mL, diluted with 3 mL of Et$_2$O, and placed at −30 °C for 1 day to get analytically pure product (**9**) as pale yellow crystals. Yield: 74% (58 mg, 0.077 mmol). Mp: 204−206 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.03−6.85 (m, *Ph*, 8H), 3.85 (s, *OMe*, 3H), 3.81 (s, *OMe*, 3H), 2.25 (m, *CH$_2$*, 2H), 1.51 (s, ^{t}*Bu*, 18H), 1.25 (m, *CH$_3$*, 3H). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 127.2 (s), 85.7 (dd, $^2J_{PP}$ = 3.9 Hz, $^2J_{pp}$ = 16.8 Hz), 35.8 (d, $^2J_{PP}$ = 17 Hz). Anal. Calcd for C$_{28}$H$_{47}$N$_2$P$_3$O$_4$PdCl$_2$: C, 45.08; H, 6.35; N, 3.75. Found: C, 45.35; H, 6.74; N, 3.34. MS (EI): 711.29 (*m*/*z* − Cl).

Synthesis of [(PdCl(η^3-C$_3$H$_5$))$_2$\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}] (10). A solution of [PdCl(η^3-C$_3$H$_5$)]$_2$ (27 mg, 0.075 mmol) in 7 mL of dichloromethane was added dropwise over a dichloromethane (5 mL) solution of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (33 mg, 0.075 mmol) at room temperature. The reaction mixture was stirred for 4 h and then concentrated to 3 mL, diluted with 3 mL of Et$_2$O, and kept at −30 °C for 1 day to get pure crystalline product. Yield: 77% (47 mg, 0.057 mmol). Mp: 162−164 °C (dec). ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58−6.88 (m, *Ph*, 8H), 5.64 (br, *CH*, 2H), 4.66 (d, syn *CH$_2$*, J_{HH} = 7.5 Hz, 4H), 3.65 (d, anti *CH$_2$*, J_{HH} = 14.7 Hz, 4H), 3.85 (s, *OMe*, 6H), 1.55 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 121.1 (s). Anal. Calcd for C$_{28}$H$_{42}$O$_4$P$_2$N$_2$Pd$_2$Cl$_2$: C, 41.19; H, 5.18; N, 3.43. Found: C, 41.30; H, 5.03; N, 3.41.

Synthesis of [RuCl$_2$(η^6-cymene)\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}] (11). A dichloromethane solution (10 mL) of [Ru(η^6-cymene)Cl$_2$]$_2$ (53 mg, 0.087 mmol) was added dropwise to a 7 mL of a dichloromethane solution of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (78 mg, 0.17 mmol) at room temperature. The reaction mixture was stirred for 6 h and then concentrated to 10 mL, diluted with 5 mL of Et$_2$O, and placed at −30 °C for 1 day to get analytically pure crystalline product. Yield: 84% (110 mg, 0.14 mmol). Mp: 168−170 °C. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.53−6.85 (m, *Ph*, 8H), 5.98 (d, cymene *Ph*, J_{HH} = 6.4 Hz, 2H), 5.75 (d, cymene *Ph*, 2H), 3.95 (s, *OMe*, 3H), 3.81 (s, *OMe*, 3H), 3.07 (septet, *CH*, 1H), 2.23 (s, *CH$_3$*, 3H), 1.40 (s, ^{t}*Bu*, 18H), 1.30 (d, *C(CH$_3$)$_2$*, J_{HH} = 6.7 Hz, 6H). ^{31}P-{^{1}H} NMR (121 MHz, CDCl$_3$): δ 133.5 (d, $^2J_{PP}$ = 8.7 Hz), 109.6 (d). Anal. Calcd for C$_{32}$H$_{46}$P$_2$N$_2$O$_4$RuCl$_2$: C, 50.79; H, 6.12; N, 3.70. Found: C, 50.33; H, 6.08; N, 3.72. MS (EI): 685.28 (*m*/*z* − 2Cl).

Synthesis of [RhCl(COD)\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}] (12). A dichloromethane (5 mL) solution of [Rh(COD)Cl]$_2$ (19 mg, 0.039 mmol) was added dropwise to *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (35 mg, 0.079 mmol) in 7 mL of CH$_2$Cl$_2$. The reaction mixture was stirred for 4 h and then concentrated to 5 mL, diluted with 2 mL of Et$_2$O, and placed at −30 °C for 1 day to get analytically pure product as yellow crystals. Yield: 87% (0.047 g, 0.068 mmol). Mp: 224−226 °C (dec). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.06−6.81 (m, *Ph*, 8H), 4.28 (d, *CH*, 4H), 3.81 (s, *OMe*, 3H), 3.81 (s, *OMe* 3H), 2.49 and 1.75 (d, *CH$_2$*, 8H), 1.52 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 131.7 (s), 102.8 (d, $^1J_{RhP}$ = 229 Hz). Anal. Calcd for C$_{30}$H$_{44}$P$_2$N$_2$O$_4$RhCl: C, 51.69; H, 6.36; N, 4.01. Found: C, 51.29; H, 6.38; N, 4.00. MS (EI): 661.32 (*m*/*z* − Cl).

Synthesis of [IrCl(COD)\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))-κP\}$_2$] (13). This was synthesized by a procedure similar to that for **12** using [Ir(COD)Cl]$_2$ (13 mg, 0.019 mmol) and *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (17 mg, 0.038 mmol). Yield: 72% (0.021 g, 0.026 mmol). Mp: 208−210 °C (dec). ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.07−6.60 (m, *Ph*, 8H), 4.43 (d, *CH*, 4H), 3.89 (s, *OMe*, 3H), 3.81 (s, *OMe* 3H), 2.37 and 1.83 (d, *CH$_2$*, 8H), 1.45 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (161 MHz, CDCl$_3$): δ 133.0 (s), 88.5 (s). Anal. Calcd for C$_{30}$H$_{44}$P$_2$N$_2$O$_4$IrCl: C, 45.82; H, 5.64; N, 3.56. Found: C, 46.03; H, 5.42; N, 3.65.

Synthesis of [Rh$_2$(CO)$_2$Cl$_2$\{(^{t}BuNP(OCH$_2$CH$_2$OMe))$_2$\}-κP]$_2$ (14). A mixture of [Rh(CO)$_2$Cl]$_2$ (30 mg, 0.077 mmol) and *cis*-[^{t}BuNP(OCH$_2$CH$_2$OMe)]$_2$ (27 mg, 0.077 mmol) in CH$_3$CN (10 mL) was stirred under reflux condition for 4 h. The solvent was removed under reduced pressure, redissolved in 3 mL of CH$_2$Cl$_2$, and diluted with 3 mL of petroleum ether. Keeping this solution at room temperature for 1 day afforded orange color microcrystals. Yield: 76% (40 mg, 0.058 mmol). Mp: 128−220 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.12 (m, *CH$_2$OP*, 4H), 3.50 (t, *OCH$_2$*, 4H, $^1J_{HH}$ = 4.64 Hz), 3.32 (s, *OMe*, 6H,), 1.73 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 116.6 (m, $|^1J_{RhP} + {}^3J_{RhP}|$ = 267, $^2J_{PP}$ = 42 Hz). FT-IR (KBr disk): ν_{CO} 2013 (s), 1998 (s) cm^{-1}. Anal. Calcd for C$_{32}$H$_{64}$N$_4$P$_4$O$_{12}$Rh$_4$Cl$_4$: C, 27.96; H, 4.69; N, 4.07. Found: C, 27.68; H, 4.54; N, 4.11.

Synthesis of [Rh(CO)Cl\{^{t}BuNP(OCH$_2$CH$_2$SMe)-$\kappa P,\kappa S$\}]$_2$ (15). A mixture of [Rh(CO)$_2$Cl]$_2$ (36 mg, 0.094 mmol) and *cis*-[^{t}BuNP-(OCH$_2$CH$_2$SMe)]$_2$ (34 mg, 0.094 mmol) in CH$_3$CN (10 mL) was stirred under reflux condition for 4 h. The solution was concentrated to 3 mL, added to 3 mL of Et$_2$O, and stored at −30 °C for 1 day to get yellow crystalline product (**15**). Yield: 79% (53 mg, 0.073 mmol). Mp: 214−216 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.36 (m, *CH$_2$OP*, 4H), 2.92 (s, *SMe*, 6H), 2.67 (t, *SCH$_2$*, $^1J_{HH}$ = 4 Hz, 4H), 1.66 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 121.9 (m, $|^1J_{RhP} + {}^3J_{RhP}|$ = 235 Hz, $^2J_{PP}$ = 45 Hz). FT-IR (KBr disk): ν_{CO} 2028 (s), 2013 (s) cm^{-1}. Anal. Calcd for C$_{16}$H$_{32}$N$_2$P$_2$O$_4$S$_2$-Rh$_2$Cl$_2$: C, 26.71; H, 4.48; N, 3.89; S, 8.91. Found: C, 27.14; H, 4.64; N, 3.67, S; 8.53. MS (EI): 683.42 (*m*/*z* − Cl).

Synthesis of [Rh(CO)Cl\{^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)-$\kappa P,\kappa N$\}]$_2$ (16). A mixture of [Rh(CO)$_2$Cl]$_2$ (32 mg, 0.084 mmol) and *cis*-[^{t}BuNP(OCH$_2$CH$_2$NMe$_2$)]$_2$ (32 mg, 0.084 mmol) in CH$_3$CN (10 mL) was stirred under reflux condition for 4 h. The solution was allowed to cool to room temperature, concentrated to 5 mL, and stored at −30 °C for 1 day to get yellow crystals of **16**. Yield: 76% (43 mg, 0.062 mmol). Mp: 218−220 °C (dec). ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.19 (m, *CH$_2$OP*, 4H), 2.72 (s, *NMe$_2$*, 12H), 2.68 (t, *NCH$_2$*, $^1J_{HH}$ = 6 Hz), 2.01 (s, *CH$_3$CN*, 3H), 1.72 (s, ^{t}*Bu*, 18H). ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 124.5 (m, $|^1J_{RhP} + {}^3J_{RhP}|$ = 259 Hz, $^2J_{PP}$ = 44 Hz). FT-IR (KBr disk): ν_{CO} 2018 (s), 1998 (s) cm^{-1}. Anal. Calcd for C$_{18}$H$_{38}$N$_4$P$_2$O$_4$Rh$_2$Cl$_2$CH$_3$CN: C, 31.84; H, 5.47; N, 9.28. Found: C, 31.98; H, 5.68; N, 9.59. MS (EI): 677.05 (*m*/*z* − Cl).

X-ray Crystallography. Crystals of **8**, **9**, **12**, **14**, and **16** were 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. A full sphere of data was collected using 606 scans in ω (0.3°/scan) at φ = 0, 120, and 240° using the

SMART software package.[27] The raw data were reduced to F^2 values using the SAINT+ software,[28] and a global refinement of unit cell parameters employing 5880−8410 reflections chosen from the full data set was performed. Multiple measurements of equivalent reflections provided the basis for an empirical absorption correction as well as a correction for any crystal deterioration during the data collection (SADABS[29]). The structures were solved by direct method and refined by full-matrix least-squares procedures using the SHELXTL program package.[30] 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.

(27) *SMART*, version 5.625; Bruker-AXS: Madison, WI, 2000.
(28) *SAINT+*, version 6.35A; Bruker-AXS: Madison, WI, 2002.
(29) Sheldrick, G. M. *SADABS*, version 2.05; University of Göttingen: Göttingen, Germany, 2002.
(30) (a) *SHELXTL*, version 6.10; Bruker-AXS: Madison, WI, 2000. (b) Sheldrick, G. M. *SHELXS97 and SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **8**, **9**, **12**, **14**, and **16**. This material is available free of charge via the Internet at http://pbs.acs.org.

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