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Aurophilic association in *endo*-dicyclopentadienechlorogold(I)

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Abstract

The complex between *endo*-dicyclopentadiene and gold(I) chloride has been prepared by a substitution reaction in dichloromethane, whereby carbon monoxide in dissolved [AuCl(CO)] has been displaced by the *endo*-dicyclopentadiene ligand. This ligand is η^2-bonded to gold(I) via the C=C bond in the norbornene ring. Crystallographic studies show that the [AuCl($C_{10}H_{12}$)] moiety undergoes aurophilic association to form a [{AuCl($C_{10}H_{12}$)}$_2$] dimer, in which the Au–Au distance is 3.4282(8) Å. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Gold(I); Aurophilic; *endo*-Dicyclopentadiene; Infrared spectroscopy; Crystal structure

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1. Introduction

Dimers, chains and clusters are stabilised by the presence of aurophilic interactions between gold centres, which in the case of gold(I) is indicated by Au···Au distances less than 3.6 Å [1–5]. Although a wealth of information exists on such interactions [1–5], including theoretical interpretations of bonding in dimers and clusters and extended arrays [1–3,6–14], little seems to be known about aurophilic contributions to the stabilisation of olefin complexes of gold(I). *endo*-Dicyclopentadienechlorogold(I) was first prepared by Hüttel et al. [15] who, on the basis of infrared and NMR measurements, suggested a linear monomeric structure in which dicyclopentadiene was bonded to gold(I) via the double bond in the norbornene ring, leaving that in the cyclopentene ring uncoordinated [15]. Two linear monomeric (olefin)AuCl molecules (olefin = *cis*-cyclooctene or norbornene) have subsequently been prepared by CO displacement from AuCl(CO) and characterised by means of crystal structure determination [16]. More recently, preferential in-plane η^2 olefin coordination to gold(I) has been demonstrated in a three-coordinated S_2Au(C=C) complex, Au_4(MNT)(dppee)$_2Cl_2$ [MNT = 1,2-dicyanoethene-1,2-dithiolate-*S,S′*; dppee = *cis*-bis(diphenylphosphino)ethylene], which complex is stabilised by aurophilic interactions [17].

It was noted by Hüttel et al. that *endo*-dicyclopentadienechlorogold(I) was among the least labile of the series of (olefin)AuCl molecules prepared and also less labile than the corresponding copper(I) analogues [15]. We have prepared and characterised the two *endo*-dicyclopentadiene complexes of copper(I) chloride, showing these to be structural isomers with distorted cubane Cu_4Cl_4 cores [18]. The existence of these two isomers is attributed to the π-acceptor properties of the ligand, a pure σ donor resulting in a single complex with a regular cubane Cu_4Cl_4 core [19]. The *endo*-dicyclopentadiene complexes of copper(I) chloride are, in their turn, labile, but less so than many other (olefin)CuCl complexes [18]. It was against this background that the preparation and structural characterisation of *endo*-dicyclopentadienechlorogold(I) was undertaken.

2. Experimental

2.1. General

All operations were carried out under argon using standard Schlenk or special low-temperature techniques [20]. Dichloromethane and dicyclopentadiene were

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dried with 4 Å molecular sieves and deoxygenated by means of freeze–pump–thaw cycles. Solid samples of $[AuCl(C_{10}H_{12})]\cdot 0.5C_{10}H_{12}$ were prepared at low temperature for infrared spectroscopy and X-ray diffraction as described in Ref. [20]. Infrared spectra were recorded for the solid and the pure ligand, using CaF_2 mull windows and a Mattson Polaris FT-IR spectrometer with a resolution of 2 cm^{-1}, varying the number of scans from 10 to 100.

2.2. Preparation of $[AuCl(C_{10}H_{12})]\cdot 0.5C_{10}H_{12}$

The compound was prepared according to the method described by Dell'Amico et al. [16]. AuCl(CO) (0.10 g, 0.38 mmol), prepared according to the method of Dell'Amico and Calderazzo [21], was dissolved in 2 ml dichloromethane and 2 ml dicyclopentadiene was added. The solution was concentrated under reduced pressure to the point of saturation and then cooled to 4°C. Colourless plates of $[AuCl(C_{10}H_{12})]\cdot 0.5C_{10}H_{12}$ were deposited from the solution after a few hours. The compound decomposes within a few seconds of exposure to the atmosphere. IR $[AuCl(C_{10}H_{12})]$: ν(C=C): 1612, 1464 cm^{-1}, $\delta(CH_2)$: 1449, 1442 cm^{-1}. $C_{10}H_{12}$: ν(C=C): 1615, 1572 cm^{-1}, $\delta(CH_2)$: 1449, 1439 cm^{-1}. The assignments involve the assumption that there is no coupling between stretching and bending modes.

2.3. X-ray crystallography

Crystal and experimental data are summarised in Table 1. A crystal of $[AuCl(C_{10}H_{12})]\cdot 0.5C_{10}H_{12}$ was mounted under argon in a glass capillary at −155°C [15] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured with a Rigaku AFC6R diffractometer, using graphite-monochromated Mo–K_α ($\lambda = 0.710\ 73$ Å) radiation from a RU200 rotating anode operated at 9 kW (50 kV; 180 mA). Data were measured at −120°C for $5 < 2\theta < 50°$, from a colourless plate-shaped crystal with approximate dimensions $0.40 \times 0.30 \times 0.10$ mm, using the ω–2θ scan mode with an ω scan rate of 16° min^{-1} and a scan width of $(1.15 + 0.30 \tan \theta)°$. Stationary background counts were recorded on each side of a reflection, the ratio of peak counting time to background counting time being 2:1. Weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections were monitored regularly after measurement of 150 reflections and indicated crystal stability in all cases. Cell constants were obtained by least-squares refinement from the setting angles of 25 reflections. Correction was made for Lorentz and polarisation effects; an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption (minimum/maximum transmission factors = 0.69/1.00). Of the 2283 unique reflections measured ($+h$, $\pm k$, $\pm l$), 1870 had $I > 3.0\sigma(I)$ and were considered observed. The structure was solved by direct methods (MITHRIL [22]) and refined using full-matrix least-squares calculations on F, with anisotropic thermal displacement parameters for all the non-hydrogen atoms. Nine of the twelve hydrogen atoms were located from difference maps and included as a fixed contribution.

The $[\{AuCl(C_{10}H_{12})\}_2]$ dimer (see below) co-crystallises with an additional non-coordinated dicyclopentadiene molecule, which is trapped in a cavity whose symmetry is $\bar{1}$; this non-coordinated dicyclopentadiene molecule is therefore disordered of necessity. It was, however, possible to model the disorder by assuming C(11), C(12) and C(13) to be alternately the three carbons associated with the disordered C=C in the cyclopentene ring and the three bridgehead carbon atoms of the norbornene ring. These atoms were refined with full occupancy, whereas the remaining carbon atoms, C(14)–C(17), were refined with half occupancy. Further details are given in the supplementary material. No hydrogen atoms associated with this disordered dicyclopentadiene molecule were included in the refinement.

Final R for 172 parameters and 1870 observed [$I > 3.0\sigma(I)$] reflections: 0.034 ($R_w = 0.042$); maximum and minimum residual electron density: 1.60; −3.13 e $Å^{-3}$. All calculations on were carried out with the TEXSAN program package [23]. Atomic scattering factors and anomalous dispersion correction factors were taken from Ref. [24]. Structural illustrations have been drawn with ORTEP [25]. Selected interatomic distances and angles are given in Table 2.

Table 1
Crystallographic data for $[AuCl(C_{10}H_{12})]\cdot 0.5C_{10}H_{12}$

Formula	$C_{15}H_{18}AuCl$
M_r	430.7
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a (Å)	6.643(1)
b (Å)	14.988(2)
c (Å)	6.6289(8)
α (°)	93.77(1)
β (°)	97.14(1)
γ (°)	93.05(2)
V ($Å^3$)	652.2(2)
Z	2
$D_{calc.}$ (g cm^{-3})	2.19
μ (Mo–K_α) (cm^{-1})	115.0
T (°C) (data collection)	−120
No. unique data	2283
No. with $I > 3.0\sigma(I)$	1870
No. parameters refined	172
R [a]	0.034
R_w [a]	0.042

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2}$.

Table 2
Distances (Å) and angles (°) for $[\{AuCl(C_{10}H_{12})\}_2]$ in $[AuCl(C_{10}H_{12})]\cdot0.5C_{10}H_{12}$ [a]

Au–C(1)	2.20(1)	Au···Au^i	3.4282(8)
Au–C(2)	2.16(1)	Au–Cl	2.276(3)
Au–X	2.07	Au···Cl^i	3.744(3)
C(1)–C(2)	1.38(1)	C(5)–C(6)	1.57(1)
C(2)–C(3)	1.52(1)	C(6)–C(7)	1.55(1)
C(3)–C(4)	1.55(1)	C(7)–C(8)	1.53(1)
C(4)–C(5)	1.54(1)	C(8)–C(9)	1.46(2)
C(1)–C(5)	1.52(1)	C(9)–C(10)	1.39(2)
C(3)–C(7)	1.57(1)	C(10)–C(6)	1.51(1)
Cl–Au–C(1)	160.9(3)	C(1)–C(5)–C(6)	103.9(7)
Cl–Au–C(2)	162.1(3)	C(5)–C(6)–C(10)	117.2(9)
Cl–Au–X	178.7	C(5)–C(6)–C(7)	103.5(8)
C(2)–C(1)–C(5)	108.0(9)	C(7)–C(6)–C(10)	106.1(8)
C(1)–C(2)–C(3)	106.5(8)	C(3)–C(7)–C(8)	117.3(8)
C(2)–C(3)–C(4)	100.8(8)	C(3)–C(7)–C(6)	103.6(8)
C(2)–C(3)–C(7)	106.0(7)	C(6)–C(7)–C(8)	105.5(8)
C(4)–C(3)–C(7)	98.5(8)	C(7)–C(8)–C(9)	106.5(9)
C(3)–C(4)–C(5)	95.5(7)	C(8)–C(9)–C(10)	113.0(9)
C(4)–C(5)–C(1)	101.1(8)	C(6)–C(10)–C(9)	109(1)
C(4)–C(5)–C(6)	98.8(8)		

[a] Symmetry code: (i): $-x$, $-y$, $-z$. X is the midpoint of the C(1)–C(2) olefin bond.

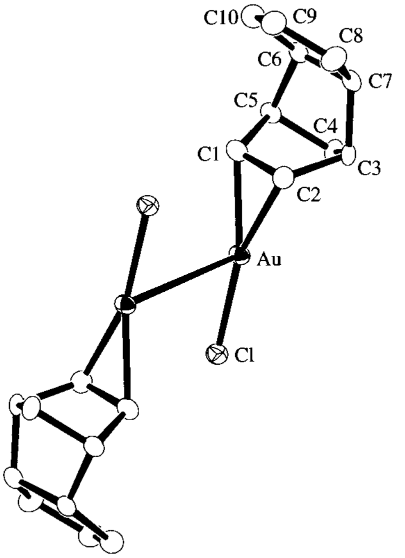

Fig. 1. View of the $[\{AuCl(C_{10}H_{12})\}_2]$ dimer showing the crystallographic numbering. The Au···Au distance is 3.4282(8) Å and the midpoint of this bond is at a centre of inversion (see Table 2). Thermal ellipsoids enclose 45% probability.

3. Results and discussion

$[AuCl(C_{10}H_{12})]$ was first prepared by Hüttel et al., but by a different route [15]. The present compound has been prepared by a substitution reaction in dichloromethane solution, whereby carbon monoxide in AuCl(CO) has been displaced by dicyclopentadiene. Our spectroscopic data is, however, in good agreement with that reported previously [15], indicating that the two complexes are identical. The solid compound prepared here differs, however, from that reported previously [15] in that each $[\{AuCl(C_{10}H_{12})\}_2]$ dimer co-crystallises with an additional molecule of dicyclopentadiene which is incorporated in a cavity in the structure.

The $[\{AuCl(C_{10}H_{12})\}_2]$ dimer is depicted in Fig. 1, which also shows the crystallographic numbering. As is seen from this figure, the *endo*-dicyclopentadiene ligand bonds to gold(I) solely through the norbornene C=C double bound. This is as was predicted by Hüttel et al. [15], and also similar to the situation for the complexes between *endo*-dicyclopentadiene and copper(I) chloride [18]. *endo*-Dicyclopentadiene acts as a tetrahapto ligand in a number of transition-metal complexes [26], but copper(I) and gold(I) are exceptions in this respect. The Cl–Au–X linkage, where X is the midpoint of the C(1)–C(2) bond is approximately linear. The lowering of the stretching frequency of C=C on coordination by 107 cm^{-1} is in good agreement with the values found for the copper(I) analogues [18]. Although lengthening of the C(1)–C(2) bond cannot be ascertained crystallographically, there is a trend in this direction. All other bond distances and angles are normal and, as is usual [18], the C=C bond of the cyclopentene ring is disordered between C(8)–C(9) and C(9)–C(10).

Perhaps the most interesting and novel feature of the structure is the dimeric aurophilic association perpendicular to the $[AuCl(C_{10}H_{12})]$ moiety, as illustrated in Fig. 1. Comparable aurophilic interaction (Au···Au = 3.4282(8) Å, see Table 2) does not seem to occur in the (cyclooctene)AuCl complex where the shortest Au···Au distance is 3.758(1) Å [16]. No detailed structural information is available for the (norbornene)AuCl analogue [16]. That the aurophilic association in $[\{AuCl(C_{10}H_{12})\}_2]$ leads to the formation of a discrete dimer and not a chain is without doubt, since other Au···Au distances are appreciably longer (of the order of 4.5 and 5.5 Å). The $[\{AuCl(C_{10}H_{12})\}_2]$ dimer is very similar to that found for $[\{2,4,6\text{-}({}^tBu)_3C_6H_2PH_2\}AuCl]$ in which there is also head-to-tail pairing with the centre of the line connecting the gold atoms (Au···Au = 3.440(1) Å) at a centre of inversion [27]. In connection with this latter structure it was noted that in gold(I) complexes structure-determining intermolecular interactions are metal to metal, whereas metal to halide interactions are the prevalent such determinators in analogous complexes containing the lighter coinage metals [27]. Indeed, the tetrameric $[Cu_4Cl_4(C_{10}H_{12})_4]$ complexes contain distorted Cu_4Cl_4 cores and are thus chloride-bridged, but with no bonding Cu···Cu interactions [18,19]. In the present structure the shortest non-bonded Au···Cl distance is to an adjacent $[\{AuCl(C_{10}H_{12})\}_2]$ dimer, viz. Au···Cl ($-x$, $-y$, $-z-1$) = 3.570(3) Å. The non bonded Au···Cl distance within the dimer is 3.744(3) Å. Recently, a unique dimeric chloride-bridged gold(I) alkyne with a strong $\text{Au–}\eta^2(\text{C}+\text{C})$ interaction has, however, been reported [28]. There would not seem to be an appreciable aurophilic interaction between the gold(I) centres in this chloride-bridged compound ($\text{Au}\cdots\text{Au} = 3.666(1)$ Å) [28].

Apart from $[\{2,4,6\text{-}(^t\text{Bu})_3\text{C}_6\text{H}_2\text{PH}_2\}\text{AuCl}]$ [27] and the present compound, dimeric aurophilic association often seems to lead to the formation of 'crossed torch' pairs (see for example Refs. [5,13,29,30]) in which the linear moieties are inclined to one another instead of being parallel. Such dimers appear to be associated with shorter $\text{Au}\cdots\text{Au}$ distances than is the case in $[\{2,4,6\text{-}(^t\text{Bu})_3\text{C}_6\text{H}_2\text{PH}_2\}\text{AuCl}]$ [27] and $[\text{AuCl}(\text{C}_{10}\text{H}_{12})]$. For a series of $[(\text{XAuPH}_3)_2]$ dimers with such C_2 symmetry, the strength of the aurophilic interaction has been shown to increase with increasing softness of the ligand X, reaching 25 kJ mol^{-1} for the softest ligand, –SCH_3 [10].

Comparison with respect to lability between $[\{\text{AuCl}(\text{C}_{10}\text{H}_{12})\}_2]$ and its copper(I) analogues: $[\text{Cu}_4\text{Cl}_4(\text{C}_{10}\text{H}_{12})_4]$ [18] is difficult since decomposition of (olefin)CuCl complexes is usually via loss of olefin, whereas in the case of the gold(I) complexes oxidation may be an important factor. Of the (olefin)CuCl complexes which we have studied, e.g. Refs. [18,19,31,32], the two $[\text{Cu}_4\text{Cl}_4(\text{C}_{10}\text{H}_{12})_4]$ compounds are among the least labile, a property which has been attributed to the unfavourable pyramidal coordination geometry which would result from loss of olefin [18]. This mechanism was first proposed to account for the resistance of $[\{\text{Cu(CO)}(\text{O}^t\text{Bu})\}_4]$ to decarbonylation [33].

Comparison as to lability in the series of known (olefin)AuCl compounds is, however, more feasible: Of those compounds between olefins and gold(I) chloride prepared by Hüttel et al., $[\text{AuCl}(\text{C}_{10}\text{H}_{12})]$ was said to be among the least labile [15], an observation which can now be better understood in terms of the demonstrated dimeric aurophilic association leading to the formation of $[\{\text{AuCl}(\text{C}_{10}\text{H}_{12})\}_2]$.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 139273. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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