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Preliminary communication

Isolation of stable hydrogen dimethylbis(2-pyridyl)aurate(III)

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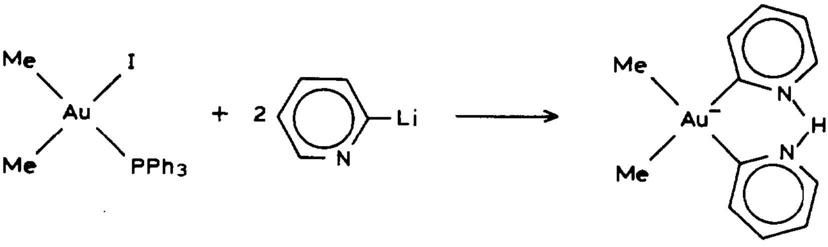
Abstract

Hydrogen dimethylbis(2-pyridyl)aurate(III), a stable anionic organogold(III) complex, has been prepared by the reaction of dimethyliodo(triphenylphosphine)-gold(III) with 2-pyridyllithium in Et_2O at −40 °C, followed by hydrolysis.

Organotransition metal ate complexes have recently attracted much attention, since they are sometimes presumed to act as active intermediates in the cross coupling reaction catalyzed by nickel and palladium complexes [1]. On the other hand, organocuprates are frequently used as highly regio- and stereo-specific alkylating reagents [2]. In spite of these facts, the structure and chemical reactivites of such organotransition metal ate complexes have been much less studied [3,4], probably because of their extreme instability toward oxygen and moisture. Here we report the preparation and some properties of stable hydrogen dimethylbis(2-pyridyl)aurate(III).

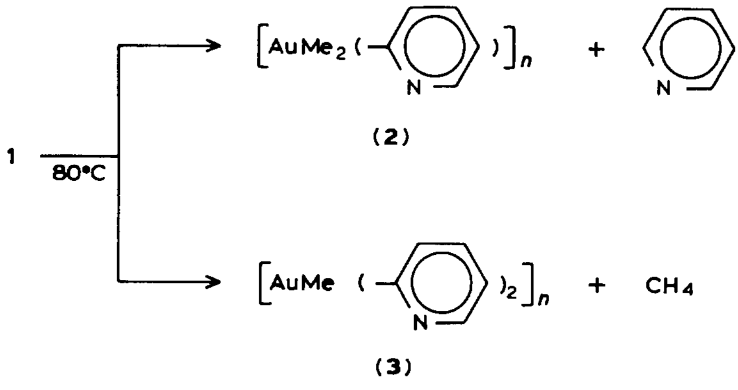
Treatment of *cis*-dimethyliodo(triphenylphosphine)gold(III) with excess of 2-pyridyllithium in Et_2O at −40 °C gave an orange homogeneous solution. Hydrolysis followed by extraction with Et_2O gave an orange solution. After removal of the solvent, the residual solid was recrystallized from Et_2O/pentane to give orange crystals of hydrogen dimethylbis(2-pyridyl)aurate(III) (**1**). Yield 55%. M.p. 139 °C (dec.). Anal. Found: C, 37.87; H, 4.04; N, 6.83. $C_{12}H_{15}N_2Au$ calcd.: C, 37.51; H, 3.93; N, 7.29%.



(1)

Complex **1** was characterized by IR and ^1H and ^{13}C NMR spectra and elemental analysis as well as by chemical reactions. It should be noted that complex **1** is surprisingly stable to oxygen and moisture and can be handled in air. It is probably formed by the hydrolysis of lithium dimethylbis(2-pyridyl)aurate(III) during the preparation. ^1H NMR of **1** in $CDCl_3$ shows a sharp singlet at 0.64 ppm due to Me-Au and multiplets at 7.16, 7.68, 8.00, and 8.43 ppm due to pyridyl ring protons in a ratio of 3/1/1/1/1. A protic hydrogen in **1** appears as a broad singlet at 4.9 ppm *. Absence of signals from the triphenylphosphine ligand is in accord with the fact that the tertiary phosphine ligand cannot coordinate to tetramethylaurate(III) [4]. $^{13}C\{^1H\}$ NMR of **1** also shows singlets at 4.61 ppm due to Me-Au and at 119.9, 134.7, 137.2, and 194.1 ppm assignable to pyridyl rings. A large deshielding of carbon attached directly to gold may arise from the large anisotropic effect of gold metal [5]. The IR spectrum of **1** showed two broad signals assignable to ν(N–H) at 2500 and 2050 cm^{-1}.

Hydrolysis of **1** with sulfuric acid liberated methane and ethane in 42 and 62% per mole of **1**, respectively. The ethane formed in this reaction may be a secondary decomposition product. Hydrogen chloride also reacted with **1** in Et_2O to give methane in 134% yield. Thermolysis of **1** at 80 °C during 5 h gave methane and pyridine in 26 and 15%, respectively. The proton source of methane was unequivocally determined as an intramolecular proton in complex **1**. Thus, the thermolysis of **1**, which had previously been treated with D_2O, gave only CH_3D and the thermolysis of **1** in C_6D_6 liberated only CH_4. These results suggest the existence of an intramolecular proton in **1**. The reaction is considered to proceed by intramolecular electrophilic attack of the proton on the methyl or pyridyl ligand. Thermolysis of **1** in C_6D_6 was followed by ^1H NMR spectroscopy. Two sets of two new Au-methyl signals at 0.44 and 1.11, and 0.51 and 1.06 ppm in ca. 1/1 ratio gradually increased with time in addition to the signals due to pyridine and methane formed. These complexes are tentatively assigned as polymeric dimethyl(2-pyridyl)gold and methylbis(2-pyridyl)gold complexes (**2** and **3**).



In $^{13}C\{^1H\}$ NMR of **2** and **3**, large low field chemical shifts of pyridyl carbons directly bonded to gold (202.7 and 204.0 ppm) were observed, suggesting the

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* The chemical shift of protic hydrogen varied from 4–10 ppm, depending on the amount of water present in $CDCl_3$.

coordination of the pyridyl ring as bridging ligand. Such an unusual chemical shift of the bridging pyridyl ligand has been previously reported [6]. Further thermolysis of **1** at 190 °C liberated ethane and α-picoline besides methane and pyridine, probably by reductive elimination of the polymeric species. Attempts to cleave the pyridyl bridge were made. Although triphenylphosphine showed no interaction with these polymers, addition of tertiary phosphine ligands such as PMe_2Ph and PEt_3 in C_6D_6 caused instantaneous transformation of the polymer to *cis*-dimethyl(2-pyridyl)(phosphine)gold(III) *, supporting the polymeric structure of **2**. However, the structure of **3** is not clear at present, since **3** remained intact in these reactions.

Further studies on the structure and reactivities of tetraalkylaurates having various organic groups are now in progress.

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* ^1H NMR data: 0.25 ppm, d, $J(HP)$ 8.1 Hz and 0.95, d, $J(HP)$ 0.95 Hz for Au-Me of the $PPhMe_2$ complex; 0.29, d, $J(HP)$ 6.8 Hz and 0.85, d, $J(HP)$ 8.8 Hz for Au-Me of the PEt_3 complex. Formation of the *cis*-dimethylgold(III) complex suggests that **1** has a *cis* structure, although it is not completely clear at present.