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DIMETHYLGOLD(III) COMPLEXES OF SALICYLALDIMINE SCHIFF-BASES

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SUMMARY

Dimethylgold complexes with bidentate *N*-alkyl- and *N*-aryl-salicylaldimines, $Me_2AuSal{=}N{-}R$, as well as bridged complexes of the quadridentate ligands *N,N'*-ethylenebis(salicylaldimine) and *N,N'*-*o*-phenylenebis(salicylaldimine), $(Me_2Au)_2$Salen and $(Me_2Au)_2$Salophen, have been synthesized. The latter is the first example of a compound in which Salophen behaves as a bridging ligand. ^{1}H NMR, infrared and mass spectra have been measured. The gold–carbon bond in these compounds does not appear to undergo reaction without complete decomposition of the complex.

INTRODUCTION

The only complexes of gold with Schiff-base chelate ligands reported to date have been mixed valence compounds of the type $[Au^{III}(Sal{=}N{-}R)_2][Au^{I}Cl_2]$[1] ($Sal{=}N{-}R$ = *N*-substituted-salicylaldiminato anion). We report here the preparation and properties of organogold salicylaldimine chelates, $Me_2AuSal{=}N{-}R$, which are the first examples of organogold Schiff-base complexes. Related acetylacetone complexes have been reported[2,3], these being less stable than the salicylaldimine compounds. This paper also describes some binuclear dimethylgold derivatives containing bridging quadridentate ligands. Spectral measurements have been made on both the mono and binuclear derivatives, and some attempts made to obtain reactions of the gold–carbon bond.

RESULTS AND DISCUSSION

Syntheses

$[Me_2AuI]_2$[3] in methanol reacts with the thallium(I) salts of Schiff bases $TlSal{=}N{-}R$ ($R{=}CH_3$, C_6H_{11}, C_6H_5), Tl_2Salen [SalenH_2 = *N,N'*-ethylenebis-(salicylaldimine)] and Tl_2Salophen [SalophenH_2 = *N,N'*-*o*-phenylenebis(salicylaldimine)] to give the complexes $Me_2AuSal{=}N{-}R$, $(Me_2Au)_2$Salen and $(Me_2Au)_2$-Salophen. The pale yellow mononuclear compounds are readily soluble in methanol and are isolated from the solution after filtering off the thallium(I) iodide. They are also readily soluble in most organic solvents, though only slightly in hexane, and presumably have the square planar structure shown in Fig. 1. $(Me_2Au)_2$Salen and $(Me_2Au)_2$Salophen are much less soluble (particularly the Salen complex) and are separated from thallium(I) iodide by dichloromethane extraction. They are expected to have the binuclear bridged structure proposed for compounds of rhodium[4], iridium[4], palladium[5,6] and platinum[6]. The formation of the Salophen complex is particularly interesting as it was previously believed that Salophen was not sufficiently flexible to permit a bridging configuration[4]. However it is clear from the formation of this compound that it is possible for Salophen to distort sufficiently for bridging to occur, although the nature of this distortion is not clear.

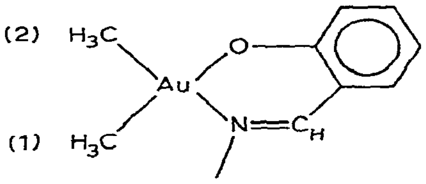

Fig. 1.

All the complexes show enhanced thermal stability, compared to other gold organometallic compounds, decomposing above 100°. They are also fairly stable to light, in contrast to the acetylacetone derivative[3], although solutions slowly decompose in direct sunlight and more rapidly under UV irradiation.

Spectra

The ^1H NMR spectra of the complexes are shown in Table 1. Low solubility prevented measurement of the NMR spectrum of the Salen complex. The methyl group(1) is assigned as that *cis* to the nitrogen donor of the Schiff base because of its shift to higher field when an *N*-alkylsalicylaldimine is replaced by the Sal=N–C_6H_5 ligand, while Me(2) remains almost unaffected. This anisotropic shielding effect of the aromatic ring on a nearby proton has previously been used to assign the structures of other organometallic Schiff base complexes[5,6]. Hence the more shielded of the two methyl groups is that *trans* to the oxygen of the Schiff base, suggesting that this is a better donor than the nitrogen. That the oxygen is in fact a stronger donor should

TABLE 1

^1H NMR SPECTRA[a]

Complex	*δ Values (ppm downfield from internal TMS)*				
	Me(1)	*Me(2)*	*Aromatic*	*CH=N*	*Other*
$Me_2AuSal=N\text{-}CH_3$	0.97	1.19	6.42–7.43	8.08	CH_3[b] 3.52
$Me_2AuSal=N\text{-}C_6H_{11}$	0.91	1.20	6.43–7.42	8.18	C_6H_{11} 1.2–3.9
$Me_2AuSal=N\text{-}C_6H_5$	0.49	1.22	6.46–7.50	8.22	
$(Me_2Au)_2$Salophen	0.39	1.08	6.43–7.48	8.16	

[a] In deuterochloroform. [b] Doublet. $J(CH=N\text{-}CH_3)$ 1.3 Hz.

not be surprising in view of the fact that in the salicylaldiminato anion the negatively charged oxygen is far more readily protonated than the neutral nitrogen atom. In allylpalladium Schiff base compounds[5] the protons attached to the carbon *trans* to the oxygen are also more shielded, but here the effect may also be rationalized in terms of σ and π bonding contributions for the two ends of the allyl group, as in related phosphine complexes[7,8]. These effects illustrate that care must be taken when discussing *trans* effects, particularly when π systems are involved. In the case of the gold complexes described here the results clearly indicate that the oxygen of the salicylaldimine produces greater shielding in the methyl group *trans* to it (presumably due to a higher electron density) although the precise effects in terms of bond strengths, polarization or even π bonding contributions from the imine nitrogen cannot be considered as clear. The starting material $(Me_2AuI]_2$ which has an iodide bridged structure shows the methyl group resonance at δ 6.08 ppm, indicating much less shielding than in the Schiff base complexes, consistent with the much weaker coordinating properties of the iodide ion, but again it would be difficult to predict the precise electronic effects.

In $(Me_2Au)_2$Salophen the methyl group (1) displays a similar upfield shift to that in $Me_2AuSal{=}N{-}C_6H_5$, suggesting that the orientation of the molecule is such as to enable the bridging phenylene group to exert an anisotropic shielding effect on this methyl. As only two methyl resonances are observed both ends of the molecule must be magnetically equivalent, at least in solution on the NMR time scale.

The infrared spectra of the complexes in the region 1700–1100 cm^{-1} are typical of those expected for salicylaldimine chelate complexes and are shown in Table 2. All show two fairly strong bands between 1640 and 1580 cm^{-1}, and a further fairly intense band between 1540 and 1530 cm^{-1}. Assignments of infrared spectra

TABLE 2

INFRARED SPECTRA (IN REGION 1700–1100 CM^{-1})[a]

Complex	*Bands* (*cm*$^{-1}$)
$Me_2AuSal{=}N{-}CH_3$	1635s, 1602m, 1539m. 1472m, 1454m, 1400w, 1360m, 1329m, 1255w, 1233w, 1204w, 1192m, 1156m, 1128w
$Me_2AuSal{=}N{-}C_6H_{11}$	1615s, 1600m, 1538m, 1470s, 1452s, 1414m, 1364w, 1354m, 1346m, 1309w, 1297w, 1264w, 1244w, 1237w, 1203w, 1191m, 1180w, 1144m, 1124w
$Me_2AuSal{=}N{-}C_6H_5$	1614s, 1598m, 1536s, 1513w, 1493m, 1470m, 1449s, 1397m, 1362m, 1330m, 1250w, 1226w, 1206m, 1177m, 1155m, 1132m
$(Me_2Au)_2$Salen	1626s, 1601m, 1537s, 1468m, 1450m, 1411m, 1360m, 1334m, 1302w, 1253w, 1214m, 1188m, 1153m, 1133m
$(Me_2Au)_2$Salophen	1610s, 1589m, 1531m, 1485w, 1463m, 1449w, 1438m, 1393m, 1384m, 1361w, 1349w, 1326m, 1266w, 1245w, 1209m, 1181m, 1170m, 1150m, 1130m, 1100w

[a] KBr disc.

of Schiff base complexes have proved difficult and uncertain, due to coupled vibrations and complexity of the spectra, most studies having been made on copper(II) complexes of arylsalicylaldimines[9-11]. On the basis of ^{15}N substitution the principal bands in Cu^{II}(Sal=N–$C_6H_4CH_3$-*p*)$_2$ have been assigned[11]. There are three bands in the region 1640 to 1580 cm^{-1}, two assigned to ν(C=N) and one to ν(C=C), whereas the gold complexes show only two bands. However the higher frequency band is very intense and somewhat broadened, indicating that overlap may be occurring. The starting material [Me_2AuI]$_2$ displays two sharp bands at 1215 and 1185 cm^{-1} which are presumably due to $\delta_s(CH_3)$. Bands due to this vibration will occur in a similar region in the Schiff base complexes but it is impossible to decide which bands these are.

All the complexes display the parent ion in the mass spectrum. The mononuclear complexes of the bidentate ligands also show clearly the ions AuSal=N–R$^+$ and Sal=N–R$^+$. Metastable peaks corresponding to the fragmentation Me_2AuSal=N–R$^+$→AuSal=N–R$^+$ are observed. The complexes of the quadridentate ligands give peaks corresponding to the ions $Me_2AuLCH_3^+$, Me_2AuLH^+, MeAuL$^+$ and AuL$^+$ (L = Salen, Salophen).

Reactions

Reactions with several reagents which may be expected to react with a metal–alkyl bond were performed but none of the products hoped for could be obtained. Liquid SO_2 produced only complete decomposition, metallic gold being evident, and no insertion product could be isolated, although insertion has been observed for a trimethylgold compound[12]. Attempts to replace the methyl groups with heptafluoropropyl groups (which may be expected to bond more strongly to the metal) by heating with heptafluoropropyl iodide either neat or in methanol led only to recovery of starting material. A similar reaction in methanol under UV irradiation produced extensive decomposition with formation of metallic gold, but no evidence for perfluoroalkyl groups in the product could be obtained, starting material still being apparent. It appears that once the gold–carbon bond is ruptured a new bond is not readily formed and only metallic gold will result.

EXPERIMENTAL

Instrumentation

^{1}H NMR spectra were measured on a Varian Associates HA-100 spectrometer and infrared spectra on a Perkin–Elmer 521 spectrophotometer. Mass spectra were obtained with a Hitachi–Perkin–Elmer RMU-6E instrument using an ion chamber temperature of 200° (except for Me_2AuSal=N–CH_3 where 90° was used) and an electron energy of 70 eV.

Starting materials

[Me_2AuI]$_2$ was prepared as in the literature[3]. The thallium(I) Schiff bases were obtained by reaction of the ligand with thallium(I) ethoxide in ethanol[13].

Syntheses

Me_2AuSal=N–R (R = CH_3, C_6H_{11}, C_6H_5). [Me_2AuI]$_2$ (200 mg, 0.28 mmol)

in methanol (40 ml) was treated while stirring with the stoichiometric quantity of the appropriate thallium(I) Schiff base compound. After stirring for approx. 1½ h the mixture was filtered and the methanol solution evaporated under reduced pressure. Recrystallization of the residue from dichloromethane/hexane gave the pure compound.

$(Me_2Au)_2$Salen and $(Me_2Au)_2$Salophen. These were formed as above from $[Me_2AuI]_2$ (200 mg, 0.28 mmol) and Tl_2Salen or Tl_2Salophen (0.28 mmol) in methanol (50 ml), the reaction time being increased to 3 h. Due to their lower solubility they were isolated by filtering off the solid (in the case of the Salen complex) or evaporating to dryness (Salophen complex), extracting the mixture with dichloromethane and reducing the volume of the solution under reduced pressure after addition of hexane.

Analytical data, molecular weights, melting points and yields for all the compounds are given in Table 3.

Reactions

Sulphur dioxide

SO_2 was condensed onto $Me_2AuSal{=}N{-}C_6H_5$ at −78° and then allowed to evaporate at 0°. Some metallic gold was evident and no insertion product could be isolated.

C_3F_7I

(*a*). $Me_2AuSal{=}N{-}C_6H_5$ and $(Me_2Au)_2$Salen were each heated under reflux with C_3F_7I both alone and with addition of methanol (to increase solubility). In the latter case some darkening due to formation of metallic gold occurred after approx. ½ h, but in all cases only unchanged starting material could be recovered from the mixture.

(*b*). $Me_2AuSal{=}N{-}C_6H_5$ (100 mg) dissolved in methanol (50 ml) was treated with C_3F_7I (2 ml) and irradiated with a UV lamp for 3 h. Substantial decomposition

TABLE 3

ANALYTICAL DATA, MOLECULAR WEIGHTS, MELTING POINTS AND YIELDS

Complex	*Formula*	*Analyses found (calcd.) (%)*				*m/e found (Calcd.)*	*M.p. (°C)*	*Yield (%)*
		C	*H*	*N*	*Au*			
$Me_2AuSal{=}N{-}CH_3$	$C_{10}H_{14}NOAu$	33.32 (33.25)	3.78 (3.91)	3.67 (3.88)	53.9 (54.5)	361 (361)	103 (sl. dec.)	62
$Me_2AuSal{=}N{-}C_6H_{11}$	$C_{15}H_{22}NOAu$	42.17 (41.97)	5.28 (5.17)	3.76 (3.26)	46.5 (45.9)	429 (429)	114 (dec.)	52
$Me_2AuSal{=}N{-}C_6H_5$	$C_{15}H_{16}NOAu$	42.21 (42.56)	3.87 (3.81)	3.11 (3.31)	46.8 (46.5)	423 (423)	154 (dec.)	75
$(Me_2Au)_2$Salen	$C_{20}H_{26}N_2O_2Au$	33.18 (33.35)	3.81 (3.64)	3.71 (3.89)	54.5 (54.7)	720 (720)	Dec. at 180–200[a]	70
$(Me_2Au)_2$Salophen	$C_{24}H_{26}N_2O_2Au_2$	37.71 (37.51)	3.43 (3.41)	3.65 (3.65)	51.0 (51.3)	768 (768)	Dec. at 190–200[a]	71

[a] Decomposes without melting.

occurred, as evidenced by the formation of metallic gold. The infrared spectrum of the residue obtained by evaporating the filtered solution indicated that it consisted largely of starting material, no CF vibrations being apparent.

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