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Preliminary communication

Convenient preparative method and crystal structures of (triphenylphosphine)gold(I) enolate and homoenolate complexes

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Abstract

Trimethylsilyl ethers of enol and cyclopropanol react with (triphenylphosphine)gold(I) chloride in the presence of cesium fluoride to give regioselectively carbon-bound (triphenylphosphine)gold(I) enolate and (triphenylphosphine)gold(I) homoenolate complexes. The first X-ray crystallography of these gold(I) complexes elucidated linear C–Au–P structures.

Transition-metal enolates have recently attracted much attention from synthetic and structural points of view [1]. Two types of transition metal enolates, O-bound and C-bound metal enolates have so far been generated and isolated. Concerning Group IB metal enolates, copper(I) and silver(I) enolates are generated as short-living intermediates and utilized in organic syntheses [2]. On the other hand, some gold(I) enolates of methyl ketones are prepared as stable solids and identified spectroscopically to be C-bound gold(I) enolates [3]. For instance, the (acetylmethyl)(triphenylphosphine)gold(I) complex can be prepared by reactions of acetone with $[(Ph_3P)Au^I]_3O^+\ BF_4^-$ or with $(Ph_3P)Au^ICl$ and Ag_2O [4]. We now wish to report a general and simple method for preparation of regioselectively C-bound gold(I) enolates (**1**) and gold(I) homoenolate (**2**) and the X-ray crystallography of **1a** (R = H, R′ = Ph) and 2.

The preparation of **1a** was carried out as follows. To a suspension of anhydrous cesium fluoride (0.5 mmol) and (triphenylphosphine)gold(I) chloride (0.10 mmol) in methylene chloride (2.0 ml), 1-(trimethylsilyloxy)styrene (0.13 mmol) was added and the mixture was stirred overnight at room temperature, then filtered to remove insoluble inorganic salts. The filtrate was evaporated and the residue was recrystallized from a mixed solvent of methylene chloride and hexane to give (benzoylmethyl)(triphenylphosphine)gold(I) (**1a**) [3] as colorless needles in 82% yield (m.p. 123–125 °C (decomp.); IR (KBr): ν(CO) 1632 cm^{-1}; ^1H NMR ($CDCl_3$): δ 3.16 (d, J(PH) 11.0 Hz, 2H), 7.19–7.63 (m, 18H), 8.10–8.22 (m, 2H); ^{13}C NMR ($CDCl_3$): δ

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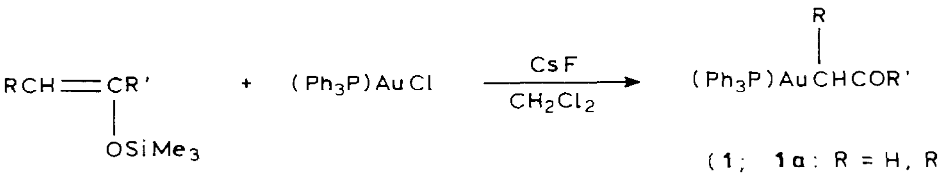
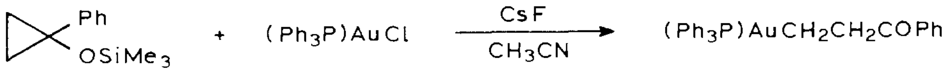


$$RCH{=}C(OSiMe_3)R' + (Ph_3P)AuCl \xrightarrow[CH_2Cl_2]{CsF} (Ph_3P)AuCH(R)COR'$$

(1; **1a**: R = H, R' = Ph)



$$+ (Ph_3P)AuCl \xrightarrow[CH_3CN]{CsF} (Ph_3P)AuCH_2CH_2COPh$$

(**2**)

43.1 (d, *J*(PC) 66.0 Hz), 127.5, 127.7, 128.7, 128.8, 129.8, 130.3, 130.4, 131.0, 131.1, 133.9, 134.0, 140.1, 202.3 (d, *J*(PC) 4.4 Hz)).

The molecular structure of **1a** as determined by X-ray crystallography, is shown in Fig. 1, together with selected bond lengths and bond angles. The structure of

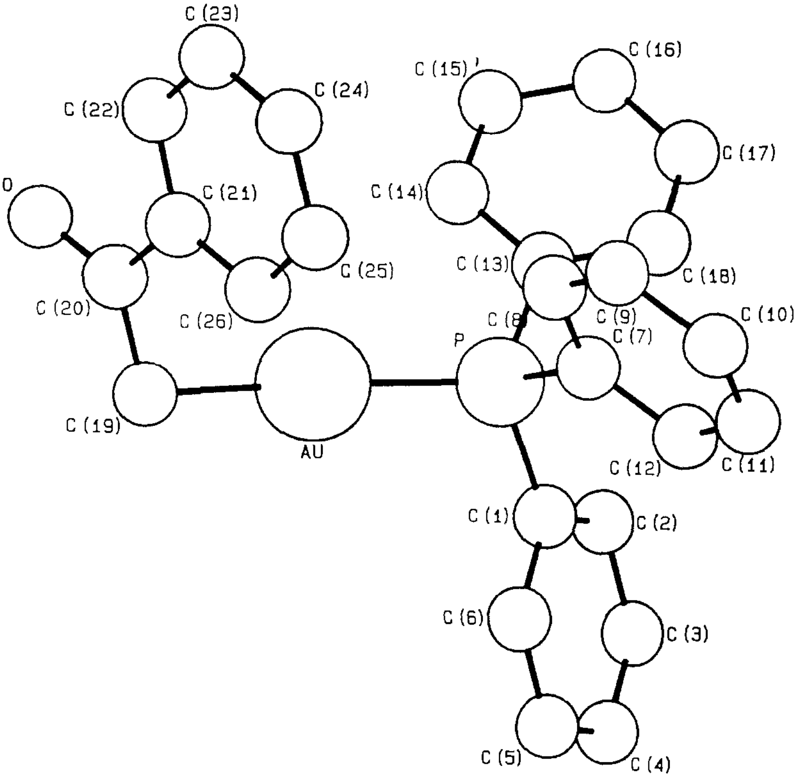


Fig. 1. Molecular structure of **1a**. Selected bond lengths and angles are: Au–P 2.283(1), Au–C(19) 2.101(5), P–C(1) 1.819(5), P–C(7) 1.824(5), P–C(13) 1.814(6), C(19)–C(20) 1.459(8), C(20)–O 1.225(6) Å; P–Au–C(19) 172.4(2), Au–P–C(1) 113.3(2), Au–P–C(7) 107.4(1), Au–P–C(13) 117.3(1)°.

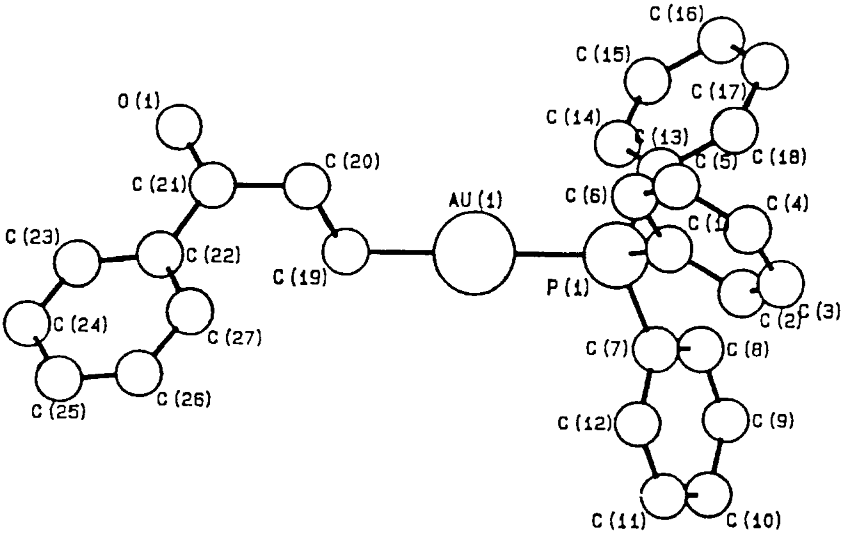
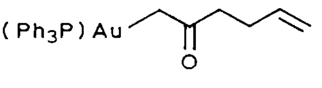


Fig. 2. Molecular structure of **2**. Selected bond lengths and angles are: Au(1)–P(1) 2.292(3), Au(1)–C(19) 2.077(9), P(1)–C(1) 1.818(8), P(1)–C(7) 1.813(6), P(1)–C(13) 1.816(7), C(19)–C(20) 1.51(2), C(20)–C(21) 1.51(1), C(21)–O(1) 1.24(1) Å; P(1)–Au(1)–C(19) 177.0(2), Au(1)–P(1)–C(1) 116.3(2), Au(1)–P(1)–C(7) 112.0(2), Au(1)–P(1)–C(13) 112.6(3)°. There are two independent molecules in the asymmetric unit, only one is shown.

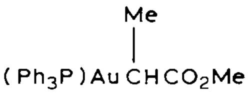
C-bound gold(I) enolate (**1a**) with almost linear C–Au–P (172.4(2)°) is consistent with the IR and NMR data. Crystal data for **1a**: $C_{26}H_{22}AuPO$, $M = 578.41$, monoclinic, space group $P2_1/n$, a 18.777(3), b 8.539(1), c 14.055(3) Å, β 101.01(1)°, U 2211.9 Å^3, $Z = 4$, D_c 1.737 g/cm^3. $R = 0.025$, $R_w = 0.032$, Enraf–Nonius CAD-4 diffractometer; 5056 reflections measured, 3035 with $I > 3\sigma(I)$ used in the refinement. Programs: SDP/VAX (Enraf–Nonius).

Similarly, C-bound gold(I) homoenolate, [β-(benzoyl)ethyl](triphenylphosphine)-gold(I) (**2**) (m.p. 121–122°C (decomp.); recrystallised from hexane/methylene chloride) was prepared in 76% yield by the reaction of 1-(trimethylsilyloxy)-1-phenylcyclopropane with (triphenylphosphine)gold(I) chloride in the presence of cesium fluoride. The X-ray molecular structure of **2** is shown in Fig. 2. Crystal data for **2**: $C_{27}H_{24}AuPO$, $M = 592.43$, triclinic, space group $P\bar{1}$, a 14.558(3), b 18.512(3), c 8.933(2) Å, β 106.55(2)°, U 2298.2 Å^3, $Z = 4$, $D_c = 1.327$ g/cm^3. $R = 0.035$, $R_w = 0.043$, Enraf–Nonius CAD-4 diffractometer; 10517 reflections measured, 5510 with $I > 3\sigma(I)$ used in the refinement.

Some other organogold(I) complexes **1b**–**1d** were prepared with good yields from trimethylsilyl ethers of enols, and identified spectroscopically.

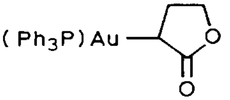


(1b)



$(Ph_3P)Au\,\overset{Me}{\overset{|}{C}}HCO_2Me$

(1c)



(1d)

References

1 J.J. Doney, R.G. Bergman, and C.H. Heathcock, J. Am. Chem. Soc., 107 (1985) 3724; and ref. therein.

2 Y. Ito, T. Konoike, and T. Saegusa, J. Am. Chem. Soc., 97 (1975) 649; Y. Ito, T. Konoike, T. Harada, and T. Saegusa, ibid., 99 (1977) 1487.

3 R.J. Puddephatt, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 2, Pergamon Press, Oxford, 1982, p. 765.

4 A.N. Nesmeyanov, E.G. Perevalova, K.I. Grandberg, and D.A. Lemenovskii, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 1124; A.N. Nesmeyanov, E.G. Perevalova, D.A. Lemenovskii, V.P. Dyadchenko, and K.I. Grandberg, ibid., (1974) 1661.