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AN INFRARED AND NMR STUDY OF THE STRUCTURE OF CYCLOPENTADIENYL COMPOUNDS OF GOLD(I)

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Summary

Cyclopentadienyl- and methylcyclopentadienyl-(triphenylphosphine)gold(I) and cyclopentadienyl(triethylphosphine)gold(I) have been characterized by infrared and variable temperature proton magnetic resonance spectroscopy. The compounds are suggested to have *monohapto* (i.e. σ-bonded) rings, in contrast with the analogous copper(I) derivatives.

Introduction

The structure and reactions of compounds in which gold(I) is bonded to an organic moiety have been little investigated hitherto. Like Ag^I and Cu^I, Au^I may be σ-bonded to a carbon atom, as in the alkyl derivatives, or π-bonded to a carbon—carbon double bond, as in the olefin derivatives.

This paper is intended to provide a contribution to the elucidation of the structure of cyclopentadienyl(triphenylphosphine)gold(I). This molecule is isoelectronic with the corresponding compound of Cu^I, which was recently shown to have a *pentahapto*-cyclopentadienyl ring [1], a conclusion contrary to that of several previous investigations.

Experimental

General

All the organometallic compounds were prepared, stored, and handled under dry nitrogen. All the solvents were carefully dried and distilled. Infrared spectra were recorded with potassium bromide pellets or Fluorolube and Nujol mulls on a Perkin—Elmer 257 or a Beckmann IR 20 spectrometer. NMR spectra were recorded at 60 MHz on a Jeol C-60 HL spectrometer.

Syntheses

(a). Cyclopentadienyl(triphenylphosphine)gold(I). This was prepared by the method of Hüttel et al. [2] except that instead of the sodium derivative, cyclopentadienyllithium, which was obtained more easily from cyclopentadiene and butyllithium, was used. White crystals were usually obtained. On standing at room temperature, they became dark brown after few days. (Analysis found: C, 52.45; H, 3.55. $C_{23}H_{20}AuP$ calcd.: C, 52.69; H, 3.84%.)

(b). Methylcyclopentadienyl(triphenylphosphine)gold(I). This compound readily undergoes decomposition [3], and several preparations were unsuccessful. Particular care must be devoted to the temperature, which must be as low as possible.

A white slurry of methylcyclopentadienyllithium in anhydrous diethyl ether was obtained from freshly depolymerized methylcyclopentadiene (1.2 g, 15 mmol) and butyllithium (Merck), in dry ice under nitrogen. A slurry of (triphenylphosphine)gold(I) chloride [4], was added very slowly under nitrogen, the temperature being kept at —70°. The mixture was stirred for twenty minutes, the temperature was slowly raised to —30°, and the supernatant liquid removed. On evaporation of the solvent under vacuum at —30° a powdery, yellowish substance was obtained. For purification it was dissolved in THF/acetone at —20° and ice was slowly added. (Analysis found: C, 53.28; H, 3.75. $C_{24}H_{22}AuP$ calcd.: C, 53.54; H, 4.12%.)

(c). Cyclopentadienyl(triethylphosphine)gold(I). It was prepared in the same manner of the methylcyclopentadienyl(triphenylphosphine)gold(I), by the reaction at —70° of 2.1 g (6 mmol) of triethylphosphinegold(I) chloride [4], suspended in 100 ml of anhydrous diethyl ether, with 2.7 g (10 mmol) of cyclopentadienylthallium. The compound was isolated as white crystals. It appears to be less stable than the triphenylphosphine analogue. (Analysis found: C, 34.53; H, 5.03. $C_{11}H_{20}AuP$ calcd.: C, 34.75; H, 5.30%.)

Results and discussion

At room temperature, the NMR spectrum of cyclopentadienyl(triphenylphosphine)gold(I) in $CDCl_3$ shows a well-defined singlet at τ 3.8 ppm due to the cyclopentadienyl ring and a complex pattern from the three phenyl groups centered at τ 2.6. The integrated intensities ratio is 5/15. On lowering the temperature from +30 to —60°, the singlet of the Cp ring remains unchanged except for a small upfield shift (at —60° the singlet is at τ 3.9 ppm) and a slight broadening at the lowest temperatures. The latter change is probably due to the temperature effect, since the signals of the phenyl rings and of TMS also appear to be slightly broadened. No signals in the τ 7 ppm region, due to methylenic hydrogens, appear. At —80° the single NMR absorption splits into a doublet. Such behaviour is observed only if traces of free triphenylphosphine are excluded from the solution; successive addition of amounts of this ligand to the sample leads to a collapse of the Cp doublet, which is replaced by a sharp singlet even at —100°.

The room temperature NMR spectrum of methylcyclopentadienyl(triphenylphosphine)gold(I) in $CDCl_3$ shows three distinct signals of the Cp ring at τ 3.9, 4.15 and 7.7 ppm (integrated intensities ratio 2/2/3). On cooling, the resonance at τ 4.15 broadens, giving a well resolved doublet at —90°, while the signal at τ 3.9 does not show any splitting.

TABLE 1

INFRARED DATA FOR CYCLOPENTADIENYL(TRIETHYLPHOSPHINE)GOLD(I) AND RELATED COMPOUNDS

$(C_5H_5)Au^I(C_2H_5)_3$	$(C_2H_5)_3Au^ICl$	$(C_5H_5)(CH_3)_2Au^{III}$-$P(C_6H_5)_3$ [a]
3091–3075 m		
2945–2890 ms	2950–2885 ms	
1475 m	1475 m	
1398 m		1382 m
1365 m	1365 m	
1065 m	1065 m	
998 m		977 m
		889 vs
808 s		818 m
737 s		742 vs
690 m	695 m	
645 m		632 vs

[a] Data from Ref. 5 Only the peaks arising from the C_5H_5Au portion are listed.

The infrared spectral data of cyclopentadienyl(triethylphosphine)gold(I) are reported in Table 1, together with those of (triethylphosphine)gold(I) chloride and $(C_5H_5)(CH_3)_2Au^{III}P(C_6H_5)_3$ [5]. The former compound was chosen in order to obtain essential infrared data [6], which cannot be obtained from the spectra of the triphenylphosphine derivative because of the interference between the phenyl groups vibrations and those of the Cp ring [6].

The NMR data are consistent with a *monohapto*-cyclopentadienyl structure, since the splitting of the Cp ring at low temperatures must be due to the coupling of the ^{31}P nucleus with the ring hydrogens. This situation is analogous to that observed for (trimethylphosphine)methylgold(I) [7]. The NMR results can be understood in terms of a rapid exchange process of the triphenylphosphine ligand at the metal centre, the rate of which is strongly dependent on the concentration of the free triphenylphosphine. The mechanism of ligand exchange at the C_5H_5Au moiety is believed to be associative, and to include an intermediate with sp^2-hybridized gold atoms of coordination number three. The concentration dependence of the NMR spectra is consistent with this proposal.

The NMR spectrum of methylcyclopentadienyl(triphenylphosphine)gold(I) is also in agreement with the *monohapto*-type of bonding. For the h^1-C_5H_5 structure, three signals would be expected, when the rotation is sufficiently fast on the NMR time scale, as in bis(methylcyclopentadienyl)mercury [8], these arising from the methyl group and the two types of olefinic hydrogens. Further, the resonances appear to fall in the typical olefinic region (the ring hydrogens of 1,1′-dimethylferrocene fall at τ 6.0 [9]), although $(h^5$-$C_5H_5)(C_6H_5)_3PCu$, the structure of which has been determined by X-ray diffraction [10], shows the singlet of the Cp ring at τ 4.3 [6]. However, the broadening and the splitting of one of the two olefinic resonances at low temperature can be understood only in terms of a rapidly rearranging h^1-bonded structure, although a rapid interconversion of h^1-C_5H_5 and h^5-C_5H_5 molecules may also occur.

Fundamental criteria based on IR data for a clear distinction between *pentahapto*- and *monohapto*-cyclopentadienyl metal derivatives have been recently suggested by Cotton and Marks [1, 6]. Their papers should be consulted for details, and we need mention only certain features. The IR spectrum of an

h^5-C_5H_5 system is very simple in the range of 600—3500 cm^{-1}, as it consists of a medium band at 3050—3100 cm^{-1}, a strong band at ca. 1000 cm^{-1} and a broad, strong band at 800 ± 50 cm^{-1}; two more bands are possible at 1400 and 1100 cm^{-1}. In contrast, for the *monohapto*-cyclopentadienyl system a very rich and complex spectrum is predicted; in particular multiple olefinic C—H stretching bands should be observed in the 3000—3100 cm^{-1} region. Thus the infrared spectrum of cyclopentadienyl(triethylphosphine)gold(I) appears to exhibit the spectral pattern characteristic of a *monohapto*-cyclopentadienyl system, although a more complex spectrum would have been predicted in the 600—1400 cm^{-1} region. It is particularly noteworthy that the infrared bands due to the C_5H_5Au portion of cyclopentadienyl(triethylphosphine)gold(I) closely resemble those observed for $(h^1$-$C_5H_5)(CH_3)_2Au^{III}P(C_6H_5)_3$ [5] (see Table 1), for which the *pentahapto*-cyclopentadienyl ring was ruled out. This indicates that the bonding of the Cp group is similar in the two compounds.

Thus it appears that, in contrast with the analogous copper(I) system, gold(I) forms *monohapto*-cyclopentadienyl derivatives, in agreement with its well-known tendency to give linear two-coordinated compounds. However, since solvents may consistently modify the nature of the Cp-ring—metal bonding through their donor properties [1, 11]*, crystallographic studies are necessary to establish whether the *monohapto*-cyclopentadienyl structure persists in the solid state.

From a theoretical point of view, it is interesting to note that the conclusions reached in this work are in accordance with the predictions based on the Woodward—Hoffmann rules as extended to the stereochemically non-rigid organometallic compounds [12].

Finally, we wish to point out that Cotton's criteria apply very well to a number of cyclopentadienylmetal compounds, such as $(h^1$-$C_5H_5)_3As$ [13], $(h^5$-$C_5H_5)_3Bi$ (black modification) [13], $(h^5$-$C_5H_5)TiCl_3$ [14], h^5-C_5H_5Tl and $(h^1$-$C_5H_5)(CH_3)_2Tl$ [15] and $(h^1$-$C_5H_5)GeH_3$ [16]. We have also noted that for such molecules as $(C_5H_5)_3Sb$ and $(C_5H_5)Bi$ (orange modification) [13], for which a rapid interconversion between h^5- and h^1-C_5H_5 rings was suggested, the infrared spectra show a complex pattern in the 600—1400 cm^{-1} region, and only a single absorption in the 3000—3100 cm^{-1} region.

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* The solvent effects on the fluxional behaviour of organometallic compounds are currently being investigated in this laboratory.

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