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Dimethylgold(III) Aryloxides and Alkoxides Having a Triphenylphosphine Ligand

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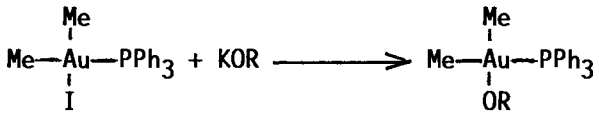
Cis-dimethyl(aryloxo or alkoxo)(triphenylphosphine)gold(III), cis-$AuMe_2(OR)(PPh_3)$ (R=Ph, tol, CH_2CF_3, $CH(CF_3)_2$) were isolated by the reaction of cis-$AuMe_2I(PPh_3)$ with corresponding potassium aryloxides or alkoxides. Nucleophilic phenoxogold(III) smoothly traps phenol by hydrogen bond and can abstract a proton from methyl cyanoacetate, malononitrile and phenyl acetylene to give corresponding cis-dimethyl(organo)(triphenylphosphine)gold(III) complexes, cis-$AuMe_2(R')(PPh_3)$.

Transition metal alkoxides have recently attracting growing interests, since they not only play important roles in various metal mediated catalyses such as carbonylation of alcohol, metathesis, stabilization of organocuprates, Tishchenko reaction and alkoxy exchange reaction,[1] but also act as versatile ligands of models for metal oxides as catalysis.[2] Among them early transition metals have a diverse family of alkoxides, whereas late transition metal alkoxides are relatively less explored.[3] Especially gold-alkoxides are rare and only a few gold(I) alkoxides such as trimethylsiloxo and phenoxo derivatives of gold(I)[4,5] and polymeric trimethylsiloxogold(III) complex[6] are known. On the other hand, in the alkoxycarbonylation of dimethylgold(III) complexes, formation of a dimethyl(methoxo)gold(III) intermediate has been tentatively assumed and the attempted isolation of this methoxogold(III) complex leads to formation of trimethyl(triphenylphosphine)gold(III).[7] We now report the isolation of novel cis-dimethyl(aryloxo or alkoxo)gold(III) complexes having a triphenylphosphine ligand.

The reaction of cis-dimethyliodo(triphenylphosphine)gold(III)[8] with potassium phenoxide in THF at room temperature gave cis-dimethyl(phenoxo)(triphenylphosphine)gold(III), **1** in 72% yield. Analogous reactions of the above dimethyliodogold(III) complex with various potassium aryloxides and fluoroalkoxides also gave corresponding aryloxo and alkoxogold(III) complexes, respectively.

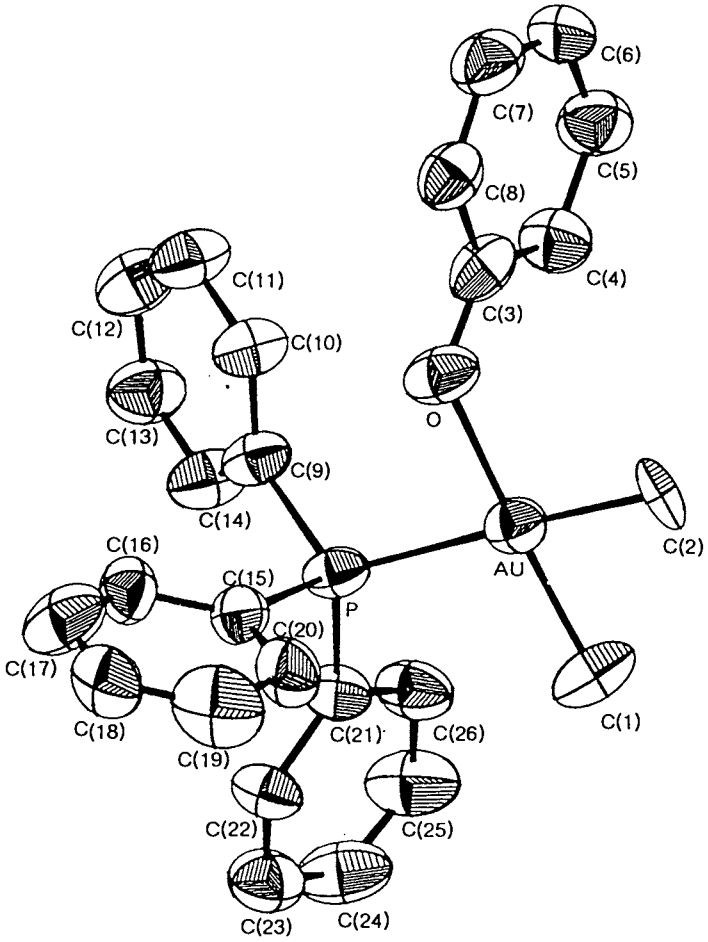


(1)

R=Ph(**1**), tol(**2**), CH_2CF_3(**3**), $CH(CF_3)_2$(**4**)

These complexes were purified by recrystallization from ether and characterized by IR and NMR spectroscopy and elemental analyses as well as by chemical reactions.[9] These complexes are air and thermally stable.

Formation of aryloxo or alkoxo-gold bond is supported by their IR spectra showing a typical strong ν(C-O) band at ca. 1250 cm^{-1}. ^1H NMR spectra of these complexes show two sets of doublets assignable to two gold-methyls, suggesting that they all have square planar cis structure. The molecular structure of **1** has been unequivocally determined by X-ray structure analysis.[10] Figure 1 shows ORTEP drawing of **1**. As suggested, **1** has typical square planar configuration and the phenoxo ligand lies on the site cis to triphenylphosphine. Bond distances and angles are quite normal and no unusual intra and inter molecular contacts were observed.



Selected bond distances(Å)

Au-C(1)=2.03(3), Au-C(2)=2.00(1)
Au-O=2.09(1), Au-P=2.402(4)
O-C(3)=1.33(2), P(1)-C(9)=1.83(2)
P-C(15)=1.83(1), P-C(21)=1.82(1)

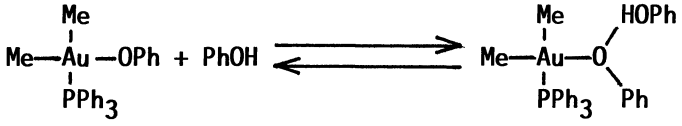
Selected bond angles(°)

C(1)-Au-C(2)=85.2(8)
C(1)-Au-P=94.9(7)
C(2)-Au-O=90.6(6)
O-Au-P=88.9(4)
Au-O-C(3)=122.9(9)
Au-P-C(9)=119.5(4)
Au-P-C(15)=107.9(5)
Au-P-C(21)=115.7(5)

Fig. 1. ORTEP drawing of $AuMe_2(OPh)(PPh_3)$, **1** with selected bond angles and distances.

When **1** was recrystallized in the presence of free phenol, one mole of phenol was incorporated to give a cis-dimethylphenoxo(phenol)(triphenylphosphine)gold(III) complex **1a**. The phenol is considered to link with the phenoxo group by hydrogen bonding; ^1H NMR of **1a** shows two sets of triplets at 6.71 and 6.78 ppm assignable to para hydrogens of phenoxy groups in both phenoxo ligand and hydrogen bonded phenol. Observation of both signals due to the phenoxo ligand and hydrogen bonded phenol even at 50 °C suggests that they are not exchanging mutually in the

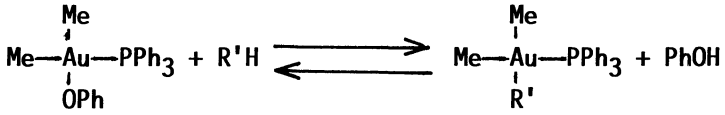
NMR time scale. Hydroxyl hydrogen of the hydrogen bonded phenol was observed as an extensively broad signal at ca. 8.5 ppm under these conditions. When phenol was added to the solution of **1** in C_6D_6 at room temperature, all signals due to hydrogen bonded phenol gradually shifted to the direction of the signals of free phenol. The broad signal for the hydrogen bonded OH group gradually sharpened with increase in the amount of free phenol. IR spectrum of **1a** also shows characteristic bands due to hydrogen bonded phenol at 2600-2900 cm^{-1}, supporting also the hydrogen bond. These results imply the high nucleophilicity of phenoxo ligand. Examples of such hydrogen bonds in palladium, rhodium and ruthenium phenoxide have also been recently demonstrated in detail by Osakada and Yamamoto,[11] and Bergman[12] independently.



(2)

1 **1a**

Complex **1** can reversively abstract acidic proton from various organic compounds such as methyl cyanoacetate, malononitrile and phenyl acetylene by virture of its high nucleophilicity. The reactions proceed in non-polar solvents such as benzene at room temperature. The reactions are highly regio and stereospecific and gold products were always cis-dimethyl(organo)(triphenylphosphine)gold(III), **5-7**.[13] In the reaction of methyl cyanoacetate, equilibrium mixture (K=130) was obtained, whereas the latter two gave complete conversion into **6** and **7**.



(3)

R'=CH(CN)(COOMe) **5**
CH(CN)$_2$ **6**
C≡CPh **7**

Further investigations concerning chemical reactivities of these aryloxo and alkoxo complexes are now in progress.

References

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9) **1**: 72% yield. mp 159-160 °C. IR: 1238 cm^{-1}. ^1H NMR(C_6D_6 at r.t.): δ 0.75 (d, J=8.3 Hz, Au-Me cis to P), 1.57 (d, J=9.0, Au-Me trans to P), 6.73 (t, J=7.3, H_p), 7.03 (d, J=7.3, H_o), 7.23 (t, J=7.3, H_m). Anal. Found: C, 53.27; H, 4.67%. Calcd for $C_{26}H_{26}OPAu$: C, 53.62; H, 4.50%. **2**: 36% yield. mp 129-131 °C. IR: 1240 cm^{-1}. ^1H NMR(C_6D_6 at r.t.): δ0.74 (d, J=8.3 Hz, Au-Me cis to P), 1.52 (d, J=8.6, Au-Me trans to P), 2.27 (s, Me), 6.9-7.1 (m, OC_6H_4-p-Me). Anal. Found: C, 53.70; H, 4.88%. Calcd for $C_{27}H_{28}OPAu$: C, 54.37; H, 4.73%. **3**: 58% yield. mp 98-100 °C. IR: 1105, 1120, 1145, 1190, 1270, 1415 cm^{-1}. ^1H NMR(C_6D_6 at r.t.): δ0.63 (d, J=8.3 Hz, Au-Me cis to P), 1.38 (d, J=9.0, Au-Me trans to P), 4.43 (q, J=9.5, CH_2). Anal. Found: C, 44.58; H, 3.93%. Calcd for $C_{22}H_{23}F_3OPAu$: C, 44.91; H, 3.94%. **4**: 38% yield. mp 115-116 °C. IR: 1090, 1175, 1205, 1255, 1275, 1365 cm^{-1}. ^1H NMR(C_6D_6 at r.t.): δ0.63 (d, J=8.6 Hz, Au-Me cis to P), 1.15 (d, J=8.5, Au-Me trans to P), 5.08 (septet, J=6.6, CH). Anal. Found: C, 42.27; H, 3.15%. Calcd for $C_{23}H_{22}F_6OPAu$: C, 42.09; H, 3.38%. **1a**: 48% yield. mp 153-154 °C. IR: 2600, 2700, 2900 cm^{-1}. ^1H NMR(C_6D_6 at r.t.):δ0.78 (d, J=8.3 Hz, Au-Me cis to P), 1.56 (d, J=9.0, Au-Me trans to P), 6.71 (t, J=7.3, H_p of OPh), 6.78 (d, J=7.3, H_p of PhOH), 8.6 (br, OH). Anal. Found: C, 57.12; H, 4.86%. Calcd for $C_{32}H_{32}O_2PAu$: C, 56.81; H, 4.77%.

10) The crystal Data for **1**, $AuMe_2(OPh)(PPh_3)$: Fw=582.4, triclinic $P\bar{1}$, a=10.008(2) Å, b=13.199(4) Å, c=9.279(4) Å, α=107.41(3)°, β=90.14(4)°, γ=100.37(3)°, V=1148.3(7) $Å^3$, Z=2, d_{calcd}=1.69 gcm^{-3}, radiation Mo K_α(0.71068 Å), $3° < 2\theta < 50°$, no. of data collected 5255, heavy atom method, All the non-hydrogen atoms were refined anisotropically. Hydrogens which were found in the differential map except for methyl hydrogens were included in the calculation. Current R values were R=0.085, R_w=0.115 for the observed 5002 reflections ($|F_o| > 3\sigma|F_o|$).

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13) ^1H NMR($CDCl_3$ at r.t.): **5**: δ0.66 (d, J=8.3 Hz, Au-Me cis to P), 1.27 (d, J=8.6, Au-Me trans to P), 2.83 (d, 10.5, CH), 3.61 (s, OMe). **6**: δ0.78 (d, J=8.3 Hz, Au-Me cis to P), 1.44 (d, J=8.3, Au-Me trans to P), 2.18 (d, 9.3, CH). **7**: δ0.33 (d, J=8.3 Hz, Au-Me cis to P), 1.44 (d, J=9.3, Au-Me trans to P), 7.0-7.2 (m, CCPh).; S. Komiya and A. Shibue, Organometallics, **4**, 684 (1984).

14) The quilibrium constant K=[**5**][PhOH]/[**1**][$NCCH_2COOMe$], where [PhOH] was the sum of free and hydrogen bonded phenols, was obtained from ^1H NMR in C_6D_6 at rt. **1**, 0.144 mol/l; $NCCH_2COOMe$, 0.144 mol/l.

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