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Synthesis and Characterization of Cyclotetraphosphato Complexes of Rh(I), Ir(I), Ru(II), and Pd(II)

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The cyclotetraphosphate ion ($P_4O_{12}{}^{4-}$) as a PPN (PPN = $(PPh_3)_2N^+$) salt reacts with $[MCl(cod)]_2$ (M = Rh, Ir; cod = 1,5-cyclooctadiene) to give the dinuclear complexes $(PPN)_2[\{M(cod)\}_2(P_4O_{12})]$, in which the two metal moieties are situated *trans* to each other with respect to the P_4O_4 ring in the solid state. In solution, however, these complexes exist as mixtures of *trans* and *cis* isomers. On the other hand, the $P_4O_{12}{}^{4-}$ ion reacts with 4 equiv of $[Rh(cod)(MeCN)_x]^+$ cation to give the tetranuclear complex $[\{Rh(cod)\}_4(P_4O_{12})]$, where the four Rh(cod) fragments are bound to the P_4O_{12} platform alternately on both sides of the P_4O_4 ring. Dinuclear P_4O_{12} complexes of ruthenium and palladium are also synthesized.

Organometallic derivatives of polyoxoanions are now receiving much attention as soluble models of metal species bound on oxide surfaces. For example, a considerable number of silsesquioxane- and polyoxometalate-supported transition metal complexes have been synthesized[1] and found to exhibit unique reactivities[2] and catalysis.[3] Among such *O*-donor ancillary ligands, our research group has taken note of the cyclophosphate $(P_nO_{3n})^{n-}$ family, whose compounds are composed of *n* corner-sharing PO_4 tetrahedra and have oxygen donor atoms in a regularly cyclic arrangement.[4] With the cyclotriphosphate ion ($P_3O_9{}^{3-}$), there have so far been synthesized several transition metal complexes, where each P_3O_9 ligand is coordinated to a single metal center typically in a κ^3-fashion.[5−7] In contrast, there has been no example for organometallic derivatives of the cylotetraphosphato (P_4O_{12}) ligand. We have expected that, owing to the flexible eight-membered ring structure, the $P_4O_{12}{}^{4-}$ ion can behave as a unique scaffold to bind metal center(s) to form a series of complexes whose coordination structures are very different from those of P_3O_9 complexes. In this Communication, we describe the syntheses of di- and tetranuclear P_4O_{12} complexes of rhodium, iridium, palladium, and ruthenium.

Since the known inorganic P_4O_{12} salts are insoluble in most organic solvents, we have prepared $(PPN)_4(P_4O_{12})\cdot 5H_2O$ (PPN = $(PPh_3)_2N^+$) by anion metathesis of $Na_4P_4O_{12}$ with PPNCl to use as the starting material. This salt smoothly reacts with 1 equiv of $[MCl(cod)]_2$ (M = Rh, Ir; cod =1,5-cyclooctadiene) in MeCN to form the anionic dinuclear complexes $(PPN)_2[\{M(cod)\}_2(P_4O_{12})]$ (M = Rh (**1a**), Ir (**1b**)), which were isolated[8] in 68−82% yield and structurally characterized by X-ray crystallography. The structures of **1a** and **1b** are similar to each other (Figure 1; only **1a** is shown).[9] Thus, complexes **1** adopt a *trans* structure with respect to the P_4O_4 ring in the solid state, where the two

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(8) Mononuclear species could not be detected even in the reactions with 0.5 equiv of $[MCl(cod)]_2$.

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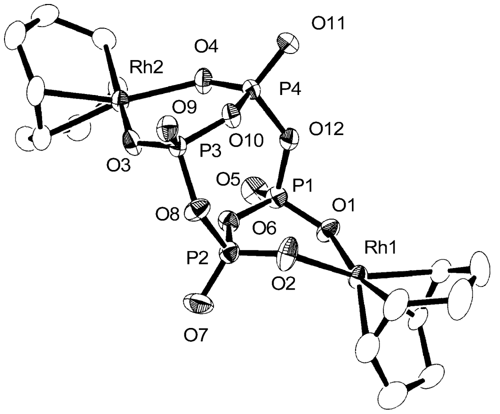


Figure 1. ORTEP drawing of the anionic part of $(PPN)_2[\{Rh(cod)\}_2(P_4O_{12})]\cdot 2MeCN$ (**1a**·2MeCN). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−O(1), 2.082(5); Rh(1)−O(2), 2.083(5); Rh(2)−O(3), 2.093(5); Rh(2)−O(4), 2.079(5); O(1)−Rh(1)−O(2), 88.3(2); O(3)−Rh(2)−O(4), 89.9(2).

metal centers are bound to the respective axial oxygen atoms and the cod ligands with a square-planar geometry. The P_4O_4 ring attains a chair conformation. The metal bound P−O bonds (av 1.489 Å (**1a**); 1.493 Å (**1b**)) are only slightly longer than the uncoordinated P−O bonds (av 1.454 Å (**1a**); 1.455 Å (**1b**)). The MP_2O_3 chelate rings adopt a planar or skew-boat conformation and form large dihedral angles with the P_4 plane (124.3°, 97.9° (**1a**); 123.8°, 97.9° (**1b**)). These conformational features form a striking contrast to those of structurally related V_4O_{12} complexes $[\{M(cod)\}_2(V_4O_{12})]^{2-}$ (M = Rh, Ir),[10] where the chelate rings take a chair conformation and are strongly folded toward the V_4O_4 ring.

In contrast to the solid state structure, the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 18 °C) spectra of **1** demonstrate two singlets (**1a**, δ −18.4, −18.5 (1:8, P_4O_{12}); **1b**, δ −16.2, −16.7 (1:3, P_4O_{12})). We have tentatively concluded that the complexes **1** in solution exist as an equilibrium mixture of *cis* and *trans* isomers (Scheme 1), since only these structures are in agreement with the high symmetry suggested by the $^{31}P\{^1H\}$ NMR spectrum. The *cis* coordination structure is observed as the local structure of the tetrarhodium derivative (vide infra). It should also be mentioned that the isomerization process is considered to include no intermolecular exchange process, because the $^{31}P\{^1H\}$ NMR spectrum of a mixture of **1a** and **1b** shows no signals assignable to the metal-scrambled product. Interestingly, the intensity ratio of the two signals exhibits reversible temperature dependence (Figure 2). For example, the intensity ratio for **1a** was 1:8 at 18 °C, while it changed to 5:4 at −60 °C. Unfortunately, we have not succeeded in determining which signal corresponds to the structurally characterized *trans* isomer.

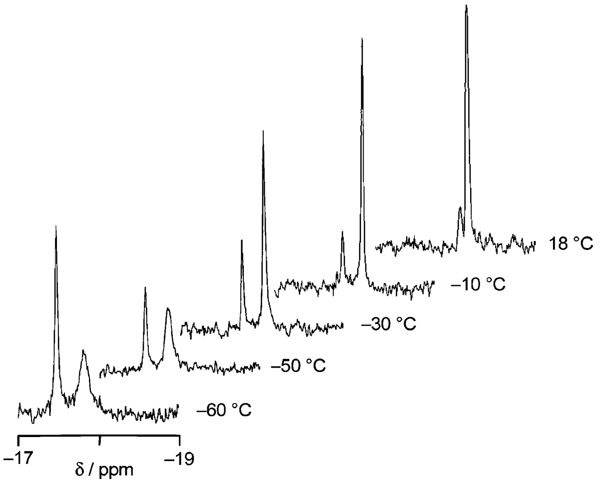
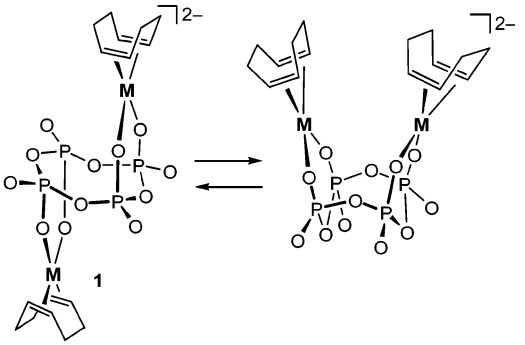
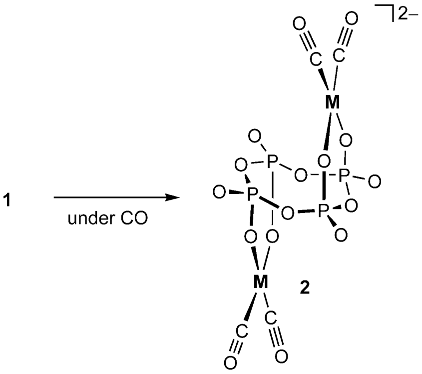


Figure 2. Variable temperature $^{31}P\{^1H\}$ NMR ($CDCl_3$) spectra of **1a**.

Scheme 1



Scheme 2



Complexes **1a** and **1b** react with CO to afford $(PPN)_2[\{M(CO)_2\}_2(P_4O_{12})]$ (M = Rh (**2a**), Ir (**2b**)) (Scheme 2). The X-ray analysis[11] of **2b** (see ORTEP in Supporting Information) demonstrates that the coordination structure is similar to those of **1a** and **1b**. The Ir−O bonds in **2b** (Ir(1)−O(1) = 2.065(6) Å and Ir(1)−O(2) = 2.042(7) Å) are slightly shorter than those in **1b** (av 2.078 Å). The $^{31}P\{^1H\}$ NMR

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(9) Crystal data for **1a**·2MeCN: formula $C_{92}H_{90}N_4O_{12}P_8Rh_2$, M = 1897.34, triclinic, $P\bar{1}$, a = 12.087(2) Å, b = 14.469(3) Å, c = 25.105(5) Å, α = 83.73(2)°, β = 82.65(1)°, γ = 82.92(1)°, V = 4301(1) Å^3, Z = 2, μ = 5.96 cm^{-1}, D_c = 1.465 g cm^{-3}, R = 0.053, R_w = 0.053 [7531 data, $I > 3\sigma(I)$]. For **1b**·2MeCN: formula $C_{92}H_{90}Ir_2N_4O_{12}P_8$, M = 2075.97, triclinic, $P\bar{1}$, a = 12.114(1) Å, b = 14.482(2) Å, c = 25.103(3) Å, α = 83.798(9)°, β = 82.657(10)°, γ = 83.010(9)°, V = 4316.0(8) Å^3, Z = 2, μ = 33.01 cm^{-1}, D_c = 1.597 g cm^{-3}, R = 0.040, R_w = 0.041 [11746 data, $I > 3\sigma(I)$].

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(11) Crystal data for **2b**·$C_2H_4Cl_2$: formula $C_{78}H_{64}Ir_2N_2O_{16}P_8$, M = 1988.50, triclinic, $P\bar{1}$, a = 11.480(3) Å, b = 12.974(4) Å, c = 13.437(4) Å, α = 76.05(3)°, β = 87.91(2)°, γ = 88.59(3)°, V = 1940.7(1) Å^3, Z = 1, μ = 37.36 cm^{-1}, D_c = 1.701 g cm^{-3}, R = 0.061, R_w = 0.078 [6739 data, $I > 3\sigma(I)$]. For **3**: formula $C_{32}H_{48}O_{12}P_4Rh_4$, M = 1160.24, monoclinic, $C2/c$, a = 16.451(3) Å, b = 17.487(4) Å, c = 15.173(4) Å, β = 121.43(1)°, V = 3724(1) Å^3, Z = 4, μ = 19.71 cm^{-1}, D_c = 2.069 g cm^{-3}, R = 0.030, R_w = 0.030 [3048 data, $I > 3\sigma(I)$].

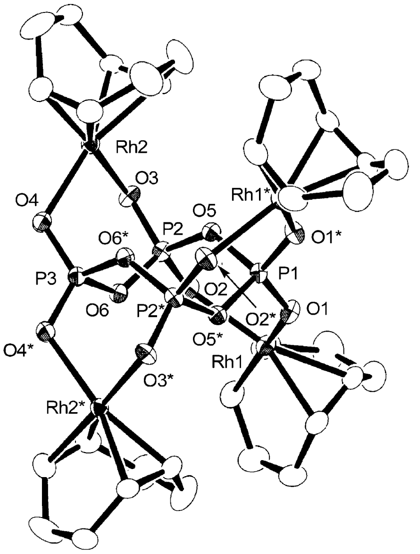
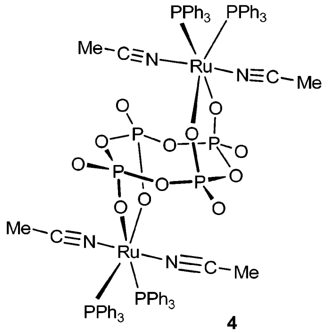


Figure 3. ORTEP drawing of $[\{Rh(cod)\}_4(P_4O_{12})]$ (**3**). Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Rh(1)−O(1), 2.119(3); Rh(1)−O(2), 2.138(3); Rh(2)−O(3), 2.158(3); Rh(2)−O(4), 2.151(3); Rh(1)···Rh(2)*, 5.662(1); O(1)−Rh(1)−O(2), 91.1(1); O(3)−Rh(2)−O(4), 89.1(1).

(CD_2Cl_2) spectra of **2** exhibit two singlets attributable to the P_4O_{12} ligand at room temperature (**2a**, δ −20.6, −22.1 (1:1, P_4O_{12}); **2b**, δ −22.5, −24.0 (1:1, P_4O_{12})), but their intensity ratios do not show notable temperature dependence.

Although the reaction of $(PPN)_4(P_4O_{12})\cdot 5H_2O$ with an excess amounts of $[RhCl(cod)]_2$ failed to give complexes with higher nuclearity, its treatment with 4 equiv of cationic solvated complex $[Rh(cod)(MeCN)_x]^+$ was found to produce the tetrarhodium complex $[\{Rh(cod)\}_4(P_4O_{12})]$ (**3**). This species is also generated by the reaction of **1a** with 2 equiv of $[Rh(cod)(MeCN)_x]^+$. The X-ray diffraction study has confirmed the tetranuclear structure of **3** (Figure 3).[11] The molecule has a crystallographic C_2 axis passing through the P(1) and P(3) atoms. The four $Rh(cod)^+$ fragments are bound to the P_4O_{12} ligand alternately on both sides of the P_4O_4 ring, and the Rh−O bonds (av 2.142 Å) are longer than those of the dinuclear complex **1a** (av 2.084 Å). The Rh(1)···Rh(2)* separation (5.662(1) Å) suggests that there is no direct interaction between the two Rh atoms on the same side of the P_4O_4 ring. The P_4O_{12} ligand now adopts a saddle conformation to accumulate four metal fragments, which reflects the flexibility of the P_4O_{12} ring. It should also be pointed out that a part of the structure of **3** corresponds to the *cis* form of **1a** and indirectly supports the above-mentioned *trans*−*cis* isomerization of **1** in solution. Attempted synthesis of the iridium analogue by reacting $P_4O_{12}{}^{4-}$ with $[Ir(cod)(MeCN)_x]^+$ ended in the formation of an uncharacterized unstable product.

On the other hand, the reactions of $[RuCl_2(PPh_3)_3]$ and $[Pd(C_3H_5)Cl]_2$ with $(PPN)_4(P_4O_{12})\cdot 5H_2O$ afford $[\{Ru(MeCN)_2(PPh_3)_2\}_2(P_4O_{12})]$ (**4**) and $(PPN)_2[\{Pd(C_3H_5)\}_2(P_4O_{12})]$ (**5**), respectively. Preliminary X-ray analysis of **4** has revealed the *trans* structure related to that of complexes **1** and **2b**. Each Ru atom is coordinated by two PPh_3, two MeCN, and two oxygen atoms of the P_4O_{12} ligand with a typical octahedral geometry, where the MeCN ligands occupy the mutually *trans* positions. This coordination environment around the Ru centers in **4** agrees with its NMR (CD_2Cl_2 + CD_3OD, 18 °C) spectrum; the ^1H NMR displays two distinct resonances due to the MeCN ligands (δ 2.20, 2.01 (s, 6H each)), while the $^{31}P\{^1H\}$ NMR displays one PPh_3 singlet (δ 51.7). Only one singlet (δ −20.6) is observed for the $^{31}P\{^1H\}$ NMR signal of the P_4O_{12} ligand over the temperature range of 18 to −80 °C, indicating that complex **4** does not undergo *trans*−*cis* isomerization. This observation implies that the sterically bulky hexacoordinated ruthenium centers cannot be bound on the same side of the P_4O_{12} face. Complex **5** has been characterized by a preliminary X-ray study as well as the ^1H and $^{31}P\{^1H\}$ NMR spectra which exhibit features similar to those of **1**. The orientation of the allyl group is severely disordered in the solid state. The $^{31}P\{^1H\}$ NMR resonance due to the P_4O_{12} ligand appeared as two singlets (δ −19.1, −19.4) in a temperature independent intensity ratio (10:1), which suggests again that **5** undergoes the *trans*−*cis* isomerization in solution.



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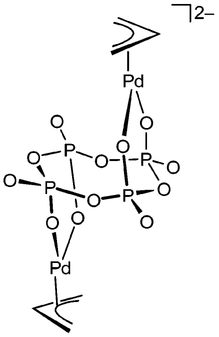

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In summary, we have synthesized the first organotransition metal P_4O_{12} complexes and demonstrated that the P_4O_{12} ligand changes its conformation from the chair form in dinuclear complexes **1** to the saddle form in tetranuclear complex **3**. This flexibility of the P_4O_4 ring and the ability to accumulate more than two metal centers on the P_4O_4 face are the notable characteristics of the P_4O_{12} ligand.

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Supporting Information Available: Experimental details describing the synthesis, and characterization data; a table of crystal data for **1a**, **1b**, **2b**, **3**, **4**, and **5**, including additional ORTEP drawings and tables of selected bond distances and angles of **1b**, **2b**, **4**, and **5**; complete X-ray structural data for **1a**, **1b**, **2b**, **3**, **4**, and **5** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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