Preparation of Mixed-metal Polynuclear Complexes by Stepwise Phosphine-bridging Reaction

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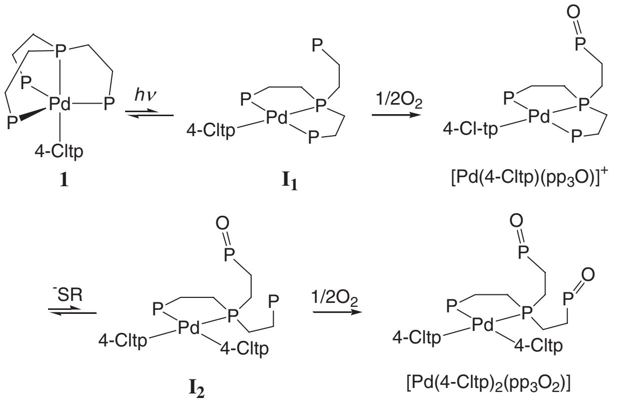
The phosphine-bridged Pd(II)–Pt(II)–Pd(II) trinuclear and Rh(III)–Pd(II)–Pt(II)–Pd(II)–Rh(III) pentanuclear complexes with tris[2-(diphenylphosphino)ethyl]phosphine (pp_3) ligands were successfully prepared by stepwise phosphine-bridging reaction of the terminal phosphino groups of the pp_3 ligands on the Pd(II) cores.

Phosphine ligands have widely used for the bound ligand of various metal catalysts and the characteristics of the catalytic action depend on the metal ions in the catalysts and cocatalysts. Therefore, if one can prepare the mixed-metal polyphosphine complexes with intended sequence of the metal ions, the cooperative effect of the different metal centers of the catalysts and cocatalysts can be investigated systematically. Recently, we have found that one terminal phosphino group of five-coordinate trigonal-bipyramidal Pd(II) complex, $[Pd(4\text{-Cltp})(pp_3)]^+$ (**1**) (4-Cltp = 4-chlorothiophenolate, pp_3 = tris[2-(diphenylphosphino)ethyl]phosphine) is selectively oxidized by photolysis and another terminal phosphino group can be oxidized by the reaction with an equimolar amount of 4-Cltp$^-$ (Scheme 1).[1] Expecting that the intermediates with a dissociated terminal phosphino group ($\mathbf{I}_1$ and $\mathbf{I}_2$) are formed, we have designed the stepwise phosphine-bridging reaction with different metal ions instead of the stepwise oxidation. As a few phosphine-bridged complexes with two kinds of metal ions have been reported recently,[2] we have tried to arrange three kinds of metal ions, Pd(II), Pt(II), and Rh(III), in intended order.



Scheme 1.

The mixed-metal trinuclear complex with alternate arrangement of Pd(II) and Pt(II) (**2**) was prepared by the reaction of **1** (0.103 mmol) with *trans*-$[PtCl_2(NCC_6H_5)_2]$ (0.052 mmol) as the metal complex to be bridged in acetonitrile at room temperature.[3] The single crystals of **2** for X-ray crystallography were obtained by slow evaporation of the chloroform solution.[4]

The linear trinuclear structure with Pd(II)–Pt(II)–Pd(II) metal sequence of **2** was confirmed by X-ray crystallography (Figure 1). The obtained structure revealed that the monodentate thiolato and chloro ligands were exchanged between the Pd(II) and Pt(II) moieties. The ^{31}P and ^{195}Pt NMR spectra of **2** in chloroform are consistent with the crystal structure. By comparison with the ^{31}P NMR spectrum of $[Pd(4\text{-Cltp})(pp_3O)]^+$ (Scheme 1),[1] the signals at 118.3 and 47.2 ppm coupled with each other ($^3J_{\text{P-P}} = 7.3$ Hz) are reasonably assigned to those for the central and two terminal phosphorus atoms of pp_3 coordinated to the square-planar Pd(II) terminals, respectively. The other signal at 14.4 ppm with a pair of satellite peaks due to ^{195}Pt ($^1J_{\text{P-Pt}} = 2767$ Hz) coupled with the central phosphorus atom ($^3J_{\text{P-P}} = 55$ Hz) is assigned to the other terminal phosphorus atom bound to Pt(II). The triplet of ^{195}Pt NMR with coupling constant equal to the above $^1J_{\text{P-Pt}}$ value indicates the equivalent two terminal phosphorus atoms on the Pt(II) center. The NMR spectral simulation[5] revealed a strong coupling between the two phosphorus atoms through the Pt(II) center ($^2J_{\text{P-P}} = 500$ Hz) that shows *trans*(*P*) geometry around the Pt(II) center (Scheme 2).

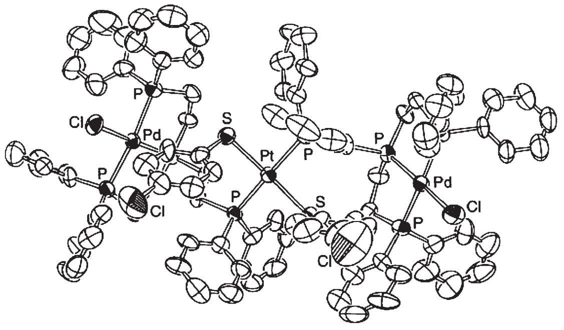
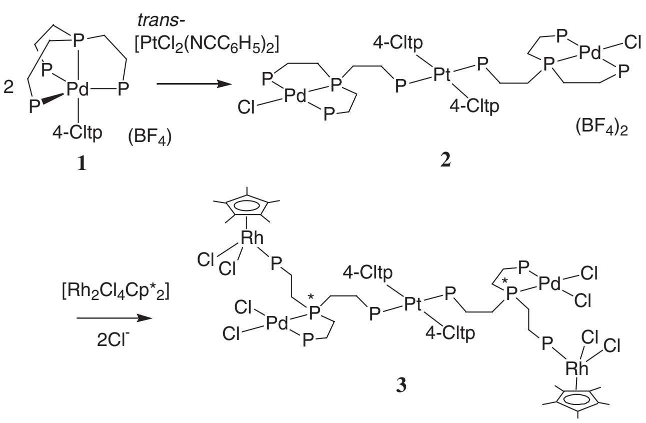


Figure 1. ORTEP diagram of the complex cation of **2**.

The absorption spectral change during the formation of **2** indicated two-step successive reactions exhibiting shift of isosbestic points. Because the lower energy d–d absorption band ($^1A_1' \rightarrow {}^1E'$) characteristic of the five-coordinate trigonal bipyramidal Pd(II) complexes[6] disappeared in the first step, the bridging of the terminal phosphorus of pp_3 in **1** proceeded initially and the monodentate ligands, 4-Cltp$^-$ and Cl$^-$, on the Pd(II) and Pt(II) cores were exchanged subsequently. This mechanism was confirmed by change in the ^{31}P and ^{1}H NMR spectra where chemical shifts of the bound pp_3 and 4-Cltp$^-$ ligands for the initially formed trinuclear complex[7] change gradually to those for the final product **2**. Benzonitrile dissociated from Pt(II) by the initial bridging reaction probably acts as the attacking ligand that is required for substitution on four-coordinate square-planar d^8 metal complexes.[8]

In order to give the mixed-metal pentanuclear complex,



Scheme 2.

Rh(III) was used to extend the metal-sequence. The trinuclear complex **2** (0.037 mmol) was allowed to react with [Rh_2Cl_4-Cp^*_2] (Cp^* = pentamethylcyclopentadienyl) (0.068 mmol) and tetra-*n*-butylammonium chloride (NBu_4Cl) (0.133 mmol) in chloroform, and the orange crystals of the Rh(III)–Pd(II)–Pt(II)–Pd(II)–Rh(III) pentanuclear complex (**3**) were obtained from the concentrated reaction solution by adding ethanol and water.[9]

The ^{31}P NMR spectrum of **3** in chloroform exhibits two sets of signals for each four phosphorus atom of the pp_3 ligand corresponding to formation of the meso and racemic isomers by combination of the chiral central phosphorus atoms in the two Pd(II) moieties (Scheme 2). Multiplets at 88.6 and 89.5 ppm and doublets at 68.1 and 68.5 ppm coupled with each other ($^3J_{\text{P-P}} = 12$ Hz) can be assigned to the central and terminal phosphorus atoms on the Pd(II) square-planes, respectively, by comparison with the spectrum of [Pd(4-Cltp)(pp_3O_2)] (Scheme 1).[1] Signals at 14.3 and 14.7 ppm showing coupling with ^{195}Pt ($^1J_{\text{P-Pt}} = 2647$ Hz) and the central phosphorus atom ($^3J_{\text{P-P}} = 49$ Hz) are assigned to the terminal phosphorus atoms bound to the Pt(II) center. The NMR spectral simulation[5] determined large coupling constant ($^2J_{\text{P-P}} = 550$ Hz) between the two equivalent terminal phosphorus atoms through the Pt(II) center, consistent with the *trans*(*P*) geometry around the Pt(II) square-plane. Agreements of the ^{31}P NMR chemical shifts for the terminal phosphorus atoms on the Pt(II) center and AB splitting pattern of ^1H NMR for the bound 4-$Cltp^-$ ligands between **2** and **3** indicate the same coordination environment around the Pt(II) center. The other signals at 27.6 and 27.7 ppm coupled with Rh(III) ($^1J_{\text{P-Rh}} = 144$ Hz) and the central phosphorus atom ($^3J_{\text{P-P}} = 54$ Hz) are assigned to the terminal phosphorus atoms bound to the Rh(III) terminals by comparison with the reported ^{31}P NMR chemical shifts and $^1J_{\text{P-Rh}}$ values for the Rh(III) complexes having [$RhCl_2Cp^*L$] (L = diphenylphosphino group) moieties with a three-legged piano-stool structure.[10] The ^1H NMR chemical shifts (1.34 ppm) and $^2J_{\text{H-Rh}}$ (3.2 Hz) values for the bound Cp^* are also in good agreement with those for the [$RhCl_2Cp^*L$] moiety.[10] These facts indicate that the bridging reaction successfully proceeds to give the pentanuclear structure of Rh(III)–Pd(II)–Pt(II)–Pd(II)–Rh(III) by using the trinuclear complex **2**, retaining the geometry of the Pt(II) center and the three-legged piano-stool structure of the Rh(III) moieties (Scheme 2).

The ^{31}P NMR spectra of the reaction solutions obtained for the preparation of the polynuclear complexes reported above coincided with those of the corresponding isolated complexes with little impurity. It is confirmed from this fact that the present polynuclear complexes with intended metal sequences were formed quantitatively. Since we have found high activity of the Pd-catalyzed cross-coupling reactions[11] for the present type of polynuclear complexes, further investigation is in progress to clarify the details of the catalytic action.

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References and Notes

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3 Yield 76%. Anal. Found: C, 49.77; H, 4.11; N, 0.00%. Calcd for $C_{96}H_{92}B_2Cl_4F_8P_8Pd_2PtS_2 \cdot H_2O$: C, 50.15; H, 4.12; N, 0.00%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): σ (relative to external D_3PO_4) 14.4 (t, 2P, $^1J_{\text{P-Pt}} = 2767$ Hz, $^2J_{\text{P-P}} = 500$ Hz, $^3J_{\text{P-P}} = 55$ Hz), 47.2 (d, 4P, $^3J_{\text{P-P}} = 7.3$ Hz), 118.3 (tt, 2P). Crystallizing water was confirmed by ^1H NMR.

4 Crystallographic data for **2**: formula, $C_{98}H_{94}B_2Cl_{10}F_8P_8Pd_2$-$PtS_2$; fw = 2519.76; space group, $P - 1$; $a = 15.510(2)$, $b = 15.854(3)$, $c = 22.923(3)$ Å, $\alpha = 97.53(1)$, $\beta = 102.72(1)$, $\gamma = 96.58(1)°$; $V = 5390(1)$ Å^3; $Z = 2$; $\rho_{\text{calcd}} = 1.552$ g cm^{-3}; no. of unique reflections is 7502; $R = 0.050$, $R_w = 0.086$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-244383. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/ retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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7 $^{31}P\{^1H\}$ NMR ($CHCl_3$): σ (relative to D_3PO_4 in external D_2O) 13.7 (t, 2P, $^1J_{\text{P-Pt}} = 2570$ Hz, $^2J_{\text{P-P}} = 450$ Hz, $^3J_{\text{P-P}} = 44$ Hz), 47.8 (d, 4P, $^3J_{\text{P-P}} = 16.7$ Hz), 109.8 (tt, 2P).

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9 Yield 29%. Anal. Found: C, 46.80; H, 4.34; N, 0.00%. Calcd for $C_{116}H_{122}Cl_{10}P_8Pd_2PtRh_2S_2 \cdot 2CHCl_3$: C, 46.70; H, 4.12; N, 0.00%. $^{31}P\{^1H\}$ NMR ($CHCl_3$): σ (relative to external D_3PO_4) 14.3, 14.7 (t, 2P, $^1J_{\text{P-Pt}} = 2647$ Hz, $^2J_{\text{P-P}} = 550$ Hz, $^3J_{\text{P-P}} = 49$ Hz), 27.6, 27.7 (dd, 2P, $^1J_{\text{P-Rh}} = 144$ Hz, $^3J_{\text{P-P}} = 54$ Hz), 68.1, 68.5 (d, 2P, $^3J_{\text{P-P}} = 12$ Hz), 88.6, 89.5 (m, 2P).

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