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The coordination and polymerisation of cyclic dienes by gold(I) cations

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Experimental

Equipment and Materials.

All reactions were performed under an atmosphere of nitrogen or argon using standard Schlenk or glove box techniques; solvents were dried using an Anhydrous Engineering Grubbs-type system (alumina columns). Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. Gold complexes $AuCl(P(Bu^t)_2$(*o*-biphenyl)), Bu^t_3PAuCl, Ph_3PAuCl, $(MeO)_3PAuCl$, Cy_3PAuCl and Me_2SAuCl were prepared according to literature procedures.[S1]

^{1}H NMR, and ^{13}C NMR spectra were obtained with Varian 400 and 500 spectrometers. ^{1}H and ^{13}C chemical shifts (δ) were reported in parts per million (ppm). ^{1}H resonances were referenced internally to residual protonated solvent resonances and ^{13}C resonances were referenced internally to deuterated solvent resonances. Assignments of ^{1}H and ^{13}C chemical shifts were based on HMBC, HSQC 2D NMR spectroscopy. ^{31}P NMR spectra were obtained with Jeol Eclipse 300MHz multinuclear spectrometer. ^{31}P resonances were referenced externally to H_3PO_4. Melting points were measured using Stuart SMP3 melting point apparatus in open capillaries. Elemental analyses were performed using a Eurovector EA3000 CHN Analyzer. Gel Permeation Chromatography was carried out using a Viscotek VE 2001 Triple Detector Gel Permeation Chromatograph, equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven (30 °C). The elution columns consist of styrene divinyl benzene gel with pore sizes of 500 Å and 100,000 Å. Detection was conducted by mean of a VE 3580 refractometer, a four capillary differential viscometer, and a 90° and low angle (7°) laser light ($\lambda_0 = 670$ nm) scattering detector, VE 3210 and VE 270. A

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0.025 % butylated hydroxytoluene stabilized THF (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min. Samples were dissolved in the eluent (2 mg/mL) and filtered (Acrodisc, PTFE membrane, 0.45 μm) before analysis. The calibrations were made from a polystyrene standard from Viscotek (triple-detection) and from polystyrene standards from Aldrich (conventional calibration). This equipment allows the exact measure of homopolymers molecular weights and polydispersity indexes (PDIs) using triple-detection calibration, or molecular weights relative to polystyrene for block copolymers using conventional calibration. Differential Scanning Calorimetry (DSC) analyses were performed on a Q100 from TA instruments coupled to a refrigerated cooling system (RCS90). The samples, placed in nonhermetic aluminium pans, were tared using a XT220A Precisa microbalance.

X-ray Crystallography

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.

Single-crystal X-ray structural studies of **1** and **2** were performed using a Bruker-AXS SMART APEX three circle diffractometer equipped with an Oxford Instruments low-temperature attachment. Data were collected at 100(2) K using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software package,[S2] and the data were corrected for absorption using the SADABS program.[S3]

Synthesis of $[(\eta^2\text{-CpH})Au(P(Bu^t)_2(o\text{-biphenyl})]^+[SbF_6]^-$ (1)

To a solution of $[AuCl(P(Bu^t)_2(o\text{-biphenyl}))]$ (0.053 g, 0.10 mmol) and $AgSbF_6$ (0.034 g, 0.10 mmol) in dichloromethane (2 mL) was added cyclopentadiene (0.01 g, 0.15 mmol). The solution was stirred for 5 min. in the absence of light and then filtered through Celite, and washed with dichloromethane (3 × 3 mL). The resulting solution was then dried *in vacuo* to yield a white solid. The white solid was redissolved in dichloromethane (~1 mL) and layered with *n*-hexane. After storage at 4 °C for 48 h, 0.04 g (50%) of **1** was obtained as analytically pure crystalline material.

^{1}H NMR (400 MHz, 22 °C, CD_2Cl_2) δ 1.31 (d, *J* = 17 Hz, 18H), 3.22 (d, *J* = 26 Hz, 1H), 3.33 (d, J = 26 Hz, 1H), 6.41 (m, 2H), 6.58 (m, 2H), 7.20-7.35 (m, 3H), 7.57-7.72 (m, 5H), 7.81-

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7.94(m, 1H) ppm; $^{13}C\{^1H\}$NMR (100 MHz, 22 °C, CD_2Cl_2) δ 31.05 (d, $^2J_{CP}$=7), 38.40 (d, $^1J_{CP}$=23Hz), 46.30 (s), 132.28 (HC=**C**H–CH_2), 133.93 (=**C**H), 128.49, 129.99, 130.54, 130.89, 143.75 (*o*-biphenyl) ppm; $^{31}P\{^1H\}$NMR (162 MHz, 22 °C, CD_2Cl_2) δ 66.02 ppm. Elemental Analysis: Found: C 38.01%, H 4.27%.; Calculated C 37.66 %, H 4.17%.

Melting Point: Decomposes to black solid at 188 °C.

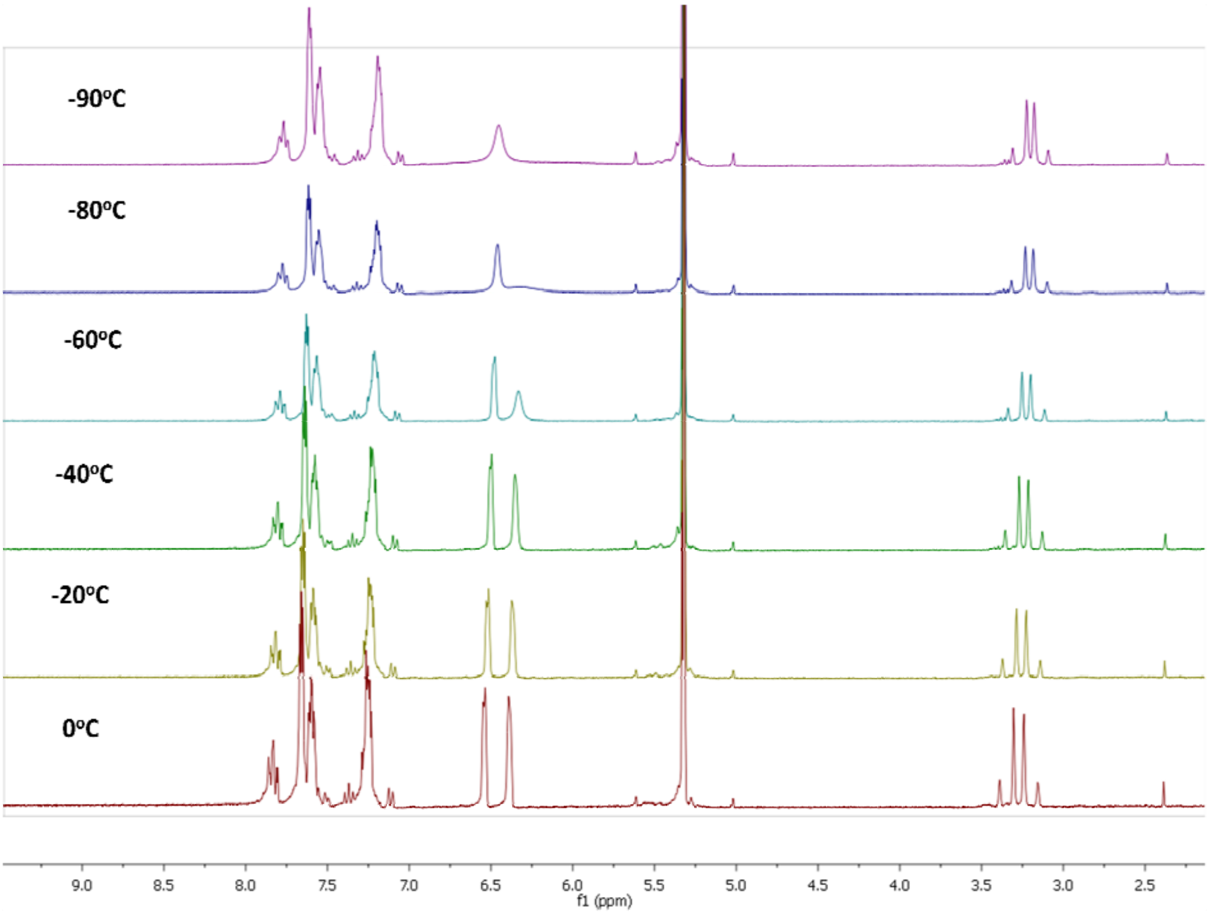

Figure S1. Variable temperature ^1H NMR (300 MHz, CD_2Cl_2) of **1**.[a]

[a] 15 mg of **1** dissolved in 0.7 mL of CD_2Cl_2

Synthesis of $[(\eta^2\text{-}(CpH)_2)Au(P(Bu^t)_2(o\text{-biphenyl}))]^+ [SbF_6]^-$ (2)

To a solution of $[AuCl(PBu^t_3)]$ (0.043 g, 0.10 mmol) and $AgSbF_6$ (0.034 g, 0.10 mmol) in dichloromethane (3 mL) was added dicyclopentadiene (0.05g, 0.40 mmol). The solution was stirred for 16 h in the absence of light and then filtered through Celite, washing with dichloromethane (3 × 3 mL). The resulting solution was then evaporated to dryness *in vacuo* to get a white solid. The solid was redissolved in dichloromethane (~1 cm^3) and layered with diethyl ether. After storage for 16 h at -18 °C, **2** was isolated and dried *in vacuo* to get 0.035 g (40%) of a white microcrystalline solid.

^{1}H NMR (400 MHz, 22 °C, $CDCl_3$) δ 1.24-1.33 (m, 1H), 1.54 (d, *J*=14Hz, 27H), 1.60-1.73 (m, 1H), 1.83-2.04 (m, 1H), 2.17-2.33(m, 1H), 2.97 (br.s, 1H), 3.41-3.69 (m, 3H), 5.57 (br.s, 2H), 6.55 (br.s, 1H), 6.74 (br.s, 1H) ppm; $^{13}C\{^1H\}$ (125 MHz, 22 °C, $CDCl_3$) δ 32.34 (d, *J*=4 Hz), 33.37, 40.59 (d, *J*=18.00 Hz), 41.70, 46.94, 48.10, 49.01, 55.27, 129.75, 131.75,133.25,136.33 ppm; $^{31}P\{^1H\}$NMR (162 MHz, 22 °C, $CDCl_3$) δ 97.96 ppm.

Elemental analysis: Found C 34.71 % H 5.10 %; Calculated C 34.44 % H 5.12 %.

Melting Point: Decomposes to a grey/black solid above 120 °C.

Synthesis of polycyclopentadiene

The polymerisation of cyclopentadiene has been accomplished using different catalyst loadings. A representative synthesis of polycyclopentadiene is as follows: To a stirred solution of 2 mol% $Ph_3PAuCl/AgSbF_6$ in CH_2Cl_2 (1 mL) was added cyclopentadiene (0.08 g, 1.2 mmol) dropwise. The solution was stirred for 15 min. in the absence of light. The reaction was quenched by adding triethylamine (0.1 mL). Volatiles were removed *in vacuo*, resulting in a solid which was redissolved in CH_2Cl_2 (10 mL), filtered through small amount of Celite and washed with CH_2Cl_2 (4 × 3 mL). The resulting solution was evaporated to dryness *in vacuo*, washed with dry methanol (10 × 3 mL) and *n*-hexane (5 × 3 mL) and dried *in vacuo* to obtain a white solid (0.051 g, 64%).

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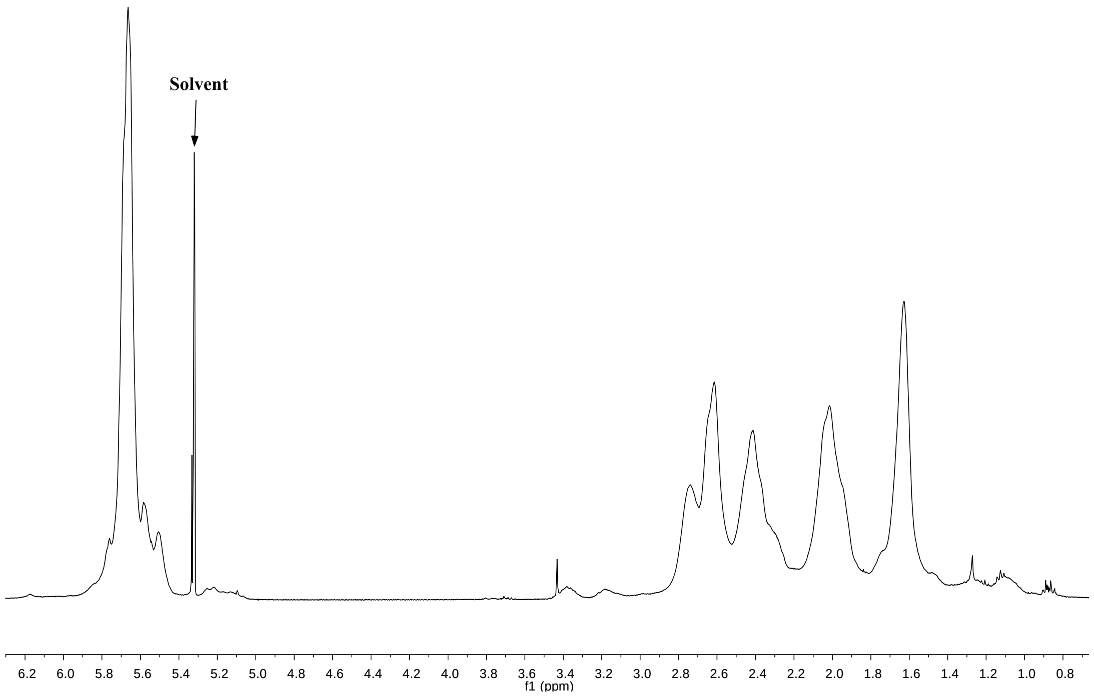

Figure 2. ^{1}H NMR (400 MHz, 22°C, CD_2Cl_2) spectra of polycyclopentadiene.

Synthesis of polycyclohexadiene

To a stirred solution 2 mol% $Ph_3PAuCl/AgSbF_6$ in CH_2Cl_2 (1 mL) was added the 1,3-cyclohexadiene (0.096g, 1.2 mmol) dropwise. The solution was stirred for 2 h in the absence of light. The reaction was quenched by adding triethylamine (0.1 mL). Volatiles were removed *in vacuo*, resulting in a solid which was redissolved in CH_2Cl_2 (10 mL), filtered through small amount of Celite and with CH_2Cl_2 (4 × 3 mL). The resulting solution was evaporated to dryness *in vacuo*. The solid was washed with dry methanol (10 × 3 mL), then with *n*-hexane (5 × 3 mL) and dried *in vacuo* to give an off-white solid (0.054 g, 56%).

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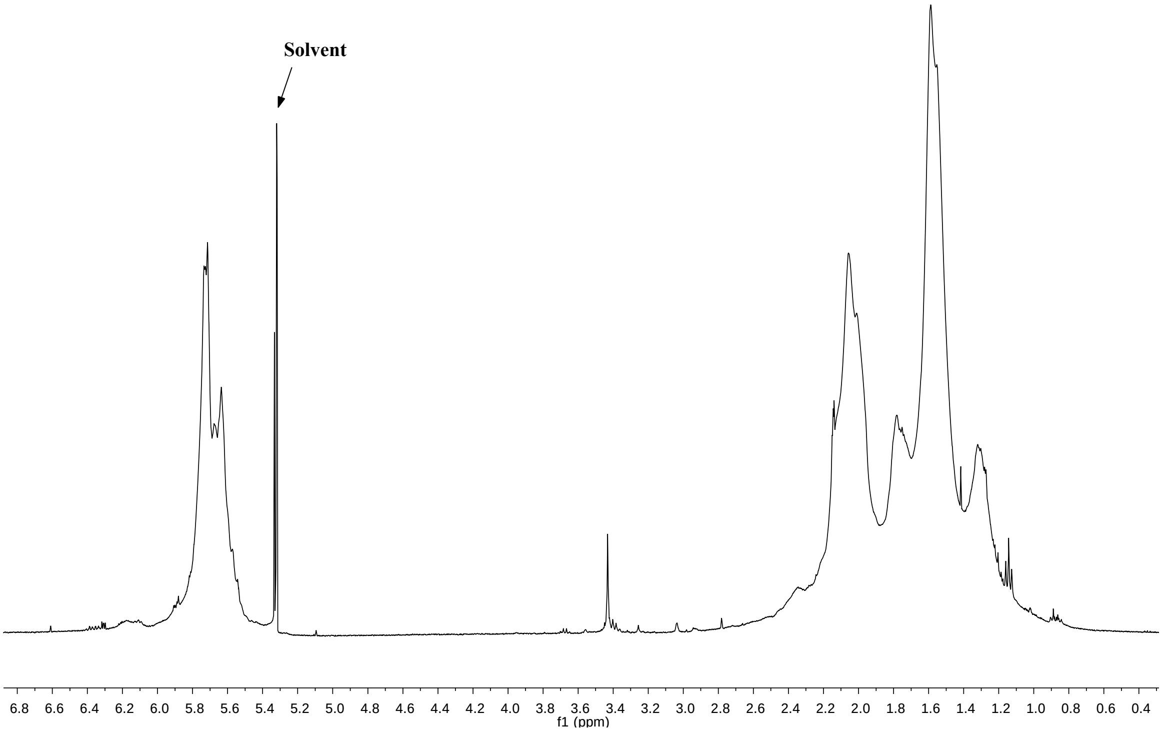

Figure 3. ^{1}H NMR (400 MHz, 22 °C, CD_2Cl_2) spectra of polycyclohexadiene.

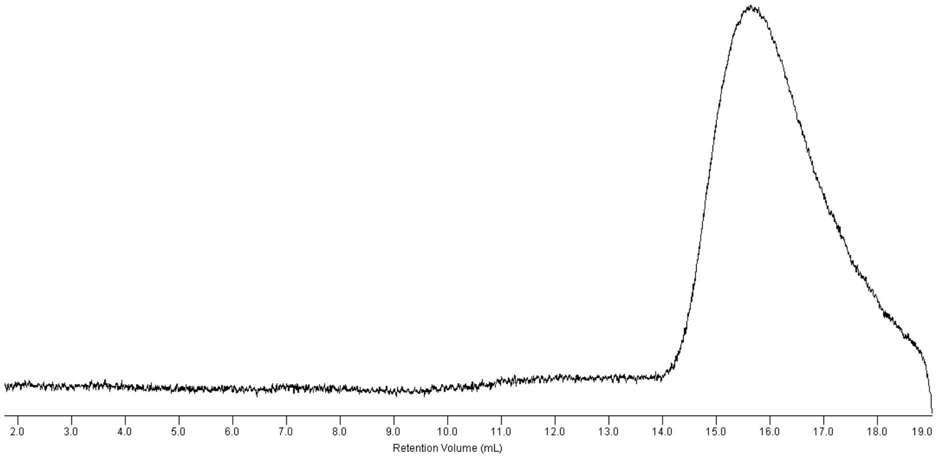

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Figure 4. GPC curve (RI response, THF as eluent) of the polycyclohexadiene polymer obtained with 5% PPh_3AuCl/5% $AgSbF_6$ catalyst system (M_n = 5.2 kDa, PDI = 1.41).

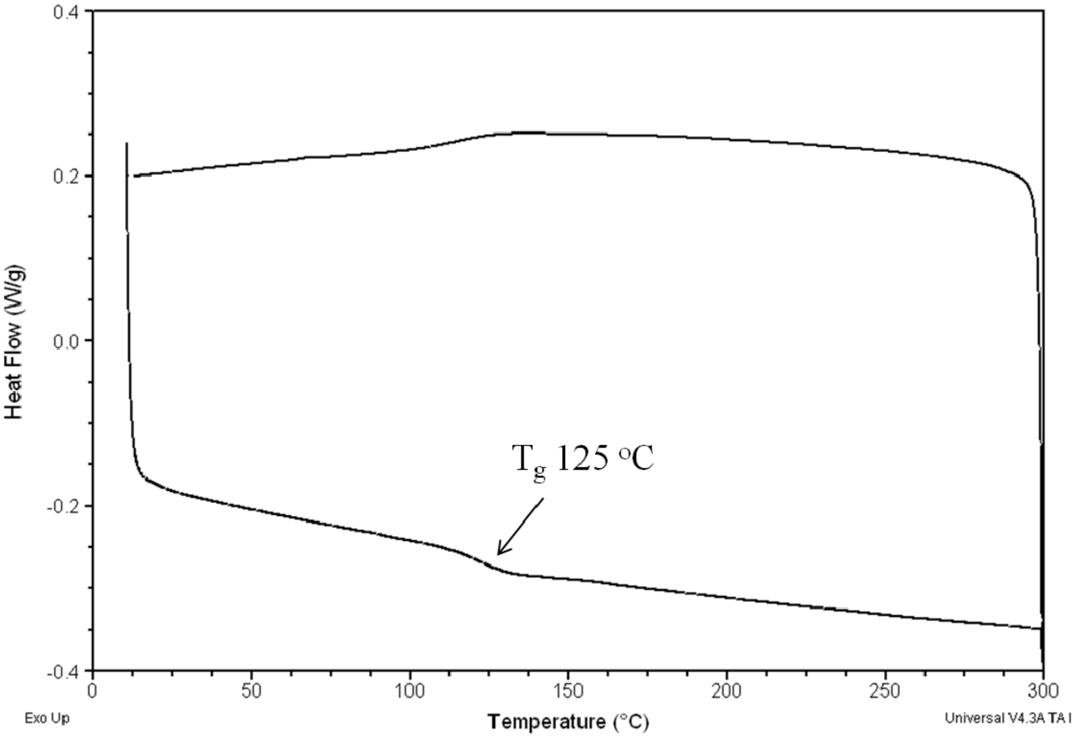

Figure 5. DSC thermogram of the polycyclohexadiene polymer (heating rate: 10 °C/min) showing T_g at 125 °C (M_n = 5.2 kDa, PDI = 1.41).

REFERENCES

S1. C. Nieto-Oberhuber, S. Lopez, and A M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178.

S2. SAINT+ Software for CCD diffractometers, Bruker AXS, Madison, WI, **2000**.

S3. G. M. Sheldrick, SADABS Program for Correction of Area Detector Data, University of Gçttingen, Gçttingen, **1999**.