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The coordination and polymerisation of cyclic 1,3-dienes by gold(I) cations†

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Cyclopentadiene and 1,3-cyclohexadiene are readily polymerised by [LAu][X]. With specific ancillary ligands polymerisation was suppressed and a molecular species involving an Au(I) cation η^2-bonding CpH was isolated and whose structure was probed in both the solid state and in solution.

The exponential growth of gold chemistry in the past decade has been exemplified by the myriad of cyclisation reactions using alkynes and allenes as the reactive substrate;[1] however, the extension of Au(I) catalysis to activate alkenes and dienes has been comparatively limited, possibly due to their propensity for side reactions.[2]

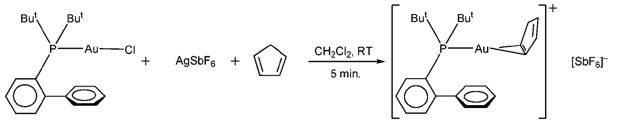
Recent work has sought to probe the coordination behaviour of cationic gold(I) complexes of the type $[\text{LAu}]^+$ (L = phosphine, NHC) with alkynes,[3] allenes,[4] alkenes[5] and acyclic 1,3-dienes[6] by careful reactions and detailed characterisation of isolated complexes. One notable omission from this list is the cyclic dienes[6b] which have a proven record as a useful class of substrate in gold catalysis. For example, cyclic dienes in general and conjugated cyclic dienes in particular have been used as substrates in Au(I) catalysed intramolecular hydroammination of 1,3-dienes to form hexahydroindoles and octahydrocyclohepta pyrroles,[7] cyclisation of unactivated 6,8-diene-1-ynes to form carbotetracycles,[8] annulations of phenols with dienes[9] and addition of active methylenes to dienes to form functionalised carbocycles.[10] Despite their utility as synthons for many Au(I) catalysed transformations, experimental evidence regarding their coordination chemistry is lacking.[6b] Herein we seek to address this issue.

As a preliminary investigation we chose to react cyclopentadiene (CpH, 1.5 equiv.) with a gold cation generated from the slurry of $[\text{P(Bu}^t)_2(o\text{-biphenyl})\text{AuCl}]/\text{AgSbF}_6$ (1 equiv.) in CH_2Cl_2 at room temperature (Scheme 1). The reaction was complete within 5 min. (as monitored by ^{31}P NMR) and immediate dilution of the reaction and filtration of the precipitate (presumably AgCl) was necessary to avoid the formation of additional unidentified products (by both ^{31}P and ^{1}H NMR). The solid was redissolved in a minimum amount of CH_2Cl_2 and layered with *n*-hexane which yielded colourless crystals of **1** (Fig. 1) which contained the desired $[(\eta^2\text{-CpH})\text{Au(P(Bu}^t)_2(o\text{-biphenyl}))]^+$ cation.‡

In the solid state, Au binds asymmetrically across one of the double bonds of CpH in a η^2 fashion (~4% slippage towards –CH_2 end). The coordinated C=C bond (1.358(5) Å) is elongated compared to the uncoordinated bond (1.332(6) Å). M···C interactions with the *o*-biphenyl unit of a M–P(Bu^t)$_2$(*o*-biphenyl) unit are well documented; for gold(I), an Au···C distance of < 2.95 Å was suggested as representing a significant interaction.[11] In **1**, the shortest Au···C contact is 3.05 Å and the P1–Au1–(C=C$_{\text{centroid}}$) angle (172.6°) deviates only slightly from linear, suggesting minimal interaction with the *o*-biphenyl unit. In contrast to the solid-state structure, the room temperature ^{1}H NMR of **1** showed only two resonances for the alkene protons (δ = 6.41 and 6.58 ppm) suggesting a fluxional process may be operating. Upon cooling, one of the peaks (6.41 ppm) broadened and began to de-coalesce into two peaks, whereas the other peak (6.58 ppm) did not de-coalesce even at −90 °C but did become broader (see ESI†). These observations are consistent with our recently proposed gliding mechanism for a $[\text{LAu}]^+$ cation over an acyclic 1,3-diene backbone.[6a]

To the best of our knowledge there are no reported examples of mononuclear metal η^2-CpH complexes (although there are a few reports with Cp derivatives[12]). The "mainstream" transition metals commonly form η^4 complexes with CpH; in addition, dinuclear bis-η^2 complexes have been observed where separate metal centres coordinate the two double bonds.[13]

In continuing our investigation, we sought to probe the role of the phosphine ligand coordinated to the gold centre. Thus we treated an excess of CpH with a mixture of $\text{Bu}^t_3\text{PAuCl}/\text{AgSbF}_6$ in CH_2Cl_2. After 16 h at room temperature, ^{1}H NMR spectroscopy showed polycyclopentadiene (*vide infra*) as the



Scheme 1 Synthesis of cyclopentadiene complex **1**.

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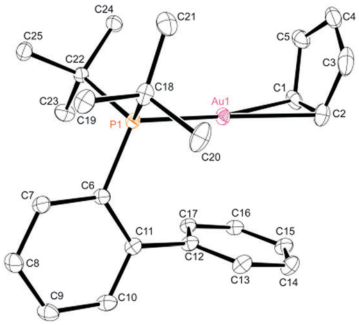


Fig. 1 Thermal ellipsoid plot of the cation of **1** shown at 50% probability level; all hydrogen atoms and the $[SbF_6]$ counter anion are omitted for clarity. Selected bond lengths (Å) and angles (°): Au1–C1 2.279(3), Au1–C2 2.311(3), Au1–P1 2.2908(6), C1–C2 1.358(5), C3–C4 1.332(6), C2–C3 1.469(5), C1–C5 1.495(4), C4–C5 1.494(5); P1–Au1–C1 167.15(9), P1–Au1–C2 156.90(9), C1–Au1–C2 34.40(12).

major product and a crystalline material, **2**, containing the $[(\eta^2\text{-}(CpH)_2)Au(PBu^t{}_3)]^+$ cation as a minor product. A rational synthesis of **2** was achieved by the direct reaction of dicyclopentadiene with a stoichiometric amount of $Bu^t{}_3PAuCl/AgSbF_6$. The structure of **2** (Fig. 2) was confirmed by X-ray crystallography showing the Au(I) cation binding to one of the C=C bonds in an *endo* fashion.

With regards to the formation of **2** it was unclear if the dimerisation of CpH was induced by metal complexation or whether complexation followed (4 + 2) dimerisation. However, the observation of oligomerisation was of special interest and we sought to study the reaction in greater detail. Thus we treated CpH with a catalytic amount of $Ph_3PAuCl/AgSbF_6$ (2 mol%) in CH_2Cl_2 at room temperature which after only 15 min. led exclusively (^1H NMR) to polycyclopentadiene formed *via* competing 1,2 and 1,4-addition reactions (Scheme 2).[14] To our knowledge, there is only a single report of a gold-catalysed olefin polymerisation, that of the Au(III)-mediated polymerisation of styrene.[15] Thus the current report contains the first examples of olefin polymerisation using a gold(I) precatalyst. In addition, the substrates employed produce hydrocarbon polymer products which are of great technological interest as new materials with high glass-transition temperature and low dielectric constant.[14,16]

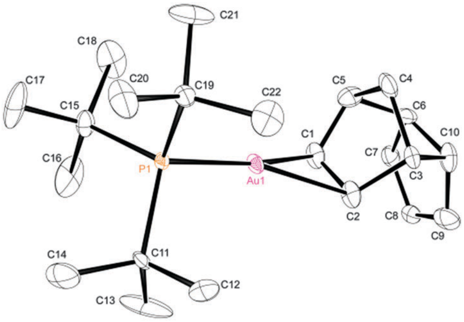
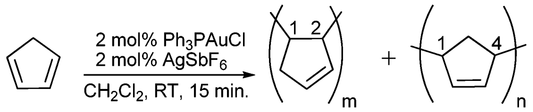


Fig. 2 Thermal ellipsoid plot of the cation of **2** shown at 50% probability level; all hydrogen atoms and $[SbF_6]^-$ anion are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Au1–C1 2.278(7), Au1–C2 2.301(7), C1–C2 1.351(11), C8–C9 1.394(11), Au1–P1 2.2964(16), C1–Au1–C2 34.3(3), P1–Au1–C1 164.5(2), P1–Au1–C2 160.2(2).



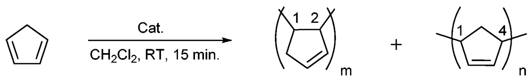
Scheme 2 Synthesis of polycyclopentadiene.

The reaction was optimised for high substrate conversion by screening potential Au(I) salts, Ag(I) salts and solvents (Table 1). As is evident from Table 1, the polymerisation reaction was sensitive to the nature of the ancillary ligand on Au(I), the counter ion and the solvent. Near quantitative conversion of CpH was observed when more Lewis acidic $[LAu]^+$ cations with the $[SbF_6]^-$ counter anion were employed as the precatalyst (entries 3 and 4). The reaction failed to occur upon employing strongly electron donating phosphines as ancillary ligands (entries 5 and 6). The $Ph_3PAuCl/AgSbF_6$ combination was found to give the highest conversion to the polymers. Control experiments using either the Au(I) or Ag(I) source alone gave no conversion.

The reaction either becomes very slow (entry 13) or shuts down (entry 11) when coordinating solvents were used. Very low conversion of CpH was observed with toluene as a solvent presumably due to both the Au(I) and Ag(I) sources being insoluble in this solvent, which in turn makes it difficult to generate the proposed active catalyst system $[R_3PAu]^+[SbF_6]^-$. CH_2Cl_2 proved to be the best solvent for the reaction.

Analysis of the polymer (Table 2) showed that a high molecular weight polymer with reasonably good molecular weight distribution (PDI) was obtained when a bulky biaryldialkylphosphine gold(I) source was employed as the catalyst (entry 5). A pronounced change in polymer chain length was observed upon changing the counter ion (entry 1). The polymer chain length decreased with increase in catalyst loadings (entries 2–4). The isolated polymer showed a glass transition temperature T_g of 68 °C (M_n = 26.8 kDa), which is consistent with literature value (Fig. 3).[14b]

Table 1 Au(I)-catalysed CpH polymerisation[a]



Entry	Au(I)	Ag(I)	Solvent	% conversion[b]
1	Ph_3PAuCl		CH_2Cl_2	0
2		$AgSbF_6$		0
3	Ph_3PAuCl	$AgSbF_6$	CH_2Cl_2	>95
4	Me_2SAuCl	$AgSbF_6$	CH_2Cl_2	>95
5	Cy_3PAuCl	$AgSbF_6$	CH_2Cl_2	0
6	$Bu^t{}_3PAuCl$	$AgSbF_6$	CH_2Cl_2	0
7	Ph_3PAuCl	AgOTf	CH_2Cl_2	86
8	Ph_3PAuCl	$AgBF_4$	CH_2Cl_2	10[c]
9	Ph_3PAuCl	Ag_2O	CH_2Cl_2	0
10	$(MeO)_3PAuCl$	$AgSbF_6$	CH_2Cl_2	0
11	Ph_3PAuCl	$AgSbF_6$	THF	0
12	Ph_3PAuCl	$AgSbF_6$	Toluene	5
13	Ph_3PAuCl	$AgSbF_6$	$MeNO_2$	5
14	$(P(Bu^t)_2(o\text{-biphenyl}))AuCl$	$AgSbF_6$	CH_2Cl_2	11

[a] CpH (1.2 mmol) was added to a CH_2Cl_2 (2 mL) solution of 2 mol% Au(I)/Ag(I) and stirred for 15 min. in the absence of light at room temp. [b] Determined by ^1H NMR spectroscopy. [c] The kinetics of this reaction were slow. After 2 h, conversion was >95%.

Table 2 Molecular weight distribution of the polycyclopentadiene[a]

Entry	Precatalyst	PDI	M_n (kDa)
1	2 mol% $Ph_3PAuCl/AgOTf$	3.42	2.1
2	2 mol% $Ph_3PAuCl/AgSbF_6$	4.00	28.9
3	5 mol% $Ph_3PAuCl/AgSbF_6$	2.89	26.8
4	10 mol% $Ph_3PAuCl/AgSbF_6$	3.74	17.6
5	5 mol% $(P(Bu^t)_2(o\text{-biphenyl}))AuCl/AgSbF_6$	2.03	71.4

[a] CpH (1.2 mmol) was added to a CH_2Cl_2 (2 mL) solution of catalyst and stirred for 15 min. in the absence of light at room temp.

To further assess the scope of Au(I) catalysed polymerisation, 1,3-cyclohexadiene was treated with 5 mol% of $Ph_3PAuCl/AgSbF_6$ in CH_2Cl_2. After 2 h, 1,3-cyclohexadiene had polymerised to yield (^1H NMR) polycyclohexadiene quantitatively with a combination of both 1,2 and 1,4-addition (Scheme 3).[17]

The polycyclohexadiene from these reactions had a relatively narrow molecular weight distribution (PDI 1.41) and moderate size with M_n of 5.2 kDa. A glass transition temperature of 125 °C was recorded, in agreement with that in the literature.[17a,e]

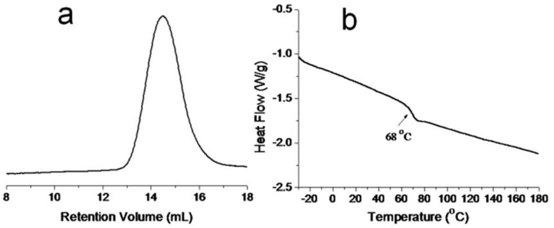
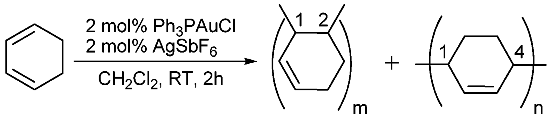


Fig. 3 (a) GPC curve (RI response, THF as eluent) of the polymer obtained with 5 mol% $(P(Bu^t)_2(o\text{-biphenyl}))AuCl/AgSbF_6$ catalyst system (b) DSC scan for a polycyclopentadiene at a scan rate of 10 °C min^{-1}.



Scheme 3 Polymerisation of 1,3-cyclohexadiene.

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Notes and references

‡ Single crystals of complexes **1** and **2** suitable for X-ray diffraction were grown from saturated CH_2Cl_2 solutions layered with *n*-hexane (**1**) or Et_2O (**2**) followed by storage at 4 °C (**1**) and −18 °C (**2**) for 48 h. Crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. Structures were solved using SHELXS and refined using SHELXL.[18]

Crystal data for 1: $C_{25}H_{33}AuF_6PSb$, M = 797.21, monoclinic, a = 9.6951(2) Å, b = 20.5032(4) Å, c = 13.9332(3) Å, β = 104.6250(10)°, V = 2679.91(10) Å^3, T = 100 K, space group $P2_1/c$, Z = 4, μ(Mo-Kα) = 6.589 mm^{-1}, 46 190 reflections measured, 6223 independent reflections (R_{int} = 0.0224). The final $R1$ [$I > 2\sigma(I)$] was 0.0188 and the final $wR(F_2)$ was 0.0491 (all data). The goodness of fit on F^2 was 1.021. CCDC 847 613.

Crystal data for 2: $C_{22}H_{39}AuPF_6Sb$, M = 767.22, monoclinic, a = 8.4126(11) Å, b = 13.2481(19) Å, c = 12.0197(15) Å, β = 103.296 (8)°, V = 1303.7(3) Å^3, T = 100 K, space group $P2_1$, Z = 2, μ(Mo-Kα) = 6.768 mm^{-1}, 14 619 reflections measured, 5644 independent reflections (R_{int} = 0.0378). The final $R1$ [$I > 2\sigma(I)$] was 0.0321 and the final $wR(F_2)$ was 0.0470 (all data). The final R_1 value was 0.0321 ($I > 2\sigma(I)$). The final $wR(F^2)$ value was 0.0666 ($I > 2\sigma(I)$). The goodness of fit on F^2 was 0.945. CCDC 847 614.

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