Auration of ruthenocene: synthesis and molecular structure of mono- and diaurated derivatives

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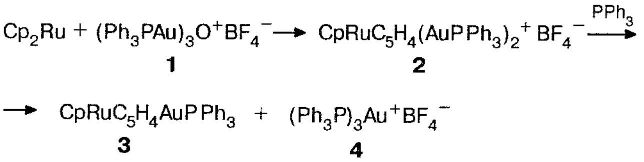
Ruthenocene, like ferrocene, reacts with $(Ph_3PAu)_3O^+BF_4^-$ to afford a *gem*-diaurated derivative $CpRuC_5H_4(AuPPh_3)_2{}^+BF_4^-$, which is converted into $CpRuC_5H_4AuPPh_3$ when treated with PPh_3. X-ray structural analysis revealed substantial Ru—Au interaction in the diaurated derivative.

Key words: ruthenocene; gold-containing oxonium salt; auration.

Cationic *gem*-diaurated derivatives of arenes[1] and ferrocene[2] have been prepared previously with the use of a new aurating reagent, namely, tris(triphenylphosphinegold)oxonium tetrafluoroborate, $(Ph_3PAu)_3O^+BF_4^-$ (**1**), as the source of electrophilic gold. In these compounds, the positive charge is localized predominantly in the Au_2C triangle, which is orthogonal to the arene plane. In the ferrocene derivative, the *endo* gold atom is necessarily brought into proximity to the iron atom.

It was of interest to study the behavior of ruthenocene in this reaction because of its known susceptibility to the formation of Ru^{IV} derivatives (*cf.* Ref. 3), in particular, haloruthenocenium salts. It was suggested that in the case of ruthenocene the direct attack of the electrophilic Ph_3PAu^+ particle on the metal atom is possible. However, this possibility is not realized. As in the case of ferrocene, the reaction affords bis(triphenylphosphinegold)ruthenocene tetrafluoroborate (**2**), from which neutral (triphenylphosphinegold)ruthenocene (**3**) is formed by the action of PPh_3.



$$Cp_2Ru + \underset{\mathbf{1}}{(Ph_3PAu)_3O^+BF_4^-} \longrightarrow \underset{\mathbf{2}}{CpRuC_5H_4(AuPPh_3)_2{}^+\,BF_4^-} \xrightarrow{PPh_3}$$

$$\longrightarrow \underset{\mathbf{3}}{CpRuC_5H_4AuPPh_3} + \underset{\mathbf{4}}{(Ph_3P)_3Au^+BF_4^-}$$

The structures of compounds **2** and **3** were established by X-ray structural analysis. Data for **2** have been reported previously.[4] In monoaurated derivative **3**, one of the hydrogen atoms of ruthenocene was replaced by $AuPPh_3$ (Fig. 1). The Au atom has a typical linear coordination. The Au(1)—C(1) (2.021(5) Å) and Au(1)—P(1) (2.279(1) Å) bond lengths are typical of complexes containing the $C(sp^2)$—Au—P fragment. The lengths of the Ru—C bonds in which the C atoms of the unsubstituted Cp ring are involved are in the range 2.162(8)—2.185(8) Å; the lengths of those bonds in which the atoms of the substituted Cp ring are involved are in the range 2.226(6)—2.170(6) Å. The C(1) atom bearing the substituent is most distant from the Ru atom.

The C(6)···C(10) ring is planar within 0.004 Å. The C(1)···C(5) ring is less planar; the maximum deviation (for the C(1) and C(2) atoms) is 0.005—0.007 Å. The Cp rings are nearly coplanar; the dihedral angle between their planes is 1.2°. The gold atom deviates from the C(1)···C(5) plane by 0.174 Å toward the ruthenium atom; however, the distance between the metal atoms is too large (3.676 Å) to provide interaction.

In diaurated derivative **2**, two $AuPPh_3$ fragments are attached to the same C(1) atom of the cyclopentadienyl ring (Fig. 2). The Au(1)C(1)Au(2) bond angle is 82°; the Au(1)···Au(2) distance (2.779 Å) corresponds to a secondary bond. The $Au_2C(1)$ triangle is nearly orthogonal to the Cp-ring plane; however, the gold atoms are located asymmetrically with respect to this plane: the Au(2) atom is displaced from this plane by 1.12 Å, whereas the displacement of the Au(1) atom is 1.63 Å. With this geometry, the distance between the Au(1) and Ru atoms approaches the bonding distance (2.820 Å). The dihedral angle between the planes of the two Cp rings is 16°.

Comparison of compound **2** with its ferrocene analog[5] shows that the gold—metal distance in both cations is nearly the same (2.820 and 2.818 Å), though the atomic radius of Ru is substantially larger[4] than that of the Fe atom. It is believed that the Ru—Au interaction is stronger and the degree of positive-charge transfer to the Ru atom is larger than in the case of the Fe—Au interaction. Note that the dihedral angle between the

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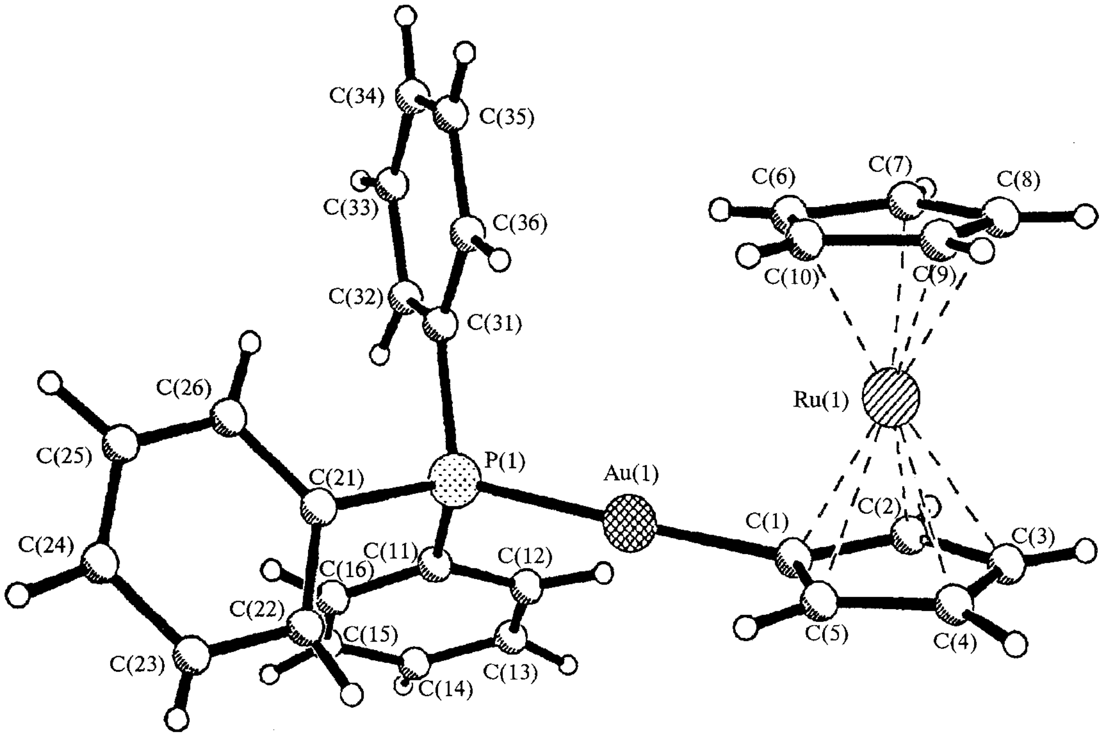

Fig. 1. Structure of $C_5H_5RuC_5H_4(AuPPh_3)$ (**3**).

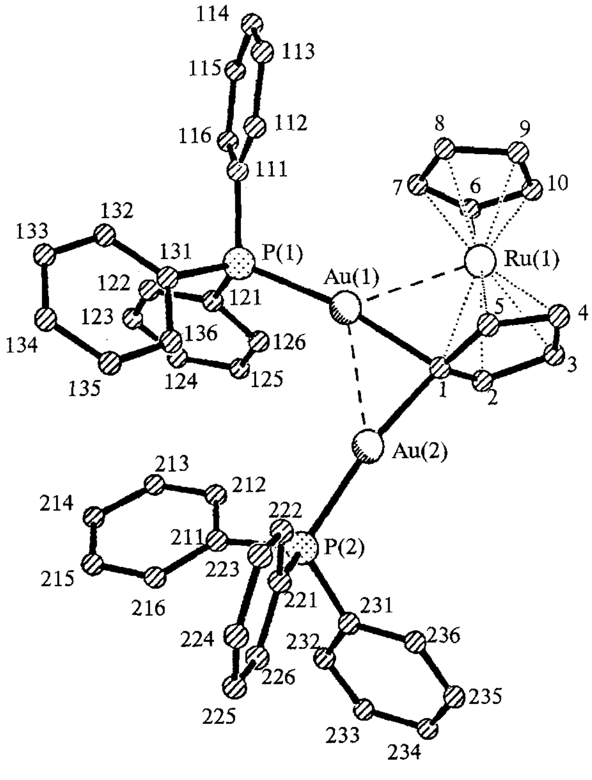

Fig. 2. Structure of $[C_5H_5RuC_5H_4(AuPPh_3)_2]^+BF_4^-$ (**2**).

Cp-ring planes in **2** and its ferrocene analog is 16°, whereas in the iodoruthenocenium cation this angle is 32.2°.[3]

Thus, the reaction of ruthenocene with electrophilic aurating reagent **1** proceeds in the same manner as the reaction of **1** with ferrocene; however, structural details of the prepared *gem*-diaurated derivative **2** indicate that ruthenocene tends to accept a positive charge to yield a Ru^{IV} complex.

Experimental

Auration of ruthenocene. 0.3 mL of a 1 *N* ethereal solution of HBF_4 was added to a solution of 0.30 g of ruthenocene and 0.30 g of **1** in 30 mL of $CHCl_3$. After 1 day, the solvent was evaporated *in vacuo* and the residue was washed several times with ether to remove the excess ruthenocene (control by TLC on Silufol). The residue was dissolved in a minimum volume of acetone; light petroleum was added, and 0.17 g (69 %) of **2** was obtained. Compound **2** is a pale yellow crystalline material whose decomposition temperature is above 200 °C; it is readily soluble in $CHCl_3$, THF, and acetone and slowly decomposes in solutions to yield a metallic film. Found (%): C, 45.28; H, 3.30; F, 5.92; P, 4.87. $C_{46}H_{39}Au_2BF_4P_2Ru$. Calculated (%): C, 44.71; H, 3.18; F, 6.15; P, 5.00. IR (vaseline oil, ν/cm^{-1}): 1060 (BF_4^-). ^1H NMR ($CDCl_3$, δ): 7.75—7.30 (m, 30 H); 5.47 (t, 2 H); 4.80 (s, 5 H); 4.45 (t, 2 H).

Synthesis of $CpRuC_5H_4AuPPh_3$ (3). 0.12 g of PPh_3 was added with stirring to a solution of 0.20 g of **2** in 30 mL of $CHCl_3$. After 30 min, the solvent was removed *in vacuo* and the solid residue was extracted with petroleum ether and then with benzene. 0.10 g of a mixture of **3** and bis(triphenylphosphine)gold tetrafluoroborate (**4**) was isolated from the benzene extract. After repeated reprecipitation (benzene—hexane), 0.03 g of **3** was obtained from the mixture, however, we failed to completely separate **3** from **4**, which is indicated by the results of elemental analysis and by the overestimated value of the integrated intensity of the aromatic protons in the ^{1}H NMR spectrum. Found (%): C, 50.13; H, 3.72. $C_{22}H_{24}AuPRu$. Calculated (%): C, 48.77; H, 3.50. ^{1}H NMR ($CDCl_3$, δ): 7.50—7.20 (m); 4.80 (t); 4.56 (s); 4.36 (t).

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References

1. A. N. Nesmeyanov, E. G. Perevalova, K. I. Grandberg, D. A. Lemenovskii, T. V. Baukova, and O. B. Afanassova, *J. Organomet. Chem.*, 1974, **65**, 131.
2. E. G. Perevalova, D. A. Lemenovskii, K. I. Grandberg, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR,* 1972, **202**, 93 [*Dokl. Chem.*, 1972, **202** (Engl. Transl.)].
3. J. S. Sohn, A. W. Schleuter, D. N. Hendrickson, and H. B. Gray, *Inorg. Chem.*, 1974, **13**, 301.
4. L. G. Kuz'mina, A. M. Abakumova, E. I. Smyslova, and K. I. Grandberg, *Zh. Neorg. Khim.*, 1993, **38**, 1004 [*Russ. J. Inorg. Chem.*, 1993, **38** (Engl. Transl.)].
5. V. G. Andrianov, Yu. T. Struchkov, and E. R. Rossinskaya, *J. Chem. Soc., Chem. Commun.*, 1973, 338.

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Homolytic addition of benzylidene bromide to trimethylvinylsilane and 1-hexene

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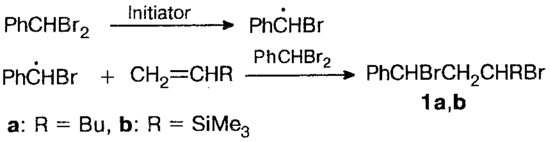
Benzylidene bromide reacts with unsaturated compounds $CH_2{=}CHR$ (R = Bu, $SiMe_3$) in the presence of benzoyl peroxide to give $PhCHBrCH_2CHRBr$ adducts.

Key words: radicals; addition; benzylidene bromide; 1-hexene; trimethylvinylsilane.

An investigation of radical addition and telomerization involving benzyl bromide has shown that it virtually does not react in the presence of peroxides, but selectively reacts at the C—Br bond with metallocomplex systems based on $Fe(CO)_5$ as initiators.[1] In the present work, in a study of radical addition of benzylidene bromide to 1-hexene and trimethylvinylsilane, we unexpectedly obtained the opposite result. When benzoyl peroxide (BP) is used as the initiator, benzylidene bromide selectively reacts at the C—Br bond to give adducts **1a,b** (Scheme 1). These adducts are not formed, however, in the presence of the $Fe(CO)_5$ + DMF system.

Scheme 1



$$\mathrm{PhCHBr_2} \xrightarrow{\text{Initiator}} \mathrm{Ph\dot{C}HBr}$$

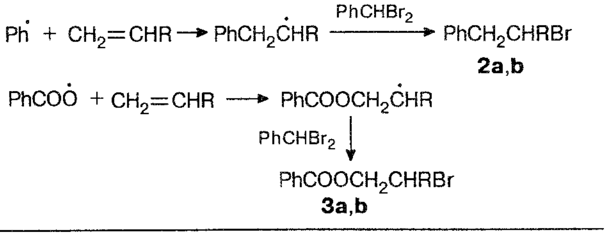
$$\mathrm{Ph\dot{C}HBr} + \mathrm{CH_2{=}CHR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCHBrCH_2CHRBr}$$

1a,b

a: R = Bu, **b**: R = $SiMe_3$

Compounds **1a,b** amount to ~80 % of the overall reaction products (Table 1). In addition to these adducts, noticeable amounts of $PhCH_2CHRBr$ (**2a,b**) and $PhCO_2CH_2CHRBr$ (**3a,b**) are formed as a result of the reaction of $CH_2{=}CHR$ with the Ph$^\cdot$ and PhCOO$^\cdot$ radicals (from BP), according to Scheme 2.

Scheme 2



$$\mathrm{\dot{P}h} + \mathrm{CH_2{=}CHR} \rightarrow \mathrm{PhCH_2\dot{C}HR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCH_2CHRBr}$$

2a,b

$$\mathrm{PhCO\dot{O}} + \mathrm{CH_2{=}CHR} \rightarrow \mathrm{PhCOOCH_2\dot{C}HR} \xrightarrow{\mathrm{PhCHBr_2}} \mathrm{PhCOOCH_2CHRBr}$$

3a,b

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