Isolation of cis-dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III)

Sanshiro. Komiya, Makoto. Ishikawa, and Satoshi. Ozaki

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the reactivity of these new systems, especially with regard to their homogeneous catalysis activity.

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Isolation of *cis*-Dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III)

Sanshiro Komiya,* Makoto Ishikawa, and Satoshi Ozaki

Department of Apllied Chemistry for Resources
Tokyo University of Agriculture and Technology
2-24-16 Nakamachi, Koganei, Tokyo 184, Japan

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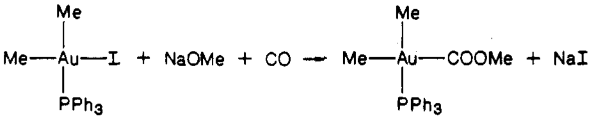
Summary: *cis*-Dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) (**1**) has been prepared by the reaction of carbon monoxide with a mixture of *cis*-dimethyliodo(triphenylphosphine)gold(III) and sodium methoxide in methanol. Thermolysis of **1** results in the competitive reductive elimination of methyl acetate and ethane.

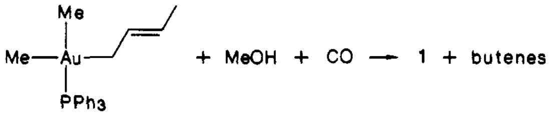
In spite of extensive investigations on the structure and chemical reactivity of organogold(III) complexes,[1] only a few insertion reactions of unsaturated molecules such as sulfur dioxide have been reported.[2] Carbon monoxide is known to be unreactive toward any type of organogold(I) or -(III) complex, but a simple carbon monoxide coordinated gold(I) compound, AuCl(CO), has been described.[3] In the course of our studies on the preparation of organogold(III) complexes,[4] we found the formation of *cis*-dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) by the reaction of dimethyliodo(triphenylphosphine)gold(III) with carbon monoxide in the presence of sodium methoxide.

A methanol solution (22 mL) of *cis*-dimethyliodo(triphenylphosphine)gold(III) (96.6 mg, 0.157 mmol) in the presence of a slight excess of sodium methoxide (12.5 mg, 0.231 mmol) was treated with an excess of carbon monoxide at atmospheric pressure at 50 °C for 30 min to give a pale yellow, homogeneous solution. After evaporation of volatiles, colorless crystals of *cis*-dimethyl(methoxycarbonyl)(triphenylphosphine)gold(III) (**1**) were obtained by recrystallization of the residual solid.[5] This is the first example of the *formal* insertion of carbon monoxide for the organogold complexes. Complex **1** is air and thermally stable. Complex **1** also was obtained by the reaction of *cis*-dimethyl(η^1-(*E*)-crotyl)(triphenylphosphine)gold(III)[6] (**2**; 100.7 mg, 0.185 mmol) with an excess of carbon monoxide at atmospheric pressure in methanol (15 mL) at 50 °C for 30 min. (59%). A facile and selective methanolysis of the η^1-crotyl group at the γ-carbon in **2** with liberation of butenes,[6] gave a dimethylmethoxogold(III) intermediate which reacted further with carbon monoxide to give **1**. Unfortunately, attempted isolation of the dimethylmethoxogold(III) intermediate was unsuccessful, and the only isolable material was trimethyl(triphenylphosphine)gold(III), probably due to the facile disproportionation of the intermediate compound.



$$\mathrm{Me{-}\overset{\displaystyle Me}{\underset{\displaystyle PPh_3}{Au}}{-}I} + \mathrm{NaOMe} + \mathrm{CO} \rightarrow \mathrm{Me{-}\overset{\displaystyle Me}{\underset{\displaystyle PPh_3}{Au}}{-}COOMe} + \mathrm{NaI} \qquad (1)$$

1



(2)

The ^{1}H NMR spectrum of **1** shows two doublets at 0.23 and 1.17 ppm, which are assignable to cis and trans gold methyl groups for a typical square-planar *cis*-dimethylgold(III) complex. A signal due to the methoxycarbonyl group appears at 3.17 ppm as a singlet, as in other transition-metal alkoxycarbonyl complexes.[7]

The ^{13}C{^{1}H} NMR spectrum of **1** also shows two doublets at 4.07 and 9.67 ppm for cis and trans gold methyl groups. The carbonyl carbon signal appears as a doublet at 210.7 ppm with a small coupling constant (^2J(P–C) = 11.9 Hz) with the phosphorus nucleus, suggesting that the methoxycarbonyl group occupies a coordination site cis to the triphenylphosphine ligand. The IR spectrum of **1** shows ν(C=O) at 1637 cm^{-1} as expected for a metallocarboxylate.[7]

At present, the mechanism of the formal insertion is not clear, whether carbon monoxide really inserts into the gold–methoxide bond or the reaction proceeds through the nucleophilic interaction of methoxide anion with coordinated carbon monoxide, since the dimethylmethoxogold(III) complex could not be isolated. However, the dimethylmethoxogold(III) complex is considered to be formed in methanol at least, since the reaction of an excess of methyl iodide with the complex prepared in situ afforded dimethyl ether (52%/Au) and *cis*-dimethyliodo(triphenylphosphine)gold(III) (52%/Au). In fact, **1** can be prepared by the reaction of carbon monoxide with a methanol solution of the dimethylmethoxogold(III) species prepared beforehand in situ. Thus, we prefer the insertion mechanism, although there is no direct experimental evidence for this. Note also that similar preferential insertion into the platinum–oxygen bond has been discussed in the case of some alkylalkoxoplatinum(II) complexes.[8]

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(5) Complex 1 was purified by recrystallization from ether/hexane: yield 59%; mp 124–125 °C dec. Anal. Calcd for $C_{22}H_{24}O_2PAu$: C, 48.19; H, 4.41. Found: C, 48.63; H, 4.60. ^{1}H NMR ($CDCl_3$): δ 0.23 (d, 3 H, ^3J(H–P) = 7.8 Hz, AuMe cis to P), 1.17 (d, ^3J(H–P) = 8.6 Hz, 3 H, AuMe trans to P), 3.71 (s, 3 H, OMe), 7.3–7.6 (m, 15 H, PPh_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 4.07 (d, ^2J(C–P) = 6.1 Hz, AuMe cis to P), 9.67 (d, ^2J(C–P) = 106.2 Hz, AuMe trans to P), 49.4 (s, OMe), 128–135 (m, PPh_3), 210.7 (d, ^2J(C–P) = 11.9 Hz, COOMe). IR (KBr): ν(C=O) 1637 cm^{-1}.

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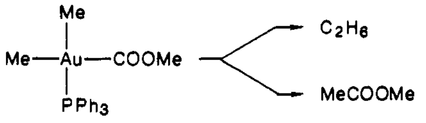
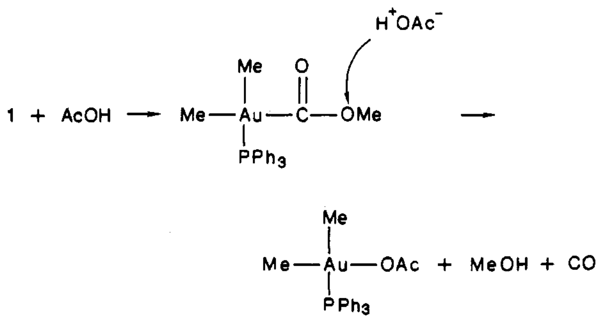
Thermolysis of 1 in C_6D_6 at 80 °C for 80 min resulted in the reductive elimination of both methyl acetate and ethane in ca. 1:1 ratio in the initial stages of the reaction (7% decomposition). Gold products are considered to be Au(I)Me(PPh_3) and Au(I)(COOMe)(PPh_3). Formation of the former was confirmed by ^1H NMR, but the latter seems to be unstable under the thermolysis conditions, since carbon monoxide and methanol were detected after the thermolysis. A prolonged thermolysis of 1 at 80 °C for 6 h gave trimethyl(triphenylphosphine)gold(III) (ca. 20%/1) accompanied by evolution of carbon monoxide in addition to the reductive elimination products, probably due to the concomitant decarbonylation of 1 giving an unstable dimethylmethoxogold(III) species (vide infra). The observed comparable rates of two possible reductive eliminations are noteworthy, since the electron-withdrawing methoxycarbonyl group is expected to be much more stable toward reductive elimination than methyl.[9] Enhanced reductive elimination in a metal–C(sp^2) bonded group has been recently invoked in reactions of organonickel(II),[10] -gold(III),[4c] and -ruthenium(II)[11] complexes. pπ-Orbitals of the sp^2 carbon might assist the reductive elimination process.[4c]



1

(3)

Acidolysis of 1 (0.027 mmol) with a stoichiometric amount of acetic acid (0.027 mmol) in C_6D_6 took place smoothly at room temperature to give *cis*-dimethyl(acetato)(triphenylphosphine)gold(III)[12] in quantitative yield with liberation of methanol and carbon monoxide.



(4)

Electrophilic attack of the acid at the methoxy group in 1 to liberate methanol, followed by decarbonylation from the resulting labile dimethylcarbonylgold(III) intermediate would give the reaction products. A mechanistic investigation of the insertion reaction is now in progress.

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Activation of a Fluorinated Carbon–Carbon Bond by Oxidative Addition of Tetrafluorocyclopropene to Platinum(0). The First Example of a Perfluorometallacyclobutene

Richard C. Hemond,[1a] Russell P. Hughes,*[,1a] David J. Robinson,[1a] and Arnold L. Rheingold[1b]

Departments of Chemistry, Dartmouth College
Hanover, New Hampshire 03755, and
University of Delaware, Newark, Delaware 19716

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Summary: Carbon–carbon bond activation of perfluorocyclopropene (**3**) by $[Pt(C_2H_4)(PR_3)_2]$ (R = Ph, Me) affords perfluorometallacyclobutene products $[Pt(C_3F_4)(PR_3)_2]$ (**4a**, R = Ph; **4b**, R = Me), characterized in solution by a combination of $^{19}F\{^{31}P\}$, $^{19}F\{^{19}F\}$, and $^{31}P\{^1H\}$ NMR spectroscopic methods. No intermediate olefin complex could be detected spectroscopically. The triphenylphosphine complex **4a** has also been characterized in the solid state by a single-crystal X-ray diffraction study.

The transition-metal chemistry of cyclopropenes is extensive.[2] Both catalytic reactions to give organic products[3-7] and stoichiometric reactions to give organometallic complexes[8-24] are known. Metal-promoted activation of a carbon–carbon bond of the cyclopropene to give an intermediate metallacyclobutene (1), or its valence tautomeric vinylcarbene relative (2), has been proposed as a key step in many of these reactions. However, no examples of the direct formation of an isolable metallacyclobutene

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