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Isolation of the First Allylic Gold(III) Complex Having a Triphenylphosphine Ligand

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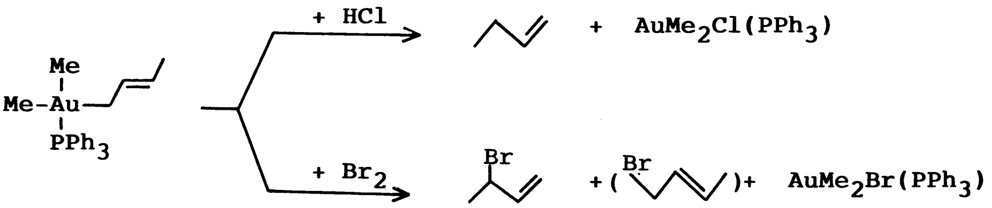
A metathetical reaction of cis-dimethyliodo(triphenylphosphine)gold(III) with 1-methylallyl Grignard reagent in ether at 0 °C gives cis-dimethyl(η^1-E-crotyl)(triphenylphosphine)gold(III), **1**. Reactions of **1** with HCl and bromine give selectively 1-butene and 1-methylallyl bromide, respectively.

Allylic derivertives of transition metals are of interest in relation to their wide applications to organic syntheses, since the structure and reactivity vary depending on the metals and coordinating ligands employed.[1,2] In spite of the previous extensive investigation of such allylic compounds of transition metals, no example of allylic gold compound has been reported so far, except for a cyclopentadienylgold(I) derivertives,[3,4] and dimethylbenzyl(triphenylphosphine)gold(III).[5] We now report the first isolation of dimethyl(η^1-crotyl)gold(III) complex having a triphenylphosphine ligand.

A metathetical reaction of cis-dimethyliodo(triphenylphosphine)gold(III) with excess 1-methylallyl magnesium chloride[6] in ether at 0 °C, followed by hydrolysis gave cis-dimethyl(η^1-E-crotyl)(triphenylphosphine)gold(III), **1** in 60% yield. Complex **1** was purified by recrystallization from a benzene-hexane mixture as pale yellow crystals and was characterized by elemental analysis and ^{1}H and ^{13}C NMR spectra as well as by chemical reactions.[7]

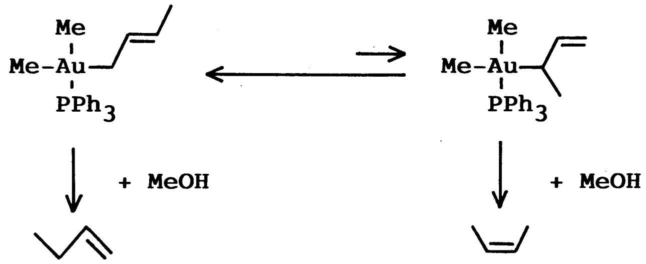
^{1}H NMR of **1** in C_6D_6 shows two doublets at 0.63 and 1.76 ppm due to cis and trans methyl groups to a triphenylphosphine ligand, which are attached directly to gold, indicating the square planar cis structure of **1**. A large coupling constant (14.9 Hz) between two vinylic protons strongly supports the E structure of the crotyl entity.[8] A small amount of Z isomer (<5%) is also detected in the ^{1}H NMR. IR spectrum of **1** shows ν(C=C) absorption band at 1643 cm^{-1} as for related platinum η^1-allyl complexes.[8]

Acidolysis of **1** with an equimolar amount of hydrogen chrolide in benzene at room temperature smoothly liberated 1-butene (91 mol%/Au) and cis-dimethylchrolo(triphenylphosphine)gold(III) (77%), suggesting the occurence of selective protonolysis at γ-carbon. Similar stoichiometric reaction of **1** with bromine also gave mainly 1-methylallyl bromide (59%/Au) in addition to crotyl bromide (10%/Au). Such γ-attack of these electrophiles on the η^1-allyl group has been well known for both transition and nontransition metal allyllic compounds.[9, 10]



(1)

On the other hand, protonolysis of **1** at 50 °C with weaker electrophiles such as methanol and ethanol afforded a mixture of 1-butene (47%) and cis-2-butene (50%). The formation of thermodynamically unstable cis-2-butene rather than trans-2-butene in addition to 1-butene suggests the involvement of the formation of reactive isomeric 1-methylallylgold(III) species, which may be derived from 1,3-transfer of gold metal in **1**. Such high reactivity of 1-methylallylgold(III) may be due to the absence of substituents on the γ-carbon. High selectivity for cis-2-butene arises during the protonolysis of 1-methylallylgold(III) isomer, presumably due to a preferred ground state conformation.[11,12)]



(2)

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7) Anal. Found: C, 52.89; H, 5.37%. Calcd for $C_{24}H_{28}PAu$: C, 52.95; H, 5.18%. Mp (dec.) 103-104 °C. ^1H NMR (C_6D_6) δ 0.63 (3H, d, J(HP)=7.1 Hz, Me-Au cis to P), 1.74 (3H, d, J(HH)=6.4 Hz, Me), 1.76 (3H, d, J(HP)=9.0 Hz, Au-Me trans to P), 2.11 (2H, t, J(HH)=J(HP)=8.8 Hz, CH_2), 4.93 (1H, dq, J(HH)=6.4, 14.9 Hz, =CH-Me), 5.74 (1H, dt, J(HH)=8.8, 14.9 Hz, CH_2-CH=), 6.8-7.5 (15H, m, PPh_3). ^{13}C NMR (C_6D_6): δ10.59 (d, J(HP)=6.1 Hz, Au-Me cis to P), 18.01 (d, J(HP)=113.5 Hz, Au-Me trans to P), 18.58 (Me), 34.49 (d, J(HP)=4.9 Hz, CH_2), 116.9 (CH_2-CH=), 128-135 (PPh_3), 135.7 (=CHMe). IR (KBr): ν(C=C) = 1643 cm^{-1}.
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