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The synthesis of resin-bound tetramethylcyclopentadienes: an evaluation of two methodologies

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Abstract—A comparison of two routes towards the synthesis of tetramethylcyclopentadienes on a range of different polymer supports is discussed. It was found that the direct displacement of the halide from halogen terminated polymers furnished a cleaner product and in fewer steps.

The use of polymeric materials as supports for metal-based catalytic species has attracted much interest over the past 30 years and has recently undergone a resurgence.[1] An important class of polymer-bound metal catalysts are those, which contain a spectator cyclopentadienyl ligand (Cp). These complexes have found utility in olefin polymerisation,[2] hydrogenation[3] and hydroformylation catalysis.[4] Analysis of the literature shows that there are five routes available for the synthesis of polymer-supported Cp ligands: (1) direct displacement of halide functionality (Cl or Br) in the resin with sodium cyclopentadienide (Na^+Cp^-);[3,5] (2) reaction of lithiated resins with either cyclopentanone[6] or (3) dimethylfulvene;[7] (4) activation of hydroxyl functionalities by conversion to a sulfonate ester,[2] followed by displacement with Na^+Cp^-; (5) reaction of nickelocene with chloro functionalised resins.[8]

Characterising the tethered species is inherently difficult when the introduced functionality, such as the Cp moiety, contains no hetero atoms. In such cases, conventional means of determining the loading or 'substitution' level of a resin (defined as mmol functional group/g resin), such as colorimetric assays,[9] titrimetric,[10] combustion elemental[11] and functional group specific derivatisations[12] cannot be applied. Prompted by these observations, we have undertaken a comparison of two routes to tetramethylcyclopentadiene (Cp″) functionalised resins on a range of different supports. Our results provide insights into reaction monitoring of, and in the characterisation of these supported species.

As part of a wider research program on the development of polymer-supported metallocene catalysts,[13] we assessed two routes towards the immobilisation of tetramethylcyclopentadiene (Cp″). The first involved activation of the hydroxyl functionality by conversion to a sulfonate ester, followed by displacement with the tetramethylcyclopentadiene anion.[2] The hydroxyl functionalised resins, ArgoGel-OH **1** (a polyethylene glycol (PEG)-grafted polymer) and ArgoPore-OH[14] **2** display a broad absorption ($\sim 3500\ cm^{-1}$) corresponding to the O–H stretching vibration in their FT-IR spectra. The CPMG ^1H MAS NMR spectrum of the ArgoGel-OH **1** exhibits a multiplet (3.69–3.75 ppm) arising from the PEG chain and signals from the C-1 (61.6 ppm) and C-2 (72.8 ppm) carbons in the terminal PEG group in the ^{13}C gel-phase NMR spectrum.

In order to determine the hydroxyl group loading (mmol OH/g resin) of resins **1** and **2**, a novel derivatisation was developed in which the resins were converted to their corresponding 3,5-dinitrobenzoates,[15] **1a**–**2a**, by reaction with 3,5-dinitrobenzoyl chloride **3** (Scheme 1).

The reactions were monitored by FT-IR spectroscopy, specifically the appearance of the carbonyl absorption ($1732\ cm^{-1}$), as well as bands corresponding to the asymmetric ($1548\ cm^{-1}$) and symmetric ($1344\ cm^{-1}$) stretching of the nitro groups in the FT-IR spectra of **1a** and **2a**. The complete disappearance of the O–H

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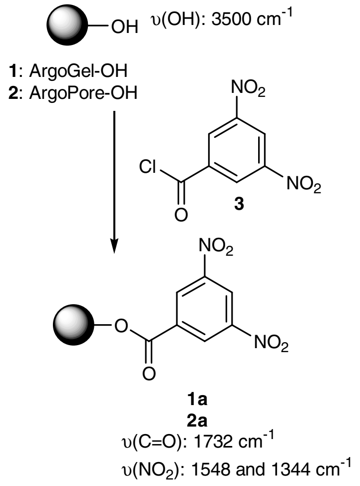


Scheme 1. Reagents and conditions: CH_2Cl_2, pyridine, rt, 6 days.

stretch confirmed that no starting material was present at the end of the synthesis. Product **1a** showed a new signal corresponding to the carbonyl carbon (159.2 ppm) and signals in the aromatic region arising from the introduced 3,5-dinitrophenyl group in the gel-phase ^{13}C NMR. Also notable was the shift in the terminal C-1 (61.6 to 64.9 ppm) in the products **1a** and **2a**. The nitro group loadings of resins **1a** (0.36 mmol NO_2/g resin) and **2a** (0.37 mmol NO_2/g resin) were calculated from nitrogen% microanalysis.

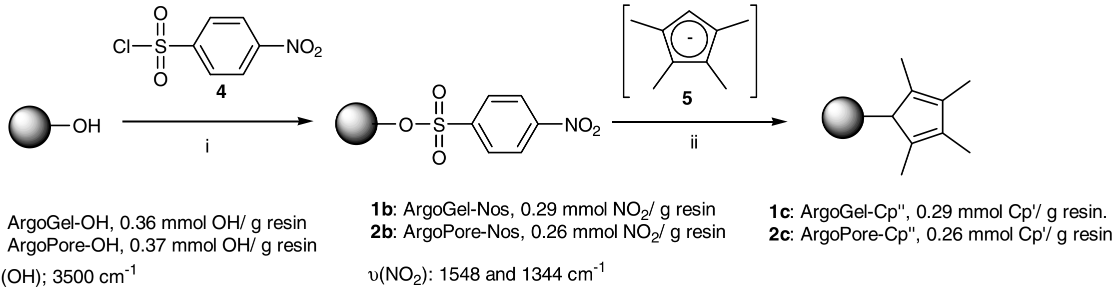
ArgoGel-OH **1** (0.36 mmol OH/g resin) and ArgoPore-OH **2** (0.37 mmol OH/g resin) were converted to their corresponding sulfonate esters[16] by treatment with 4-nitrobenzenesulfonyl chloride **4** to afford the nosylate derivatives, ArgoGel-Nos **1b** and ArgoPore-Nos **2b** (Scheme 2). The nosylate loadings (%N microanalysis) for compounds **1b** and **2b** were found to be 0.29 and 0.26 mmol NO_2/g resin, respectively. The appearance of new absorptions at 1532 and 1350 cm^{-1} in the FT-IR spectra of compounds **1b** and **2b**, assignable to the stretching modes of the nitro group, confirmed that the desired nosylates had been formed. However, the O–H stretching vibration was still present in the spectra indicating that these reactions did not reach completion.

Apart from the PEG resonances (3.51–3.86 ppm) in the CPMG ^1H HR-MAS NMR spectrum of ArgoGel-Nos **1b**, a downfield singlet (4.34 ppm) was observed for the C-1 methylene protons in the terminal PEG chain. Furthermore, two sets of doublets were observed at 8.19 and 8.45 ppm corresponding to the *ortho* and *meta* protons in the nosylate group. The gel-phase ^{13}C NMR spectrum of compound **1b** also displayed a downfield shift of the terminal C-1 carbon signals (61.0 to 66.6 ppm) and the C-2 carbon signals (72.8 to 74.9 ppm), in addition to new resonances in the aromatic region. However, a weak signal at 61.0 ppm from the starting material ArgoGel-OH **1** was still evident and verifies that product formation was incomplete.

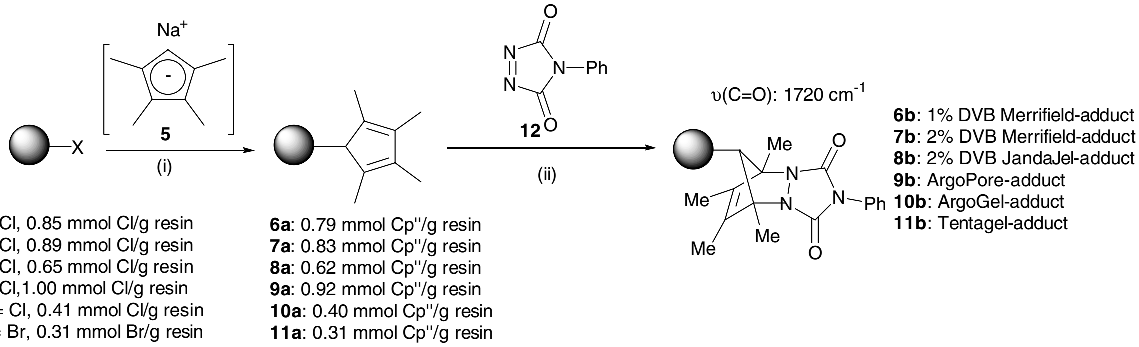
Attempts to drive these reactions to completion were unsuccessful, and the nosylates **1b** and **2b** were employed in this impure state in the next step of the synthesis. Attachment of the tetramethylcyclopentadienyl ligands (Cp'') was accomplished by reacting the nosylates **1b** or **2b** with freshly prepared sodium 1,2,3,4,-tetramethyl-1,3-cyclopentadienide[17] **5**, which resulted in Cp'' loadings of 0.29 and 0.26 mmol Cp''/g resins for compounds **1c** and **2c**, respectively (Scheme 2). This loading was confirmed by the absence of nitro group absorptions in the FT-IR spectra, aromatic resonances in the ^1H and ^{13}C NMR spectra of ArgoGel-Cp'' **1c** and finally, nitrogen in the elemental analyses of resins **1c** and **2c**.[16]

In an effort to improve the purity and loading of the Cp'' functionalised resins, a second approach was adopted, which involved the displacement of halide from the starting resin with NaCp″. 1% DVB Merrifield-Cl **6**, 2% DVB Merrifield-Cl **7**, JandaJel-Cl **8**,[18] ArgoPore-Cl **9** and the PEG resins, ArgoGel-Cl **10** and TentaGel-Br **11** were chosen for study. The supported Cp'' derivatives **6a**–**11a** were prepared by reacting the halogen terminated resins **6**–**11** with sodium 1,2,3,4-tetramethyl-1,3-cyclopentadienide **5** (Scheme 3). Reactions performed on resins **6**–**9** were easily monitored by observing the disappearance of the C–Cl absorption at 1266 cm^{-1} in their FT-IR spectra.

Complete chloride displacement was observed in all cases (%Cl microanalysis). With the exception of ArgoPore-Cp'' **9a**, compounds **6a**–**8a** were further characterised by an upfield shift of the benzylic protons (4.41 ppm) in the chlorinated resins to ~3.75 ppm in the Cp'' attached species in the CPMG ^1H MAS NMR



Scheme 2. Reagents and conditions: (i) pyridine, CH_2Cl_2, 0 °C to rt, 6 days; (ii) DMF, 80 °C, 2 days.



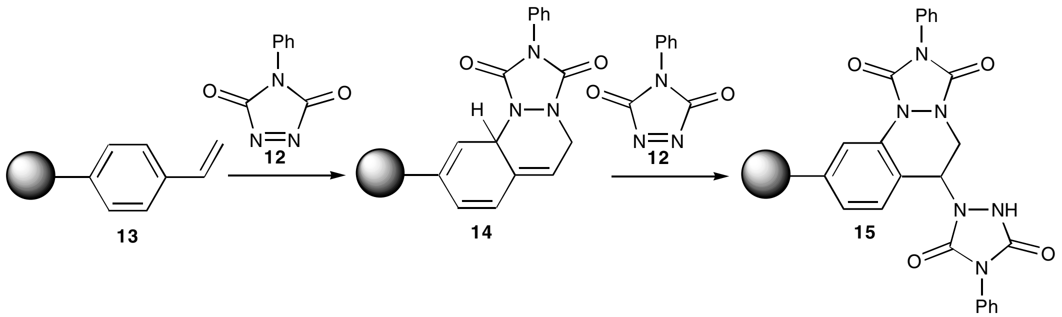
Scheme 3. Reagents and conditions: (i) DMF, 80 °C, 2 days; (ii) CH_2Cl_2, −78 °C, 12 h.

spectra.[5] New weak resonances between 14 and 16 ppm, from the cyclopentadienyl methyl groups, were also present in the gel-phase ^{13}C NMR spectra. Conversely, the reaction of the PEG based resins, ArgoGel-Cl **10** and Tentagel-Br **11** with the NaCp″ anion to produce the Cp″ derivatives **10a** and **11a** was monitored by following the disappearance of the CH_2–X (where X = Cl or Br) wag at 1281 cm^{-1} in the FT-IR spectra. Complete halide displacements were confirmed by (%Cl or %Br) microanalysis.

The ArgoGel derivative **10a** exhibited a new broad resonance (2.85 ppm) assignable to the terminal methylene C-1 protons in the PEG chain in the ^1H NMR spectra. An upfield shift of the C-1 carbon in the terminal PEG group (43.1 to 34.8 ppm), in addition to new resonances between 22.1 and 26.1 ppm, were observed in the gel-phase ^{13}C NMR spectra. A downfield shift of the C-1 carbon in the terminal PEG unit in Tentagel-Br **11** (29.5 to 34.8 ppm) was observed in the Cp″ supported product **11a** as well as the appearance of a new multiplet centred at 2.86 ppm, which corresponds to the C-1 protons in the terminal PEG unit in the CPMG ^1H MAS NMR spectra.

N-Phenyl-1,3,4-triazoline-2,5-dione (Cookson's reagent) **12** has been used in the quantitative determination of the cyclopentadienyl ligand loading on polymer supports.[2] This method of quantification was applied to a number of polymer bound Cp″ batches prepared by the direct displacement methodology. Accordingly, Diels–Alder adduct formation with Cookson's reagent[19] was conducted with several different batches of the Cp″-supported derivatives **6a**–**11a** (Scheme 3). Diels–Alder adduct formation in compounds **6b**–**11b** was confirmed by the appearance of a strong absorption at 1720 cm^{-1} (corresponding to the imide, Scheme 3) in the FT-IR spectra, although an additional unexpected signal at ~1789 cm^{-1}, of variable intensity, was observable in some spectra. The gel-phase ^{13}C NMR spectra of compounds **6b**–**11b** also exhibited a new carbonyl resonance at 159 ppm. The CPMG ^1H MAS NMR spectra, of the PEG graft supported species **6b**–**11b** were complicated, although a downfield shift of the PEG signal in the starting materials (3.47–3.87 to 4.12–4.78 ppm) was observed. Unfortunately, the Cp″ loadings determined from the % nitrogen in compounds **6b**–**11b** were far higher (in excess of 100%) than expected from loadings based on halide displacement.

Anomalously high Cp loading levels have been reported elsewhere, when Cookson's reagent was employed to assess quantitative loading.[2,8] We believed that Cookson's reagent may undergo an additional ene reaction with unreacted vinyl groups within the polymer matrix of these resins to give a compound with a structure identical to that of **14**. To test this hypothesis, an excess of Cookson's reagent **12** was reacted with vinyl polystyrene[19] **13** (Scheme 4). The reaction was monitored by observing the disappearance of the vinyl absorption (1665 cm^{-1}) and the corresponding emergence of a new strong absorption at 1789 cm^{-1} (indicative of the carbonyl group in **14**) in the FT-IR spectrum. Reaction completion was confirmed by the disappearance of the vinylic protons (5.21 and 5.71 ppm) in the CPMG MAS ^1H NMR spectrum. This observation explains the appear-



Scheme 4. Reagents and conditions: CH_2Cl_2, −78 °C, 12 h.

ance of the 1789 cm^{-1} absorption in the IR spectra of the Cookson's adduct resins **6b**–**11b**.

However, microanalysis of the new product (11.09% N) showed twice the amount of nitrogen that would be expected if the product had structure **14**. A more probable structure is the Diels–Alder ene adduct **15**,[20] which is formed by the re-aromatisation of the initial Diels–Alder product **14**, which drives a subsequent ene reaction with a second molecule of Cookson's reagent. This structure is in good agreement with the % nitrogen result. Furthermore, a new multiplet at 3.68–3.79 ppm, assignable to the saturated ring protons in **15**, was also present in the CPMG ^1H MAS NMR spectrum. This type of re-aromatisation has been noted in the Diels–Alder reaction of vinyl polystyrene derivatives with Cookson's reagent.[21]

In summary, two routes for the synthesis polymer-supported tetramethylcyclopentadiene have been evaluated. Direct displacement of halide in the starting resins (with NaCp″) was found to give clean products with superior Cp″ loadings (100% halide displacement) in a one-pot synthesis. The activation (by conversion to sulfonate esters) and subsequent displacement methodology, resulted in lower Cp″ loading. It can also be concluded that the Cookson's adduct formation is an unreliable method for the quantitative determination of the polymer-attached Cp″ loading, since a varying amount of bi-adducts, cf. **15** are formed, presumably dependent on the amount of unreacted vinyl groups, which varies in each resin batch.

Acknowledgements

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14. ArgoPore-OH **2**, a macroporous resin (Argonaut Technologies), contains nitrogen (1.18%) presumably as an artifact of nitrogen-containing activators used during the synthesis of this resin. Modified results are reported in later CHN calculations by subtracting this amount from the total microanalysis result.
15. The loading of the 3,5-dinitrobenzoate ligand is identical to the hydroxyl loading only if 100% conversion is assumed. ArgoGel-OH **1** or ArgoPore-OH **2** (40 mg) was treated with 3,5-dinitrobenzoyl chloride **3** (147.6 mg, 0.64 mmol) and pyridine (0.1 mL, 0.48 mmol) in anhydrous dichloromethane (10 mL) at room temperature under an argon atmosphere. The resulting suspensions were then shaken for 3 days, after which time identical amounts of 3,5-dinitrobenzoyl chloride **3** and pyridine were added, and the reaction was shaken for a further 3 days. The resultant polymer **1a** or **2a** was then filtered and washed with H_2O, H_2O/MeOH (1:1), MeOH, ethyl acetate, CH_2Cl_2 and pentane. Reactions were conducted twice, and the benzoate loading, determined by % nitrogen microanalysis, is the average these experiments.
16. ArgoGel-OH **1** (0.36 mmol OH/g resin, 500 mg, 0.18 mmol) or ArgoPore-OH **2** (0.37 mmol OH/g resin, 500 mg, 0.19 mmol) were suspended in dichloromethane (15 mL) and cooled to 0 °C in an ice bath. Pyridine (0.1 mL, 1.8 mmol or 0.2 mL, 1.9 mmol) and 4-nitrobenzenesulfonyl chloride **4** (320.0 mg, 1.40 mmol or 336.9 mg, 1.50 mmol) were added, and the suspension was allowed to warm to room temperature and shaken overnight. The resultant suspension was again cooled to 0 °C and identical amounts of the reactants were added. The polymer suspension was then shaken for a further 3 days. The resultant polymer was then filtered and washed with H_2O, H_2O/MeOH (1:1), MeOH, ethyl acetate, CH_2Cl_2 and pentane, and dried in vacuo to afford the nosylate derivatives ArgoGel-Nos **1b** and ArgoPore-Nos **2b**.
17. Generated by the deprotonation of 1,2,3,4,-tetramethyl-1,3-cyclopentadiene with an excess of sodium hydride. The resulting deep red suspension was transferred to a suspension of the resin in DMF, heated at 80 °C for 2 days, filtered, washed and dried in vacuo to yield the dark brown polymer-supported Cp″ resins **1c** and **2c**.
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19. In a typical reaction, Cookson's reagent **12** (32.2 mg, 0.18 mmol) was added to a CH_2Cl_2 (10 mL) suspension of the polymer-supported Cp″ compound (**9a**, 0.92 mmol Cp″/g resin, 40 mg, 36.8 μmol) cooled to −78 °C. The bright red mixture was allowed to warm to room temperature and was shaken for 12 h at room temperature. During this period the mixture decolourised, and the resultant polymer was filtered, washed sequentially with aliquots of water, water/MeOH, ethyl acetate, CH_2Cl_2 and, finally, pentane, before being dried in vacuo to yield the adducts **6b**–**11b**.
20. Compound **15** was further characterised by ^1H MAS NMR, which displayed a distinctive multiplet (3.69–3.70 ppm) arising from the ring methylene protons. The gel-phase ^{13}C NMR spectrum exhibited signals at 152.8 and 159.0 ppm arising from the carbonyl groups.
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