# Synthesis and Reactions of Water-soluble Diorganoplatinum(II) Complexes

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Ligand displacement reactions of $PtR_2(cod)$ with water soluble tertiary phosphines such as 1,2-bis{di(hydroxymethyl)-phosphino}ethane (DHMPE) or tris(hydroxymethyl)phosphine (THMP) gave new water-soluble diorganoplatinum(II) complexes $PtR_2L_2$ [$L_2 = (HOCH_2)_2PCH_2CH_2P(CH_2OH)_2$: R = Me (**1a**); Et (**1b**); Ph (**1c**), L = $P(CH_2OH)_3$: R = Me (**2a**); Et (**2b**); Ph (**2c**)] at room temperature. They were considerably stable in water and the thermolyses of **1b** and **2b** at 80 °C liberate ethylene and ethane via $\beta$-hydrogen elimination and hydrolysis.

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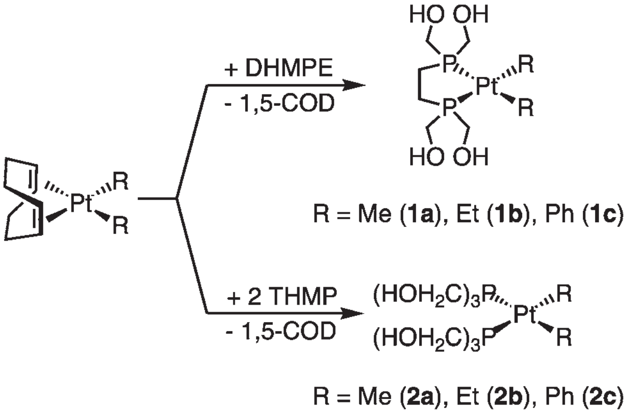
Transition metal-mediated chemical reactions in water is attracting considerable attention, since the use of water as a reaction medium is one of the promising ways to provide a new environmentally benign reaction system.[1] Although many Werner-type transition metal complexes are generally treated in water, organometallic reactions and catalyses usually avoid moisture and oxygen, because the putative intermediates ought to be hydrolyzed under the reaction conditions. Thus, only limited numbers of water soluble complexes with metal-carbon $\sigma$-bonds[2,3] have been reported so far and their reactivities are not well established in spite of their importance for understanding and developing organometallic reactions and catalyses in water.[4,5] Such metal-carbon bonds are generally believed to be very reactive toward water, since many organometals such as Grignard and Gilman reagents as well as organolithiums are violently hydrolyzed with water. In fact, Atwood reported preparation of water-soluble methyliridium(I) complexes *trans*-$IrMe(CO)[P(C_6H_4SO_3M\text{-}3)_3]_2$ (M = Na, K),[3] but they were immediately hydrolyzed in water to form corresponding hydroxoiridium(I) complexes. Although Pringle also reported *cis*-$PtMe_2(thmp)_2$ and *cis*- and *trans*-$[PtMeX(thmp)]^2$ [THMP = tris(hydroxymethyl)phosphine] with insufficient characterization due to facile decomposition during the isolation processes, reactions of these complexes are not reported.[2,6] We now describe the synthesis of a series of water-soluble diorganoplatinum(II) complexes with 1,2-bis{di(hydroxymethyl)phosphino}ethane (DHMPE)[7] or THMP ligand,[2,8] whose Pt-C bonds are considerably stable in water at room temperature. When dimethyl(1,5-cyclooctadiene)platinum(II), $PtMe_2(cod)$ was treated with one equivalent of DHMPE in acetone, DMSO or methanol, immediate ligand displacement took place to give *cis*-dimethyl[1,2-bis{di(hydroxymethyl)phosphino}ethane]platinum(II) *cis*-$PtMe_2(dhmpe)$ (**1a**) with liberation of quantitative amount of 1,5-cyclooctadiene at room temperature.[9] **1a** can be purified by recrystallization from acetone/hexane to give pure white powder. The $^{31}P\{^1H\}$ NMR spectrum of **1a** in $D_2O$ shows a singlet at $\delta$ 49.3 with $^{195}Pt$ satellites. The $^1H$ NMR showed a triplet at $\delta$ 0.50 with $^{195}Pt$ satellites assignable to the Pt-Me and a characteristic second-order multiplet at $\delta$ 1.96 ($AX_2X'_2A'$) assignable to the bridging methylene protons of the DHMPE ligand. Diastereotopic methylene protons for the coordinated DHMPE ligand appeared as an AB quartet at $\delta$ 4.14 and 4.25: the latter involved Pt satellites. The THMP analog **2a** was similarly prepared.[10] Diphenyl derivatives **1c**[11] and **2c**[12] with DHMPE or THMP ligands were also isolated and showed the *ortho*-H protons with $^{195}Pt$ satellites.[11,12] Diethylplatinum(II) analogues *cis*-$PtEt_2L_2$ with these ligands (L = DHMPE (**1b**),[13] 2 THMP (**2b**)[14]) were also obtained. Although it was difficult to isolate them as crystals, the formation was unambiguously determined by the $^1H$ and $^{31}P\{^1H\}$ NMR. Signals due to methylene and methyl protons of the ethyl group in **1b** and **2b** are very close to each other showing one multiplet at $\delta$ 1.1-1.2 accompanied by distinct $^{195}Pt$ satellites of the methylene quartet signal.[13,14] The monodentate THMP ligands in **2a**-**c** are considered to occupy the coordination sites mutually *cis* because of their relatively small $J_{Pt\text{-}P}$ values (1700 Hz for **2a**, 1470 Hz for **2b**, 1660 Hz for **2c**). Addition of free THMP to **2b** did not cause broadening of the signal due to coordinated P nuclei, but the signal of added free THMP was extensively broadened, implying a typical fast dissociative ligand exchange process, whereas DHMPE complex **2a** shows no indication of facile ligand exchange reaction.

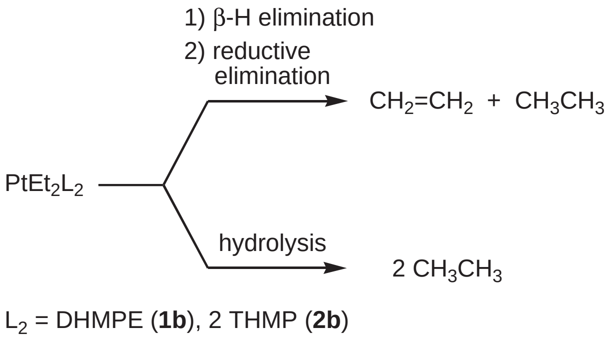


**Scheme 1.**

Diphenylplatinum(II) complexes **1c** and **2c** are soluble and stable in water for a few days at room temperature. On the other hand, dimethylplatinum(II) complexes **1a** and **2a** are relatively unstable in water, slowly liberating methane.[15] Protonolyses of **1a** and **2a** with acid such as HCl immediately liberated quantitative amounts of methane (203%/**1a**, 160%/**2a**).

Of particular interest is thermolysis of diethylplatinum(II) complexes **1b** and **2b**. Heating of **1b** and **2b** in $D_2O$ at 80 °C for 30 min evolved ethylene and ethane in 40 and 114% yields and 46 and 84% yields, respectively, suggesting that disproportionation of the ethyl groups took place in addition to protonolysis, though the mechanism is not clear at present.

The present results summarize the intrinsic thermal stability of the Pt-C bond and occurrence of a typical organometallic



**Scheme 2.**

reaction such as $\beta$-hydrogen elimination even in water, and suggest that such organometallic intermediates should be taken into account in transition metal mediated organic transformations and catalyses in water as well as in biphasic water/organic solvents.

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## References and Notes

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6 These compounds were characterized only by $^{31}$P{$^1$H}- and $^{13}$C{$^1$H} NMR spectra of the phosphorus ligands and no distinct evidence for Pt-Me moiety are described. Accordingly no chemical reactions of these complexes are reported.[2]

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9 **1a**: Yield 72%. $^1$H NMR ($D_2O$): $\delta$ 0.50 (t, $^3J_{\text{H-P}} = 7$ Hz, $^2J_{\text{H-Pt}} = 69$ Hz, 6H, Pt-*Me*), 1.96 (m, 4H, $PC_2H_4$), 4.14 (dd, $^2J_{\text{H-H}} = 14$ Hz, $^2J_{\text{H-P}} = 2.1$ Hz, 4H, $PCH_2OH$), 4.25 (d, $^2J_{\text{H-H}} = 14$ Hz, $^3J_{\text{H-Pt}} = 12$ Hz, 4H, $PCH_2OH$). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 49.3 (s, $^1J_{\text{P-Pt}} = 1640$ Hz). Anal. Calcd for $C_8H_{22}O_4P_2Pt$: C, 21.87; H, 5.05%. Found: C, 21.05; H, 4.66%.

10 **2a**: Yield 82% (by NMR). $^1$H NMR ($D_2O$): $\delta$ 0.49 (brs, $^2J_{\text{H-H}} = 66$ Hz, 6H, Pt-*Me*), 4.29 (br, 12H, $PCH_2OH$). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 13.2 (s, $^1J_{\text{P-Pt}} = 1700$ Hz).

11 **1c**: Yield 64%. $^1$H NMR ($D_2O$): $\delta$ 2.10 (m, 4H, $PC_2H_4$), 4.11 (m, 8H, $PCH_2OH$), 6.85 (t, $^3J_{\text{H-H}} = 7$ Hz, 2H, *p-Ph*), 7.08 (t, $^3J_{\text{H-H}} = 7$ Hz, 4H, *m-Ph*), 7.46 (t, $^3J_{\text{H-H}} = {}^4J_{\text{H-P}} = 7$ Hz, $^3J_{\text{H-Pt}} = 52$ Hz, *o-Ph*). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 43.9 (s, $^1J_{\text{P-Pt}} = 1600$ Hz). Anal. Calcd for $C_{18}H_{26}O_4P_2Pt$: C, 38.37; H, 4.65%. Found: C, 38.38; H, 4.81%.

12 **2c**: Yield 58%. $^1$H NMR ($D_2O$): $\delta$ 4.06 (s, $^3J_{\text{H-Pt}} = 11$ Hz, 12H, $PCH_2OH$), 6.79 (t, $^3J_{\text{H-H}} = 7$ Hz, 2H, *p-Ph*), 7.01 (t, $^3J_{\text{H-H}} = 7$ Hz, 4H, *m-Ph*), 7.41 (d, $^3J_{\text{H-H}} = 7$ Hz, $^3J_{\text{H-Pt}} = 57$ Hz, 4H, *o-Ph*). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 4.5 (s, $^1J_{\text{P-Pt}} = 1660$ Hz). Anal. Calcd for $C_{18}H_{28}O_6P_2Pt$: C, 36.19; H, 4.72%. Found: C, 36.46; H, 4.50%.

13 **1b**: Yield 86% (by NMR). $^1$H NMR ($D_2O$): $\delta$ 1.25 (q, $^3J_{\text{H-H}} = 8$ Hz, $^2J_{\text{H-Pt}} = 71$ Hz, 4H, Pt-$CH_2CH_3$), 1.26 (m, 6H, Pt-$CH_2CH_3$), 1.88 (m, 4H, $PC_2H_4$), 4.09 (dd, $^2J_{\text{H-H}} = 14$ Hz, $^2J_{\text{H-P}} = 3$ Hz, 4H, $PCH_2OH$), 4.22 (d, $^2J_{\text{H-H}} = 14$ Hz, $^3J_{\text{H-Pt}} = 11$ Hz, 4H, $PCH_2OH$). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 48.3 (s, $^1J_{\text{P-Pt}} = 1460$ Hz).

14 **2b**: Yield 89% (by NMR). $^1$H NMR ($D_2O$): $\delta$ 1.14 (m, 6H, Pt-$CH_2CH_3$), 1.2 (q, 4H, $^3J_{\text{H-H}} = 8$ Hz, $^2J_{\text{H-Pt}} = 129$ Hz, Pt-$CH_2CH_3$) 4.33 (brs, 12H, $PCH_2OH$). $^{31}$P{$^1$H} NMR ($D_2O$): $\delta$ 8.9 (s, $^1J_{\text{P-Pt}} = 1470$ Hz).

15 Pt products were not characterized.