

Enhanced Reductive Elimination of Dialkylgold(III) Complexes in Water

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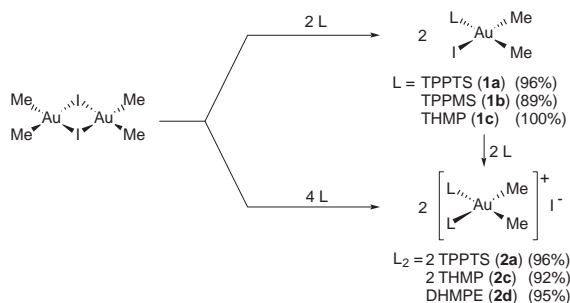
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Neutral and cationic dimethyl- or diethylgold(III) complexes having a water-soluble phosphine ligand, AuR_2XL and $[\text{AuR}_2\text{L}_2]\text{X}$ ($\text{R} = \text{Me}$ or Et ; $\text{X} = \text{Br}$ or I ; $\text{L} = \text{TPPTS}$, TPPMS , THMP , or DHMPE), are prepared. Reductive elimination involving C–C bond formation at Au(III) in water is faster than those in organic solvents.

Water has recently attracted attention as safe, cheap, and environmentally benign reaction medium.¹ If transition metal-mediated organic reactions and catalyses are carried out in water as in organic solvents, it will be highly beneficial in developing and designing new valuable chemical processes, though some transition metal-catalyzed reactions in water have been known.^{1c,2} However, since putative organometallic intermediates are simply believed to be unstable in water, very few reports concerning synthesis and reactions of water-soluble complexes having metal–carbon σ bonds are known to date in spite of their intrinsic importance both in fundamental aspects and applications.³ We previously reported the synthesis and preferential β -hydrogen elimination of water-soluble diorganoplatinum(II) complexes $\text{cis}[\text{PtR}_2\text{L}_2]$ ($\text{L} = \text{TPPTS}$ [3,3',3''-phosphinidynetris(benzenesulfonic acid) trisodium salt], THMP [tris(hydroxymethyl)phosphine], or DHMPE {1,2-bis[di(hydroxymethyl)phosphino]ethane}) even in aqueous medium.^{3d,3e} We now report the synthesis of water-soluble dialkylgold(III) complexes which show enhanced reductive elimination including C–C bond formation in water.

After treatment of dimethylgold(III) dimer, $[\text{AuMe}_2\text{I}]_2$ ⁴ with two equivalents of TPPTS in $\text{H}_2\text{O}/\text{acetone}$ at 0 °C, excess acetone was added to give white powder of water-soluble neutral *cis*-dimethylgold(III) complex, *cis*- $[\text{AuMe}_2\text{I}(\text{TPPTS})]$ (**1a**), quantitatively (Scheme 1).⁵ Further addition of an equimolar amount of TPPTS to **1a** or reaction of the dimer with four equivalents of TPPTS gave a cationic complex *cis*- $[\text{AuMe}_2(\text{TPPTS})_2]\text{I}$ (**2a**). They were purified by reprecipitation from methanol/acetone.

Analogous dimethylgold(III) complexes having TPPMS [3-



Scheme 1.

(diphenylphosphino)benzenesulfonic acid sodium salt], THMP and DHMPE were also prepared similarly. All these complexes were soluble in water. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1a** in D_2O shows a singlet at δ 30.7. The ^1H NMR spectrum of **1a** in D_2O shows two doublets at δ 1.33 ($^3J_{\text{PH}} = 8.1$ Hz) and 1.57 ($^3J_{\text{PH}} = 8.7$ Hz) indicating the square planar *cis* configuration of **1a**. The ^1H NMR of **2a** displays a characteristic second order $\text{A}_3\text{XX}'\text{A}'_3$ multiplet centered at δ 1.31 also showing its *cis*-square planar geometry. Accordingly, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** in D_2O shows a singlet at δ 32.8.

These water-soluble dimethylgold(III) complexes having a TPPTS, TPPMS, or THMP ligand are relatively stable in organic solvent such as THF or ethanol at room temperature, but they reductively eliminated ethane in water even at room temperature, accompanied by formation of Au(I) complex (eq 1).⁶

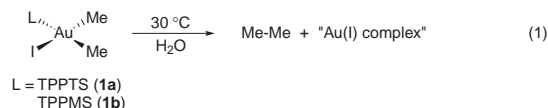


Figure 1 shows the time–yield curves of ethane for the thermolysis of **1b** having TPPMS ligand in various solvent at 30 °C, showing unexpected medium effect of water on reductive elimination.

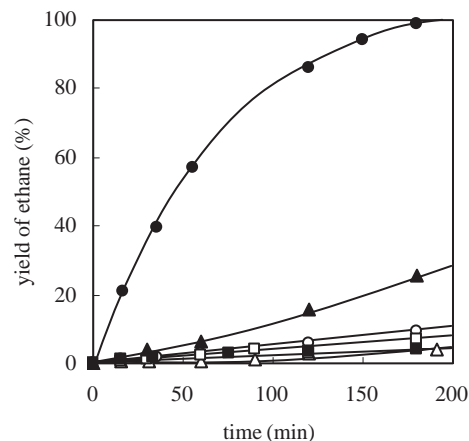
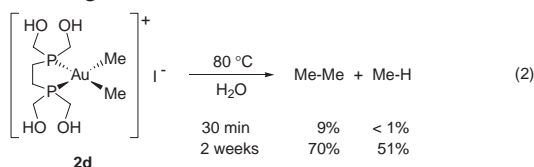


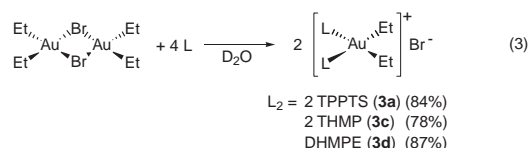
Figure 1. Solvent effect on time-courses for reductive elimination of dimethylgold(III) complex (**1b**) at 30 °C. Ethane evolved in H_2O (●), THF (▲), EtOH (■), MeCN (○), DMSO (△), and HCONHMe (□).

Complexes with TPPTS ligand **1a** and **2a** also liberated ethane in water quantitatively at 40 °C in 60 and 80 min, respectively, but they are stable in methanol and DMSO for a few hours. These results show preferential reductive elimination involving C–C bond formation over protonolysis at Au(III) in water, and more interestingly water medium enhanced reductive elimination in comparison with organic solvents. Simple in-

crease of solvent polarity may not explain the fact.⁷ Possible coordination of water to Au(III) or solvent effect might be responsible for these results. In contrast, cationic complex **2d** having DHMPE ligand was very stable in water and liberated only 1 and 9% yields of methane and ethane at 80 °C for 30 min, but after two weeks at 80 °C, the yields of methane and ethane increased to 51 and 70%, respectively (eq 2). At high temperature hydrolysis became significant relative to reductive elimination.

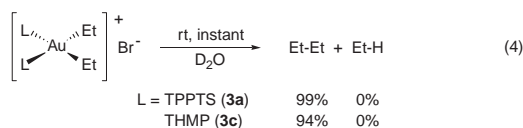


Cationic diethylgold(III) analogues *cis*-[AuEt₂L₂]Br (L₂ = 2TPPTS (**3a**), 2THMP (**3c**), and DHPME (**3d**)) were also prepared in situ by the similar reactions of [AuEt₂Br]₂⁸ with corresponding water-soluble phosphine ligands (eq 3).



It was difficult to isolate the ethyl analogues in a pure form, but the formation was unambiguously confirmed by the ¹H and ³¹P{¹H} NMR.

Reductive elimination of diethylgold(III) analogues with TPPTS or THMP was much faster than that of dimethylgold(III) complexes. They selectively liberated butane quantitatively immediately after dissolving in water at room temperature (eq 4). DHPME complex **3d** was again stable in H₂O, but at 80 °C evolved butane and ethane in 79 and 12% yields, respectively.



Addition of five equivalents of free TPPTS to **2a** effectively suppressed the reductive elimination. Such retardation effect of added tertiary phosphine ligand is well known for the reductive elimination of organogold(III)⁹ and organopalladium(II)¹⁰ complexes in organic solvent such as benzene, where a dissociation of tertiary phosphine ligand giving a 3-coordinate intermediate is the rate determining step for reductive elimination. It is notable that addition of 5 equiv. of NaI to the water solution of neutral dimethylgold(III) complex **1a** also showed significant suppressing effect on the reaction. Ionization of **1a** giving an unstable cationic 3-coordinate T-shape species such as [AuMe₂L]⁺ in water may also be another important intermediate for reductive elimination.

The present results would open opportunity and benefits to apply various nonaqueous organometallic C–C bond forming reactions and catalyses into various aqueous systems. Further detailed studies are required to elucidate the role of water in the facile reductive elimination.

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- Physical and spectroscopic data for **1a**, **1b**, and **2a** are given: [AuMe₂I(TPPTS)] (**1a**)·5H₂O: white powder from methanol/acetone. Anal. Found: C, 23.19; H, 2.58; S, 9.49%. Calcd for C₂₀H₂₈AuI Na₃O₁₄PS₃: C, 23.73; H, 2.79; S, 9.50%. IR (KBr, cm⁻¹): 3449 (ν_{OH}), 1191 (ν_{as}S=O), 1040 (ν_sS=O). ¹H NMR (D₂O, rt): δ 1.33 (d, ³J_{PH} = 8.1 Hz, 3H, Au-CH₃), 1.57 (d, ³J_{PH} = 8.7 Hz, 3H, Au-CH₃), 7.5–8.0 (m, 12H, aryl). ³¹P{¹H} NMR (D₂O, rt) δ 30.7 (s). [AuMe₂I(TPPMS)] (**1b**): white powder from THF/ether. Anal. Found: C, 34.02; H, 3.14; S, 3.61%. Calcd for C₂₀H₂₀AuI Na₃O₃PS: C, 33.44; H, 2.81; S, 4.46%. IR (KBr, cm⁻¹): 1213 (ν_{as}S=O), 1040 (ν_sS=O). ¹H NMR (CD₃OD, rt): δ 0.98 (d, ³J_{PH} = 8.1 Hz, 3H, Au-CH₃), 1.34 (d, ³J_{PH} = 9.0 Hz, 3H, Au-CH₃), 7.3–7.9 (m, 14H, aryl). ³¹P{¹H} NMR (CD₃OD, rt): δ 29.4 (s). [AuMe₂(TPPTS)₂]I (**2a**)·5H₂O: white powder from methanol/acetone. Anal. Found: C, 29.05; H, 2.60; S, 11.80%. Calcd for C₃₈H₄₀AuI Na₆O₂₃P₂S₆: C, 28.87; H, 2.55; S, 12.17%. IR (KBr, cm⁻¹): 3448 (ν_{OH}), 1195 (ν_{as}S=O), 1040 (ν_sS=O). ¹H NMR (D₂O, rt): δ 1.31 (m, 6H, Au-CH₃), 7.3–8.1 (m, 12H, aryl). ³¹P{¹H} NMR (D₂O, rt): δ 32.8 (s). Other complexes were characterized spectroscopically.
- Although complete characterization of the gold product was unsuccessful, Au(I) complex is considered to be formed, since addition of 3 equivalents of TPPTS after thermolysis of **1a** gave a broad singlet at δ 40.3 (D₂O) in ³¹P NMR, which is tentatively assigned to Na₃{Au[P(C₆H₄SO₃)₃]₃} by comparing the following reported data: W. A. Herrmann, J. Keller, and H. Riepl, *J. Organomet. Chem.*, **389**, 103 (1990).
- Dielectric constants (ε): THF (7.58), EtOH (24.55), MeCN (35.94), DMSO (46.45), H₂O (78.39), HCONHMe (182.4).
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