Tetranuclear Rhodium(I) Macrocycle Containing Cyclodiphosphazane $[Rh_2(\mu\text{-}Cl)_2(CO)_2\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}_2]$ and Its Reversible Conversion into *trans*-$[Rh(CO)Cl\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}_2]$

P. Chandrasekaran,[†] Joel T. Mague,[‡] and Maravanji S. Balakrishna*[,†]

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076, India, and Department of Chemistry, Tulane University, New Orleans, Louisiana 70118

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The 1:1 reaction between *cis*-$[^tBuNP(OC_6H_4OMe\text{-}o)]_2$ (**2**) and $[Rh(\mu\text{-}Cl)(CO)_2]_2$ affords novel tetranuclear rhodium(I) macrocycle (**3**) containing two cyclodiphosphazanes bridged by two $[Rh(\mu\text{-}Cl)(CO)]_2$ moieties, whereas the corresponding 4:1 reaction affords *trans*-$[Rh(CO)Cl\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}_2]$ (**4**).

Introduction

In recent years, there has been considerable interest in the construction of supramolecular compounds through coordination chemistry.[1] The metallamacrocycles[2] are one of the most important supramolecular architectures used in catalysis, sensors, and molecular electronics.[3] Nitrogen donor ligands with bis(pyridine) frameworks have been widely used for constructing macrocycles.[4] Macrocycles containing phosphorus centers are less extensive, mainly due to the lack of availability of suitable phosphorus(III) frameworks. Diazadiphosphetidines or cyclodiphosphazanes of the type $[RNPCl]_2$ with almost planar N_2P_2 rings are one such type of system which can form a variety of macrocycles through nucleophilic substitutions at phosphorus centers.[5] Although the main group chemistry of cyclodiphosphazanes has been extensively studied by Chivers' and Stahl's groups,[6] their utility in coordination chemistry is limited[7] and their polynuclear transition-metal complexes are even less extensive.[8] We report here the synthesis of a novel tetrarhodium(I) macrocycle containing two $[Rh(\mu\text{-}Cl)(CO)]_2$ units bridged by two cyclodiphosphazanes and of a *trans*-mononuclear rhodium(I) derivative containing two monodentate cyclodiphosphazanes.

Results and Discussion

The reaction of cyclodiphosphazane, $[^tBuNPCl]_2$ (**1**), with 2 equiv of *o*-methoxyphenol in the presence of triethylamine afforded *cis*-$[^tBuNP(OC_6H_4OMe\text{-}o)]_2$ (**2**) in quantitative yield. Compound **2** is a white solid and soluble in all common organic solvents. The ^{31}P NMR spectrum of **2** shows a single resonance at 145.7 ppm indicating the symmetric nature of two phosphorus centers. The analytical data, ^1H NMR, and mass spectral data are consistent with the structure proposed for **2**.

In the reaction of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with 1 equiv of **2,** a tetrarhodium(I) macrocycle, $[Rh_2(\mu\text{-}Cl)_2(CO)_2\{(^tBuNP(OC_6H_4OMe\text{-}o))_2\text{-}\kappa P\}]_2$ (**3),** was obtained as shown in Scheme 1. The ^{31}P NMR spectrum of complex **3** consists of an AA′XX′ multiplet[9] centered at 115.8 ppm with

* To whom correspondence should be addressed. Fax: +91-22-2572-3480. Tel: +91-22-2576-7181. E-mail: krishna@iitb.ac.in.
[†] Indian Institute of Technology.
[‡] Tulane University.

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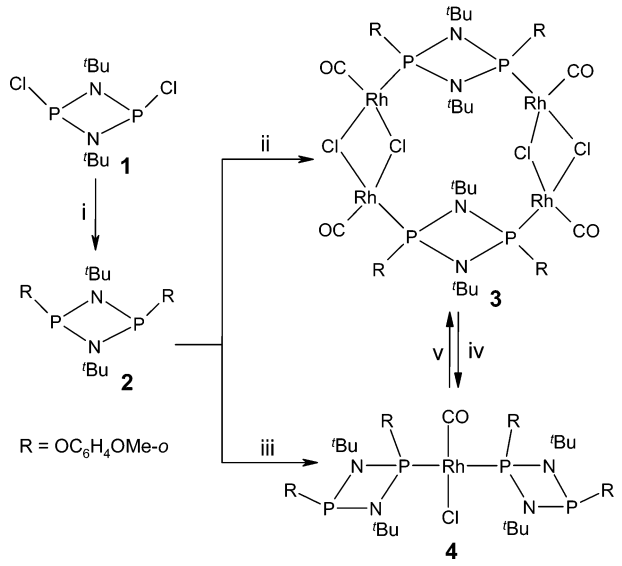
Scheme 1[a]



[a] Key: (i) $2HOC_6H_4OMe$-*o*, Et_3N/Et_2O; (ii) $[Rh(\mu\text{-}Cl)(CO)_2]_2$, CH_3CN; (iii) $0.25[Rh(\mu\text{-}Cl)(CO)_2]_2$, CH_2Cl_2; (iv) $6[^t BuNPR]_2$ (**2**), $CDCl_3$; (v) $1.5[Rh(\mu\text{-}Cl)(CO)_2]_2$, $CDCl_3$.

$|^1J_{RhP} + {}^3J_{RhP}| = 282$ Hz and $^2J_{PP} = 47$ Hz. This clearly indicates the magnetic nonequivalence of the two phosphorus centers. The noncoordinating nature of the methoxy groups was confirmed by the ^1H NMR spectrum which did not show any change in the chemical shift of the methoxy protons as compared to the same in the free ligand. The IR spectrum of **3** shows two absorptions at 2020 and 1992 cm^{-1} which is consistent with the *cis*-related CO/phosphine structures proposed for similar complexes.[10] The reaction of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ with 4 equiv of **2** in dichloromethane afforded bright yellow crystals of *trans*-[Rh(CO)Cl{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP}$_2$] (**4**) in good yield. The ^{31}P NMR spectrum of **4** shows a singlet at 130.8 ppm for uncoordinated phosphorus centers and a doublet centered at 112.5 ppm for coordinated phosphorus centers with a $^1J_{RhP}$ coupling of 187 Hz. The low $^1J_{RhP}$ is attributed to the *trans*-disposition of two phosphorus centers. The IR spectrum of **4** shows ν_{CO} at 2019 cm^{-1}. The mass spectrum of **4** shows a peak at 1031.43, which corresponds to (m/z − Cl). The structures of compounds **3** and **4** were finally confirmed by low-temperature single-crystal X-ray diffraction studies.

Perspective views of the molecular structures of compounds **3** and **4** with atom numbering schemes are shown in Figures 1 and 2, respectively. Crystal data and the details of the structure determination are given in Table 1, while selected bond lengths and bond angles appear below the corresponding Figures. The complex **3** is the first example of cyclodiphosphazanes forming a tetranuclear transition metal macrocycle (Figure 1). The structure consists of two $[Rh(\mu\text{-}Cl)(CO)]_2$ units bridged by two cyclodiphosphazanes via P(III) centers to form a centro-symmetric pentacyclic tetranuclear macrocycle with rhodium(I) centers in slightly distorted square planar environment. The Rh(1)−P(1) and Rh(2)−P(2) distances are 2.187(1) and 2.197 (1) Å, respectively. Two planar P_2N_2 rings are almost orthogonal to the slightly inward puckered $[Rh(\mu\text{-}Cl)]_2$ rings. The distances Rh(1)−Cl(1) (2.353(1) Å) and Rh(1)−Cl(2) (2.410(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 91.02(3)° and 88.60(3)°, respectively. These differences may be attributed to bond-strain reduction within the macrocycle.

The molecular structure of **4** is shown in Figure 2. The rhodium(I) center is in a slightly distorted square

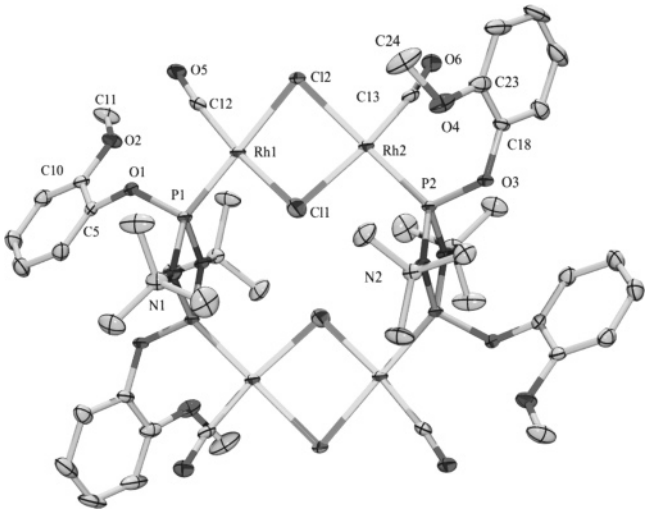


Figure 1. Molecular structure of **3** in the crystal (hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (deg): Rh(1)−P(1), 2.187(1); Rh(2)−P(2), 2.197(1); Rh(1)−Cl(1), 2.353(1); Rh(1)−Cl(2), 2.410(1); Rh(2)−Cl(1), 2.364(1); Rh(2)−Cl(2), 2.409(1); Rh(1)−C(12), 1.825(3); Rh(2)−C(13), 1.820(3); P(1)−N(1), 1.692(3); P(2)−N(2), 1.692(3); Rh(1)···Rh(2), 3.365; P(1)−Rh(1)−C(12), 89.47(11); P(1)−Rh(1)−Cl(1), 96.61(3); Cl(1)−Rh(1)−Cl(2), 84.17(3); Cl(2)−Rh(1)−C(12), 89.75(11); Rh(1)−Cl(1)−Rh(2), 91.02(3); Rh(1)−Cl(2)−Rh(2), 88.60(3).

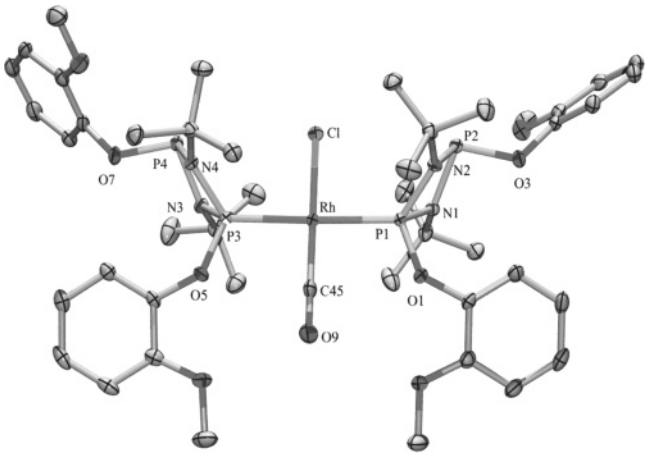


Figure 2. Molecular structure of **4** in the crystal. Selected bond lengths (Å) and angles (deg): P(1)−Rh, 2.278(1); P(3)−Rh, 2.286(1); Rh−Cl, 2.364(1); Rh−C(45), 1.825(2); P(1)−N(1), 1.677(2); P(1)−N(2), 1.680(2); P(2)−N(1), 1.723(2); P(2)−N(2), 1.720(2); O(9)−C(45), 1.145(3); P(1)−Rh−Cl, 88.96(2); P(1)−Rh−C(45), 91.34(7); P(3)−Rh−Cl, 87.84(2); P(3)−Rh−C(45), 91.80(7); P(1)−Rh−P(3), 175.73(2); Cl−Rh−C(45), 178.69(8).

(9) The ^{31}P NMR spectrum of **3** is best interpreted as the A part of an AA′XX′ nuclear spin system with $J_{XX'} = 0$.

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Table 1. Crystallographic Information for Compounds 3 and 4

	3	**4**
formula	$C_{48}H_{64}Cl_4N_4O_{12}P_4Rh_4$	$C_{45}H_{64}ClN_4O_9P_4Rh$
fw	1566.36	1067.24
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	15.642(2)	13.774(2)
b, Å	13.640(1)	11.105(1)
c, Å	14.790(1)	32.790(4)
α, deg	90	90
β, deg	112.799(1)	96.607(2)
γ, deg	90	90
V, Å^3	2909.0(5)	4982.3(10)
Z	4	4
D_{calc}, g cm^{-3}	1.788	1.423
μ (Mo Kα), mm^{-1}	1.469	0.581
F (000)	1568	2224
crystal size (mm)	0.02 × 0.11 × 0.19	0.12 × 0.15 × 0.17
T (K)	100	100
2θ range, deg	1.4−28.4	1.5−28.3
total no. reflns	25324	43664
no. of indep reflns	6967 [R_{int} = 0.036]	12003 [R_{int} = 0.038]
GOF (F^2)	1.02	1.04
R_1[a]	0.0369	0.0387
wR_2[b]	0.0985	0.0869

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

planar environment with P_2N_2 rings bending inward making the angles P(1)−Rh−Cl (88.96(2)°) and P(3)−Rh−Cl (87.84(2)°) acute. The two *trans* Rh−P bond distances in complex **4** are slightly longer than the equivalent bonds in complex **3** which is expected due to the weakening of back-bonding. The sum of the angles around the nitrogen atoms of cyclodiphosphazanes is ∼355°, which shows that the P_2N_2 rings are slightly puckered.

In an NMR tube experiment, the reaction of **3** with 6 equiv of the *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (**2**) was monitored using ^{31}P NMR spectroscopy in $CDCl_3$. The macrocycle **3** was completely converted into the mononuclear complex **4** within 1 h. Likewise, complex **4** was readily converted into tetranuclear complex **3** when treated with 1.5 equiv of [Rh(μ-Cl)(CO)$_2$]$_2$ under similar reaction conditions.

In conclusion, we have reported the first example of tetranuclear rhodium macrocycle containing cyclodiphosphazanes, which act as bridging 4-electron donor ligands. In the presence of excess cyclodiphosphazane, the Rh−Cl bridges in the tetranuclear complex **3** cleave to give the mononuclear complex **4** in a reversible reaction.

The *cis*-orientation of uncoordinated phosphorus(III) centers in complex **4** can be used to make the heteropolymetallic complexes of high nuclearity. Efforts in this direction are underway.

Experimental Section

All manipulations were performed under rigorously anaerobic conditions using Schlenk techniques. All the solvents were purified by conventional procedures and distilled prior to use.[11] The compounds [^{t}BuNPCl]$_2$[12] (**1**) and [Rh(μ-Cl)(CO)$_2$]$_2$[13] were prepared according to the published procedures. 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. 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 spectra were recorded using Waters Q-Tofmicro-YA-105. Melting points were recorded in capillary tubes and are uncorrected.

Synthesis of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (2). A mixture of 2-methoxyphenol (3.6 g, 3.2 mL, 28.72 mmol) and triethylamine (2.9 g, 4 mL, 28.72 mmol) in 50 mL of diethyl ether was added dropwise over 30 min to a well-stirred diethyl ether (125 mL) solution of **1**, [^{t}BuNPCl]$_2$ (3.95 g, 14.36 mmol), at 0 °C. The reaction mixture was stirred for 18 h at room temperature. Et_3NHCl was filtered off, and the filtrate was concentrated to 30 mL under reduced pressure and stored at −30 °C to afford **2** as a crystalline material. Yield: 96% (6.21 g, 13.7 mmol). Mp: 84−86 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−6.82 (m, Ph, 8H), 3.83 (s, OMe, 6H), 1.38 (s, ^{t}Bu, 18H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 145.6 (s). MS (EI): 451.16 (m/z + 1). Anal. Calcd for $C_{22}H_{32}N_2O_4P_2$: C, 58.66; H, 7.16; N, 6.21. Found: C, 58.33; H, 7.19; N, 6.15.

Synthesis of [Rh$_2$(CO)$_2$Cl$_2$\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}]$_2$ (3). A mixture of [Rh(μ-Cl)(CO)$_2$]$_2$ (60 mg, 0.15 mmol) and *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (70 mg, 0.15 mmol) in CH_3CN (15 mL) was stirred under reflux conditions for 4 h. The resulting yellow solution was evaporated under reduced pressure and twice washed with Et_2O (5 mL) to get yellow solid as product (**3**). Yield: 92% (112 mg, 0.071 mmol). Mp: 230−232 °C dec. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72−6.77 (m, Ph, 16H), 3.80 (s, OMe, 12H), 1.79 (s, ^{t}Bu, 36H). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ 115.8 (m, $|^1J_{RhP} + {}^3J_{RhP}|$ = 282 Hz, $^2J_{PP}$ = 47 Hz). FT-IR (KBr disk): ν_{CO} 2020 (s) cm^{-1}, 1992 (s) cm^{-1}. Anal. Calcd for $C_{48}H_{64}N_4O_{12}P_4Rh_4Cl_4$: C, 36.80; H, 4.11; N, 3.57. Found: C, 36.75; H, 4.12; N, 3.47.

Synthesis of *trans*-[Rh(CO)Cl\{(^{t}BuNP(OC$_6$H$_4$OMe-*o*))$_2$-κP\}$_2$](4). A dichloromethane (5 mL) solution of [Rh(μ-Cl)(CO)$_2$]$_2$ (22 mg, 0.056 mmol) was added dropwise to a well-stirred dichloromethane solution (10 mL) of *cis*-[^{t}BuNP(OC$_6$H$_4$OMe-*o*)]$_2$ (0.103 g, 0.227 mmol) at room temperature. The reaction mixture was stirred for 4 h. The solution was concentrated to 5 mL under reduced pressure, diluted with 3 mL of hexane, and placed at room temperature for a day to get pale yellow crystals as product. Yield: 87% (0.105 g, 0.098 mmol). Mp: 208−210 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22−6.83 (m, Ph, 16H), 3.85 (s, OMe, 6H), 3.82 (s, OMe, 6H), 1.51 (s, ^{t}Bu, 36H). ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$): δ 130.8 (s), 112.5 (d, $^1J_{PRh}$ = 187 Hz). FT-IR (KBr disk): ν_{CO} 2019 (s) cm^{-1}. MS (EI): 1031.43 (m/z − Cl). Anal. Calcd for $C_{45}H_{64}N_4O_9P_4RhCl$: C, 50.64; H, 6.04; N, 5.24. Found: C; 50.67; H, 5.99; N, 5.28.

X-ray Crystallography. A crystal of **3** or **4** 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. A full sphere of data was collected using 606 scans in ω (0.3° per scan) at φ = 0, 120, and 240° using the SMART software package.[14] The raw data were reduced to F^2 values using the SAINT+ software,[15] and a global refinement of unit cell parameters employing 7321−7383 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[16]). The structure was solved by direct methods and refined by full-matrix least-squares procedures using the SHELXTL program package.[17] Hydrogen atoms were

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placed in calculated positions and included as riding contributions with isotropic displacement parameters tied to those of the attached non-hydrogen atoms.

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Supporting Information Available: X-ray crystallographic files (CIF) for the structure determinations of **3** and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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