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Complexes of $(CH_3)_2Au^{III}$: Synthesis, PMR and IR Spectra

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The syntheses and reactivity of dimethylgold(III) complexes with multidentate ligands as TRIPHOS (i.e., 1,1,1-tris(diphenylphosphinomethyl)ethane) and TREN (i.e. 2,2',2"-triaminotriethylamine) have been examined. I.r. spectra for the compounds in the solid state, conductivity and PMR data for solutions, lead to the assignment of an ionic formula $[(CH_3)_2Au\ TRIPHOS]^+[(CH_3)_2AuCl_2]^-$ *where the gold(III) atoms are presumably four-coordinate. The complex* $(CH_3)_2AuCl$ *TREN in DMSO solution undergoes a reductive elimination reaction, as found for analogous dimethylgold(III) derivatives.*

Introduction

In the past years we have investigated the chemistry of the dimethylgold(III) moiety both in respect of complexes with N, S, P, As, Sb donor ligands[1] and reactions which take place in solution[2].

Laser-Raman spectroscopy has been essentially employed to investigate the structures of the complexes in the solid state and their reactivity in solution. In general, the dimethylgold(III) complexes have been found to possess a square planar structure, with the methyl groups arranged in a mutually "*cis*" configuration and the coordination on the gold(III) atom was four. PMR spectra at room temperature of dimethylgold(III) chloride in pyridine solution exhibit a single, unbroadened signal for the methyl protons, indicating that the six protons are equivalent. At–38° C, $(CH_3)_2AuClpy$ (py = pyridine) in $CHCl_3$ and CCl_4 solutions, shows the two signals expected for this asymmetric complex[1,2]. The addition of free pyridine causes the coalescence of the signals. The exchange process is first order in pyridine and a five-coordinate intermediate is advanced[2].

The original aim was of obtaining five-coordinate complexes in the solid state. In this note we report the complexes obtained by reaction of dimethylgold(III) chloride with multidentate ligands as TRIPHOS (1,1,1-tris(diphenylphosphinomethyl)ethane) and TREN (2,2′,2″-triaminotriethylamine). The first ligand is potentially tridentate with P donor atoms, while TREN is potentially tetradentate through its N donor atoms. The main question to be answered was whether complexes with coordination number of the gold(III) atom greater than four were formed. Conductivity measurements and PMR spectra have been obtained for the complexes in solution, while in the solid state they have been investigated by i.r. spectroscopy.

Experimental

Dimethylgold(III)chloride has been synthesized by the previously reported method[3]. The ligands TREN, TRIPHOS and TERPY have been purchased from Alfa Inorganics Ventron (Beverly, Mass.), Strem Chemicals (Danvers, Mass.) and Schuchardt (Munich) respectively and used without further purification. The solvents (cyclopentane and diethylether) have been dried with molecular sieves 3A-type.

The complexes $(CH_3)_2AuClTREN$ and $[(CH_3)_2Au\ TRIPHOS]^+[(CH_3)_2AuCl_2]^-$ have been prepared by mixing under vigorous stirring dimethylgold(III) chloride solutions (2–4 mmol in *ca.* 5 ml cyclopentane) with TREN (dissolved in 5 ml cyclopentane) in a 1:1 molar ratio or with TRIPHOS (dissolved in 5 ml diethylether) in 2:1 molar ratio. In the latter synthesis, whenever 1:1 molar amounts of organogold(III) and TRIPHOS were reacted, the above mentioned complex was obtained, instead of the expected $[(CH_3)_2Au\ TRIPHOS]^+Cl^-$.

Operating essentially in the same conditions, the synthesis of $[(CH_3)_2AuTERPY]^+[(CH_3)_2AuCl_2]^-$ has been attempted, (TERPY = 2,2′,6′,2″-terpyridine) but analytical data were unsatisfactory for the solid compound obtained and further investigation was abandoned.

The compound $(CH_3)_2AuCl$ TREN is very hygroscopic. These complexes are generally fairly stable to the daylight, and could be kept in the dark, at a temperature of ca. 2° C for some months, without any detectable decomposition. Microanalyses were performed by Laboratorio di Microanalisi, Istituto di Chimica Farmaceutica (Padova) and reported in Table I, along with equivalent conductivity data (measured at 26° C with a LKB Conductolyzer Type 5300B) for the ionic complex. PMR spectra have been obtained

TABLE I. Analytical Data [Found(Calculated)%] and Equivalent Conductivity (T = 26 °C, nitromethane) of $(CH_3)_2Au^{III}$ Complexes.

Compound	C	H	N	P	Conc. ($M \times 10^3$)	Λ_e (Ω^{-1} cm^2 equiv.$^{-1}$)
$(CH_3)_2AuCl$ TREN	23.77 (23.50)	6.09 (5.91)	13.52 (13.70)			
$[(CH_3)_2Au\ TRIPHOS]^+[(CH_3)_2AuCl_2]^-$ [a]	47.74	4.93		8.38	6.24	65.64
	(47.01)	(4.47)		(8.08)	3.12	69.62
					1.87	71.98
					1.25	73.36
					1.06	74.84

[a] Cl; 6.26 (6.17).

with a Jeol C 60 spectrometer operating at 60 MHz at 26 °C; i.r. spectra in the 4000–200 cm^{-1} region have been recorded with Beckmann IR 12 and Perkin Elmer 457 spectrometers as Nujol–halocarbon oil split mulls. A KBr liquid cell has been used for i.r. spectra of a TREN solution in benzene.

Discussion

Equivalent conductivity data support the ionic formula $[(CH_3)_2AuTRIPHOS]^+[(CH_3)_2AuCl_2]^-$. Accordingly, the i.r. spectra of the complex exhibit two bands of medium intensity at 270 and 290 cm^{-1}, which are assigned to the asymmetric and symmetric Au–Cl stretching vibrations respectively, associated with the $(CH_3)_2AuCl_2^-$ ion[10].

In the PMR spectrum of the complex, the methyl groups resonance at $\delta = 1.18$, with $^3J(^{31}P–^1H) = 5.2$ Hz coupling constant, has been assigned to the $(CH_3)_2Au^{III}$ moiety of the cationic species $[(CH_3)_2Au\ TRIPHOS]^+$ on the basis of the $[(CH_3)_2Au\ DIPHOS]^+$ spectrum[1]. The two spectra have in common this pseudotriplet, which is associated in the latter with a $A_3XX'A'_3$ spectrum[4]. $^3J(^{31}P–^1H)$ values are also very similar in both compounds (5.2 and 7.4 Hz respectively). It is known that the TRIPHOS ligand may act as tridentate[5,6,7] and bidentate[7,8] through its phosphorus atoms. As the PMR spectra of the TRIPHOS moiety in $[(CH_3)_2Au\ TRIPHOS]^+$ are markedly different from those of the free ligand especially in the phenyl groups region, this might be helpful in assessing whether the TRIPHOS ligand is tridentate or bidentate. The PMR resonances of the free ligand in $CDCl_3$ are within few tenths of ppm from those reported in the literature[7]. These resonances in the phenyl protons region are quite complicated by the super imposition of signals due to *ortho-*, *meta-* and *para-* phenyl protons of bonded and non-bonded phosphorus atoms respectively. According to the previous assignments[7] the signal at $\delta = 7.23$ ppm may be associated with the $\delta = 7.27$ ppm resonance in the free ligand due to protons of a non-bonded phosphino group, and the $\delta = 7.40$ ppm intense signal may result from the super imposition of "*ortho*" phenyl protons of non-bonded phosphorus with protons from bonded groups. The $\delta = 7.53$ ppm and 7.80 ppm signals are probably associated with bonded phosphino groups. Such non-equivalence of bonded and non-bonded signals is also found for methylene protons. The signal at $\delta = 2.03$ ppm is sufficiently broad (width at half-height *ca.* 4 Hz) to suggest the presence of an unresolved doublet due to $^2J(^{31}P–^1H)$ coupling and may arise from non-bonded groups. The complex signals between $\delta = 3.00$ and 4.00 ppm may be due to bonded phosphino groups. A similar pattern has been observed for complexes of Re(V) with a bidentate TRIPHOS ligand but similar resonances are actually exhibited also by the PMR spectrum of $[(CH_3)_2AuDIPHOS]^+$ where both phosphino groups are bonded to gold[4]. The analogy between the PMR spectra of the dimethylgold(III) moiety in both the complexes with TRIPHOS and DIPHOS suggests a similar coordination by the ligands, that is one phosphino group of TRIPHOS is uncoordinated. The i.r. spectra of the free ligand have been reported in detail[7] and on complex formation all the X-sensitive modes arising from $Ph_2P–C$ groups are shifted. Once again a similar pattern had been found for the DIPHOS complex. The highest shifts are relative to the 500–600 cm^{-1} region as for the complexes of Re(V) mentioned above[7] but also in this case no definite information on the coordination of the ligand could be drawn.

Three very strong bands in this region, due to TRIPHOS (480, 519 and 535 cm^{-1}), are obscuring $\nu(AuC_2)$ vibrations which, besides, are expected to be weak in the infrared. Raman spectra might eventually allow a direct comparison between the dimethylgold(III) moiety vibrational modes in both TRIPHOS and DIPHOS complexes. Also the deformation frequencies due to CH_3–Au groups are obscured by ligand vibrations.

TABLE II. PMR Spectra of $(CH_3)_2Au^{III}$ Complexes (TMS internal standard, solvent $CDCl_3$).

Compound	Temp. (°C)	$CH_3(Au)$		δ (CH_2) (ppm)	δ Aromatics (ppm)
		δ (ppm)	$^3J(^{31}P{-}^1H)$(Hz)		
$[(CH_3)_2Au\ TRIPHOS]^+[(CH_3)_2AuCl_2]^-$	26	1.18[b]	5.2	2.03; 3.00–4.00	7.23; 7.40 7.53; 7.80
$[(CH_3)_2Au\ DIPHOS]^+Cl^-$[a]	40	1.23	7.4	3.32	7.55 (multiplet)

[a] Ref. 1 and 4; DIPHOS = $[P(C_6H_5)_2CH_2]_2$. [b] Group of signals from δ 1.50 to 0.50 ppm enveloping δ (CH_3–Au) of the anion and δ (CH_3–C) of the ligand.

The $(CH_3)_2$AuClTREN complex is practically insoluble in noncoordinating solvents and this prevented meaningful conductivity measurements[9]. The broad band exhibited by $(CH_3)_2$AuCl TREN at 250–270 cm^{-1} is assigned to the ν(AuCl) vibration, which is present at 256 cm^{-1} in the parent $[(CH_3)_2AuCl]_2$, and at 268, 280 cm^{-1} (i.r.) in $[(CH_3)_2AuCl_2]^-$. A broad band at *ca.* 550 cm^{-1} due to TREN is present in the region where $\nu(AuC_2)$ vibrations are expected. The PMR spectra in DMSO for $(CH_3)_2$AuCl TREN exhibit a single resonance at δ = 0.20 ppm whose relative intensity bears no relationship with the other signals due to the ligand. Solutions of dimethylgold(III) complexes[1,4] in chloroform have been shown to undergo a reductive elimination reaction with the appearance of a signal at δ = 0.85 ppm, which was identified as due to ethane by the mass spectrum and by comparison of the PMR chemical shift with that of ethane resonance in a saturated $CDCl_3$ solution[4]. The reaction is favored by a high nucleophilicity of the anion and the nature of the solvent. This might as well be the case also for $(CH_3)_2$AuClTREN in DMSO solutions. Any conclusion on the nature of this complex at the present time would be largely conjectural. In view of the insolubility of the complex, it is likely that the compound is polymeric with bridging TREN.

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References

1 G.C. Stocco and R.S. Tobias, *J. Am. Chem. Soc., 93* (1971) 5057.
2 H. Hagnauer, G.C. Stocco and R.S. Tobias, *J. Organometal. Chem., 46* (1972) 170.
3 W.M. Scovell, G.C. Stocco and R.S. Tobias, *Inorg. Chem., 9* (1970) 2682.
4 C.F. Shaw, III, J.W. Lundeen and R.S. Tobias, *J. Organometal. Chem., 51* (1973) 365.
5 J. Chatt and H.R. Watson, *J. Chem. Soc.,* (1961) 4980; quoted in ref. 7.
6 A.G. Massey and R.S. Nyholm, *J. Polymer. Sci., 62* (1962) S 126.
7 R. Davis and J.E. Fergusson, *Inorg. Chim. Acta, 4* (1970) 16.
8 R. Davis and J.E. Fergusson, *Inorg. Chim. Acta, 4* (1970) 23.
9 W.J. Geary, *Coord. Chem. Rev., 7* (1971) 81.
10 W.M. Scovell and R.S. Tobias, *Inorg. Chem., 9* (1970) 945.