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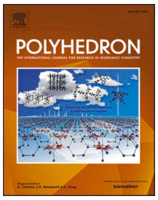

# Functionalised polymeric materials in the efficient synthesis of 2-substituted $\eta^3$-butadienyl molybdenum complexes

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ABSTRACT

Polystyrene resins functionalised with phosphonium chloride or bromide have been found to function as efficient catalysts in the synthesis of complexes of the type $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C = CH_2)L_2]$, the rate of conversion being controlled by the structure of the polymer. Subsequent addition of amines or amino acids to the resulting solutions gave amide 2-substituted $\eta^3$- butadienyl complexes, which have been investigated by NMR analysis.

## 1. Introduction

The formation of transition metal complexes containing $\eta^3$-bonded butadienyl ligands has been reported for various reactions of $\eta^2$-diynes, $\eta^3$-allyls or propargyls and $\eta^4$-dienes, and they have been identified as key intermediates in certain catalytic processes [1–7]. Typically, they are formed in dried ethers or chlorinated solvents and under a dry, inert atmosphere, being extremely sensitive to the presence of moisture. In contrast, the author has found that an $\eta^3$-butadienyl complex $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C = CH_2)L_2]$ (**1**) ($L_2 = 2,2'$-bipyridine or 1,10-phenanthroline) can be synthesised in the presence of water (Scheme 1, step 3) [8]. Whilst this introduced an environmentally benign solvent, further improvement of the overall route was required. The second step of this three-step synthetic pathway reacts $[Mo(CO)_4L_2]$ with $Ph_4PCl$ to give a more nucleophilic metal carbonyl anion for reaction with 1,4-dichloro-2-butyne to form the $\eta^3$-butadienyl complex. However, final recovery of $Ph_4PCl$ at the end of this route by chromatography was inefficient, giving low returns and adding to waste and costs. An alternative method of tethering this compound to a resin which can be reclaimed and recycled has therefore been investigated and is reported in this work.

Reduction of environmental impact and resource conservation are key tenets of the green chemistry paradigm [9,10]. The use of polymer resins as supports for chemical synthesis or as surfaces on which to perform homogeneous catalysis fits this concept, having been exploited for a wide range of synthetic purposes [11]. Such solid-phase methods for combinatorial chemistry are attractive from a green perspective, allowing one-pot serial reactions to replace conventional, multi-pot methods, simple filtration to remove resin and reduction in use of chemicals and energy during work-up [12]. Solid-supported synthesis also facilitates the move from batch to flow reactions, where steady state conditions result in improved energy transfer, reactant composition, product yield and product purity. In this work, we report the successful one-pot use of a functionalised resin to catalyse steps 2 and 3 to form **1** with reduction of waste and illustrate application of this method to significantly improve overall yields of a series of 2-substituted $\eta^3$-butadienyl complexes.

## 2. Experimental

### *2.1. Materials and methods*

The complex $[Mo(CO)_4L_2]$ was prepared from the hexacarbonyl by the published method [13]. The polystyrene resins **A**-**F** (Fig. 1) functionalised with triphenylphosphine or phosphonium halides (Table 1) were made as described below or purchased from Sigma-Aldrich. Both 1,4-dibromo-2-butyne and 1,4-diiodo-2-butyne were synthesised according to the published method [14]. Other chemicals were purchased from commercial sources and used without further purification, unless specified otherwise. Experiments were conducted under a dinitrogen atmosphere using dry solvents and liquid reagents. ATR-IR spectra were recorded on a Perkin Elmer 781 spectrometer and NMR spectra were recorded on a Bruker Neo 600 MHz spectrometer fitted with a TXO Helium CryoProbe. The specifications of commercial resins **A**, **B**, **D** and **F**

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and synthesised resins **C** and **E** used in this work are given in Table 1.

### 2.2. *Preparation of polymer-bound benzyltriphenylphosphonium bromide and methyltriphenylphosphonium iodide resins, **C** and **E**, respectively*

In a modification of the reference method [15], polymer-bound triphenylphosphine resin **A** (0.5 g) was refluxed in acetonitrile (25 $cm^3$) with excess benzyl bromide or iodomethane (1.62 mmol) for 24 hr. After filtration, the polymer was washed sequentially with ten 1 $cm^3$ aliquots of toluene, dichloromethane and diethyl ether, then dried at 70 °C under vacuum. Bromide or iodide loading of the resultant polymer was assessed by argentometric determination. DMF (5 $cm^3$) was added to the resin (0.2 g) and the suspension was stirred for 15 min to swell the polymer. After adding a solution of 5 drops concentrated $HNO_3$ in 5 ml 50 % sodium nitrate solution to the flask, the mixture was stirred for 3 hr, followed by dilution with water (100 $cm^3$). Bromide or iodide concentration was determined by titration using the Volhard method.

### 2.3. *General method for reaction of [$Mo(CO)_4L_2$] and 1,4-dichloro-2-butyne or 1,4-dibromo-2-butyne in the presence of a functionalised resin*

The resin (3–50 mg) was pre-swollen in either dichloromethane or acetone (50 $cm^3$) by refluxing for 5 min. A sample of [$Mo(CO)_4L_2$] ($4 \times 10^{-2}$ – 1.53 mmol) and 1,4-dichloro-2-butyne or 1,4-dibromo-2-butyne ($4 \times 10^{-2}$ – 1.53 mmol) were added to the flask, and the mixture was refluxed for a period (0.5–9 hr). Conversion to **1** was monitored over time by extracting a small sample of solvent at 5 min intervals and recording the IR spectrum. At complete conversion, the resin was filtered from solution, washed several times with dichloromethane or acetone and returned to the remaining solvent with further [$Mo(CO)_4L_2$] and 1,4-dichloro-2-butyne or 1,4-dibromo-2-butyne for further reaction. The yield of **1** after each use of resin could be determined by removal of solvent *in vacuo*. Conversion to the acyl substituted $\eta^3$-butadienyl complex was also confirmed by addition of an amine or amino acid ester to the mixture and isolation of the corresponding amide, as described below.

### 2.4. *Synthesis and characterisation of amide 2-substituted $\eta^3$-butadienyl complexes **3**–**6***

All complexes were characterized by IR and NMR spectroscopy and by elemental analysis, as given below. The $^{13}C$ NMR assignments are listed for the $\eta^3$-butadienyl fragment C11C12C13 = C14 and the amide carbonyl group C15. Yields based on the initial weight of [$Mo(CO)_4L_2$] used with resin were in the range 69–84 %.

Complexes **3** or **4** were obtained as follows. The acyl chloride ($L_2$ = 1,10-phenanthroline) in dichloromethane (1.0 mmol) was prepared as given in 2.3 using 1,4-dichloro-2-butyne, and the resin removed by filtration. To this solution was added dropwise excess propylamine or hexylamine (0.2 $cm^3$), and the mixture was stirred for 2 hr. Reduction in volume under vacuum and chromatography on silica (60–120 mesh) using 5 %v/v methanolic dichloromethane, followed by recrystallisation using $CH_2Cl_2$/petrol gave the products as orange rectangular crystals.

Complex **3:**

Selected ATR-IR ($cm^{-1}$): $\nu$(NH) 3441, $\nu$(C≡O) 1890, 1971, $\nu$(C=O) 1635.

Elemental analysis %found (%calculated): 51.73(52.43)C, 4.03 (3.97)H, 8.23(8.34)N.

$^1H$ NMR ($CDCl_3$, 600 MHz): 0.45(t, 3H), 0.59(m,2H), 1.32(m,H), 2.12(m,H), 2.08(s,H'$_{anti}$), 3.94(s, H'$_{syn}$), 5.11(t, H''$_{anti}$), 5.76(d,H), 6.21 (d, H''$_{syn}$), 7.80–9.25(m,8H).

$^{13}C$ NMR ($CDCl_3$): 11.07($CH_3$), 22.00($CH_2$), 40.42($CH_2N$), 49.07 (C11), 58.25(C12), 104.96(C14), 125.10–152.06(aromatics), 166.38 (C13), 175.84(C15), 218.01(C≡O), 219.70(C≡O).

Complex **4:**

Selected ATR-IR ($cm^{-1}$): $\nu$(NH) 3419, $\nu$(C≡O) 1893, 1965, $\nu$(C=O) 1652.

Elemental analysis %found (%calculated): 54.94(54.79)C, 4.80 (4.74)H, 7.56(7.67)N.

$^1H$ NMR ($CDCl_3$, 600 MHz): 0.82(t, 3H), 1.11–1.43(m,10*H*), 2.08(s, H'$_{anti}$), 3.94(s, H'$_{syn}$), 5.08 (t, H), 5.75(d, H''$_{anti}$), 6.22(d, H''$_{syn}$), 7.80–9.25(m, 8H).

$^{13}C$ NMR ($CDCl_3$): 10.97($CH_3$), 13.96($CH_2$), 22.39–31.41($CH_2$), 38.86($CH_2N$), 49.20(C11), 105.04(C14), 114.99–152.13(aromatics), 166.29(C13), 175.80(C15), 218.06(C≡O), 219.77(C≡O).

For complex **5**, a solution of the 4-nitro-L-phenylalanine methyl ester hydrochloride (5.0 mmol) in 2-propanol (50 $cm^3$) was stirred with excess potassium hydrogen carbonate (6.0 mmol, 0.600 g) for one hour. To this was added triethylamine (1.0 mmol, 0.14 $cm^3$) and freshly prepared complex **1** (1.0 mmol) obtained by removal of solvent from the resin solution in 2.3 above. The mixture was stirred for a further two hours, solvent was removed under vacuum and the residue extracted three times with aqueous dichloromethane (15 $cm^3$, 35 % v/v). The dried organic phase was chromatographed on silica gel (60–120 mesh) using 30 % v/v acetonitrile/$CH_2Cl_2$ and recrystallised from $CH_2Cl_2$/petrol at low temperature (-5 °C) to give the products as fine orange needles.

Complex **5:**

Selected ATR-IR ($cm^{-1}$): $\nu$(NH) 3400, $\nu$(C≡O) 1900, 1972, $\nu$(C=O) 1653, 1731.

Elemental analysis %found (%calculated): 51.51(51.63)C, 3.43 (3.41)H, 8.23(8.30)N.

$^1H$ NMR ($CDCl_3$, 600 MHz): 2.14(s,H'$_{anti}$), 2.68(m,H), 2.79(m,H), 2.95(m,H), 3.51(s, 3H)), 3.94(s, H'$_{syn}$), 5.76(d, H''$_{anti}$), 6.10(d, H''$_{syn}$), 6.99–9.24(m, 12H).

$^{13}C$ NMR ($CDCl_3$): 21.67($CH_3$), 37.38($C_\beta$), 48.61(C11), 52.15($OCH_3$), 53.46(C12), 57.15(Cα), 105.42(C14), 123.33–152.19(aromatics), 174.95(C15), 217.43(C≡O), 219.29(C≡O).

Complex **6** was obtained in an analogous manner to **5** using L-4-fluorophenylalanine ethyl ester, but 2-propanol was replaced by dichloromethane and triethylamine was used instead of potassium hydrogen carbonate.

Complex **6:**

Selected ATR-IR ($cm^{-1}$): $\nu$(NH) 3403, $\nu$(C≡O) 1902, 1971, $\nu$(C=O) 1655, 1731.

Elemental analysis %found (%calculated): 54.59(54.75)C, 3.65 (3.80)H, 6.46(6.39)N.

$^1H$ NMR ($CDCl_3$, 600 MHz): 1.17(t,3H), 2.12(s, H'$_{anti}$), 2.58(m,H), 2.67(m,H), 2.95(m,H), 3.92(q,2H), 3.94(s,H'$_{syn}$), 5.74(d, H''$_{anti}$), 5.75 (d,NH), 6.08(d, H''$_{anti}$), 6.79–9.26(m, 12H).

$^{13}C$ NMR ($CDCl_3$): 14.16($CH_3$), 36.58($C_\beta$), 48.80(C11), 52.42($OCH_2$), 57.34(C12), 61.14($C_\alpha$), 105.26(C14), 125.05–151.99(aromatics), 174.97(C15), 217.56(C≡O), 219.47(C≡O).

$$Mo(CO)_6 + L_2 \longrightarrow Mo(CO)_4L_2 + 2CO \qquad \text{Step 1}$$

$$Mo(CO)_4L_2 + Ph_4PCl \longrightarrow Ph_4P[MoCl(CO)_3L_2] + CO \qquad \text{Step 2}$$

$$Ph_4P[MoCl(CO)_3L_2] + ClCH_2C{\equiv}CCH_2Cl \longrightarrow \mathbf{1} + Ph_4PCl \qquad \text{Step 3}$$

**Scheme 1.** The three steps involved in synthesis of [$MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C=CH_2)L_2$] (**1**).

## 3. Results and discussion

In selecting solvents for this work, the solubility and thermal stability of the complexes $[Mo(CO)_4L_2]$, $Ph_4P[MoCl(CO)_3L_2]$ and **1**, and the physical properties of the resin, had to be considered. Both the metal tetracarbonyl and anionic tricarbonyl have good thermal stability, being synthesised in boiling toluene (110 °C), however use of solvents with boiling points above 80 °C in step 3 gives rise to the alternative complex $[MoCl_2(CO)(\eta^2\text{-}ClCH_2C\equiv CCH_2Cl)L_2]$ (**2**) [16]. Commercially available functionalised resins **A**, **B**, **D** and **F** are reported to have good thermal stability up to 125 °C, and the synthesised resins **C** and **E** were found to be stable for several hours in refluxing toluene. Polar alcohols, acetonitrile and ethyl acetate were rejected as solvents, either because they were poorly absorbed by the resin or gave **2** only. The good solubility of **1** in $CH_2Cl_2$ and excellent swelling properties of the resin in this solvent led to its use in initial studies. However, this was later replaced by acetone, another aprotic solvent with greener credentials.

The purple complex $Ph_4P[MoCl(CO)_3L_2]$ can be obtained by refluxing $[Mo(CO)_4L_2]$ and $Ph_4PCl$ in $CH_2Cl_2$ (step 2). On refluxing the triphenylphosphonium chloride resin **B** with $[Mo(CO)_4L_2]$, a light purple colouration of the polymer was observed. On repeating this process in the presence of $ClCH_2C\equiv CCH_2Cl$, the filtered and washed polymer was light red, and EDAX examination showed molybdenum had been retained within the resin. The extent of conversion of $[Mo(CO)_4L_2]$ to **1** and final reaction time were determined by periodic sampling of the reaction liquor and monitoring by IR spectroscopy. At completion, complex **1** was obtained in almost quantitative yield. It is probable that heating of the resin in solution results in swelling and release of product. On cooling, only a little product remains in the contracted architecture to give coloration. The resin could then be reused in several further reactions by adding $[Mo(CO)_4L_2]$ and $ClCH_2C\equiv CCH_2Cl$ in fresh solvent. Various relative proportions of solvent volume, weight of resin and amounts of metal carbonyl and butyne were investigated over various time periods (0.5–6 hr). In total the resin was reused ten times, with a yield of over 90 % each time. This is a significant improvement over the combined typical 50 % yield after conducting steps 2 and 3 in series, it dispenses with both the use of solvents (toluene and acetonitrile) for step 2 and with the need for solvent ($CH_2Cl_2$) and chromatography packing to remove $Ph_4P[MoCl(CO)_3L_2]$ from complex **1** in step 3. The final minimum reaction time using acetone (30 min) was shorter than the combined times required for steps 2 (90 min, reflux) and 3 (3 hr, room temperature), and significantly less than the previously reported one pot method of refluxing $[Mo(CO)_4L_2]$, $Ph_4PCl$ and $ClCH_2C\equiv CCH_2Cl$ in chlorinated solvent (6 hr) [16]. Scheme 2 shows the reaction pathway for complexes **1** and **2**, and subsequent reactions of **1** to give complexes **3**–**6**.

**Table 1**
Properties of the functionalised resins.

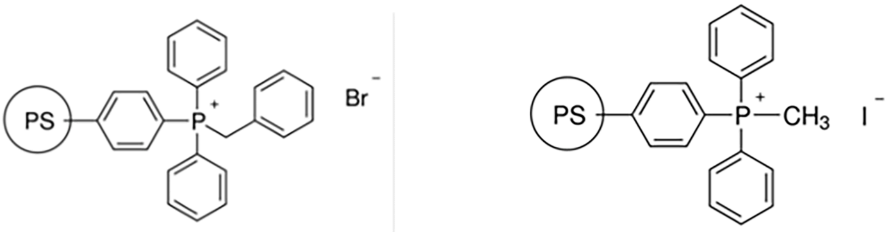
| Resin | Functionality | Mesh Size | Loading (mmol/g) | Cross-linking[a] (%) | Swelling Volume (cm$^3$/g) |
|---|---|---|---|---|---|
| **A** | $PPh_3$ | 100–200 | 1.0–1.5 | 1 | [b] |
| | | | | | 6.70[c] |
| **B** | $PPh_4^+$ $Cl^-$ | 100–200 | 0.7–1.3 | 1 | 4.02[d] |
| **C** | $PBnPh_3^+$ $Br^-$ | 100–200 | 1.0–1.5 | 1 | [b] |
| **D** | $PBnPh_3^+$ $Br^-$ | 200–400 | 1.8–2.0 | 2 | 1.43[d] |
| **E** | $PMePh_3^+$ $I^-$ | 100–200 | 1.0–1.5 | 1 | [b] |
| **F** | $PMePh_3^+$ $I^-$ | 200–400 | 1.8–2.0 | 2 | 1.61[d] |

[a] Divinylbenzene.
[b] Not specified.
[c] In $CH_2Cl_2$ (DCM).
[d] In THF.

Incorporating bromide resins C or D in reactions of $BrCH_2C\equiv CCH_2CBr$ and $[Mo(CO)_4L_2]$ was less effective however, with lower yields (45–50 %) of $[MoBr(CO)_2(\eta^3\text{-}CH_2C(COBr)C = CH_2)L_2]$ being isolated and with longer reaction time (3 hr) required. Combination of resins E or F, $ICH_2C\equiv CCH_2I$ and $[Mo(CO)_4L_2]$ under the same conditions did not form an $\eta^3$-butadienyl complex as heating led to rapid polymerization and inactivation of the alkyne. Use of bromide resins **C** or **D,** or iodide resins **E** or **F**, in reactions of $[Mo(CO)_4L_2]$ and $ClCH_2C\equiv CCH_2Cl$ formed $[MoCl(CO)_2(\eta^3\text{-}CH_2C(COCl)C = CH_2)L_2]$ only.

Resin **A**

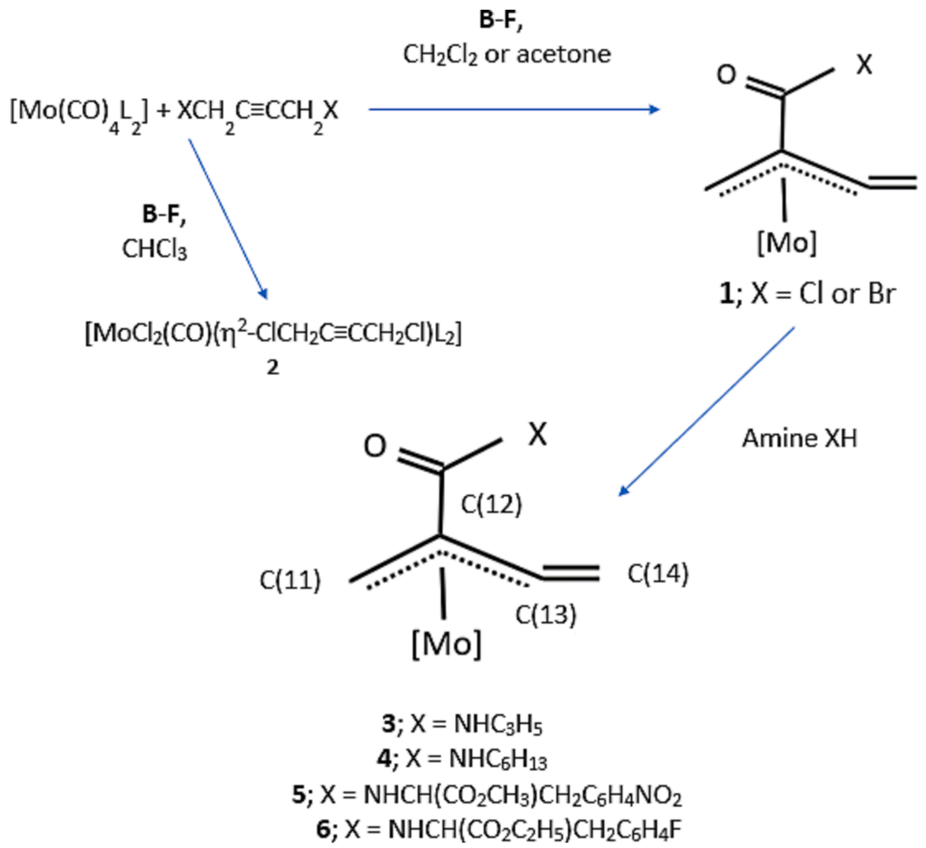
Resin **B**



Resins **C** and **D**

Resins **E** and **F**

**Fig. 1.** General structures of the functionalised polystyrene (PS) resins **A**-**F**.



**Scheme 2.** Synthesis of complexes **1** or **2** using polystyrene resins **B-F,** and subsequent formation of amide complexes **3**–**6**. The numbering of the $\eta^3$-butadienyl unit in **3**–**6** is shown to assist assignment and discussion of the $^{13}C$ NMR spectra. [Mo] = $Mo(CO)_2L_2X$, X = Cl, Br.).

The larger ionic radii of bromide and iodide ions may be less mobile within the matrix and chloride ions may effectively compete against bromide or iodide ions in the reaction. Resins **E** and **F** both required longer reaction time (9 hr) for complete conversion to **1**. The physical properties of the resin affect absorption of reactants and movement of **1** out of the polymer matrix. Initial absorption of solvent by the resin leads to swelling, until solvation of ions and the stretched matrix equals elastic forces and resistance. This swelling results in solvated areas of ionic groups and counter-ions where reaction and exchange can occur. Drying of the washed used resin before re-swelling and addition of further reactants resulted in lower yields, and examination of the resin by SEM showed the exterior surface of the beads was no longer smooth. It is probable that loss of solvent and dehydration had also caused contraction and damage of the polymer architecture, limiting subsequent reactant absorption and product egress. Fig. 2 illustrates the possible composition of swollen resin and the pathways for movement of species.

A mechanism for formation of **1** in step 3 of Scheme 1 has been proposed [17]. Halide ions are mobile within the swollen resin and can readily react with absorbed $[Mo(CO)_4L_2]$ to form $[Mo(CO)_3L_2X]^-$. This nucleophilic anion attacks 1,4-dichloro-2-butyne to form an intermediate which undergoes rearrangement with release of chloride ion. Resin **B** can be considered a true catalyst, with chloride ions being used to make anion and then released on formation of **1** for re-use. For resins **C-F**, initial reaction of bromide or iodide ion with $[Mo(CO)_4L_2]$ and 1,4-dichloro-2-butyne results in formation of chloride ion as a by-product which can be involved in further reaction. Thus once reaction has commenced, $[Mo(CO)_3L_2Cl]^-$ continues to form and **1** is produced with release of chloride until reactants are exhausted. Continual production of chloride results in this ion outcompeting the less mobile, larger bromide or iodide ions and mixed halogen complexes of the type $[Mo(CO)_2(\eta^3\text{-}CH_2COX)C = CH_2)L_2Y]$ (X or Y = Cl, Br or I) were not isolated from these resins. A possible catalytic cycle and the role of resins **B-F** in the mechanism of this reaction are shown in Fig. 3. Absorption of a solution of $[Mo(CO)_4L_2]$ into the resin results in oxidative addition of resin-bound phosphonium halide, loss of carbon monoxide and conversion to the anionic tricarbonyl, step (a). Nucleophilic attack of this

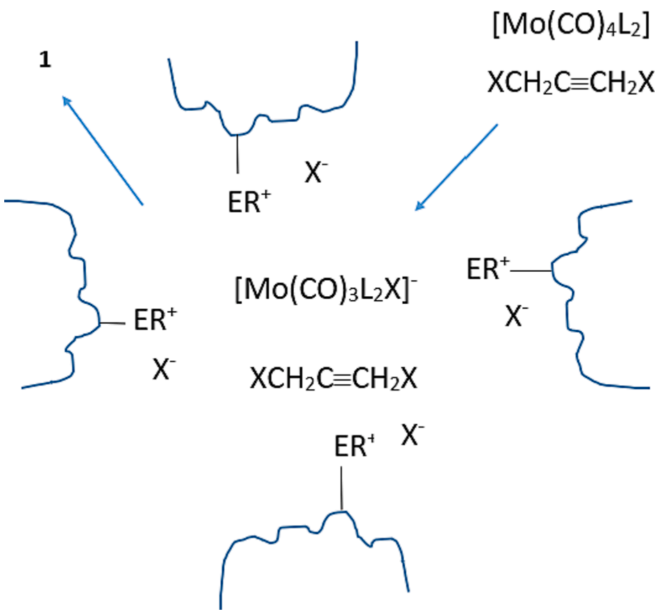


**Fig. 2.** Representation of a region of the swollen polystyrene resin showing tethered functional groups $ER^+$, mobile halide ions $X^-$ and the formation of $[Mo(CO)_3L_2X]^-$ and $[Mo(CO)_2(\eta^3\text{-}CH_2C(COX)C = CH_2)L_2X]$ **1**. For resin **B**, ER = $PPh_4$, for resins **C** or **D**, ER = $PBnPh_3$ and for resins **E** and **F**, ER = $PMePh_3$.

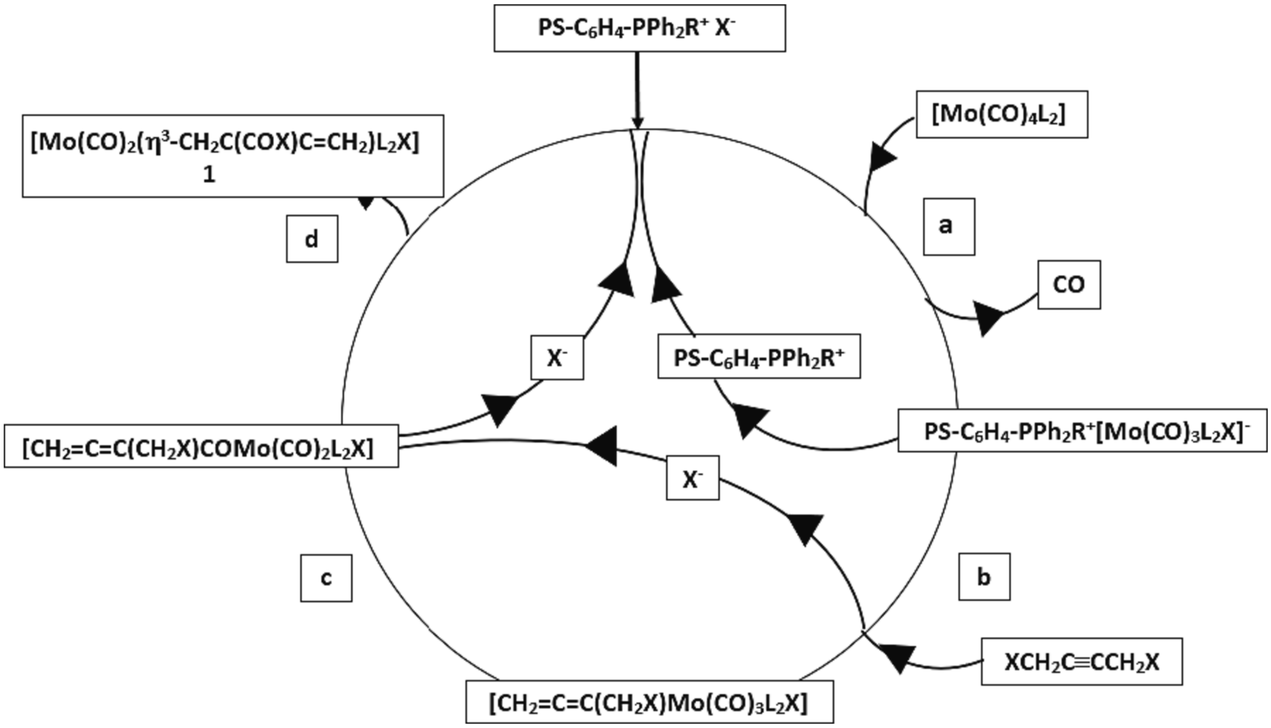


**Fig. 3.** Proposed catalytic cycle for use of a functionalised polystyrene (PS) polymer in the synthesis of complex **1**.

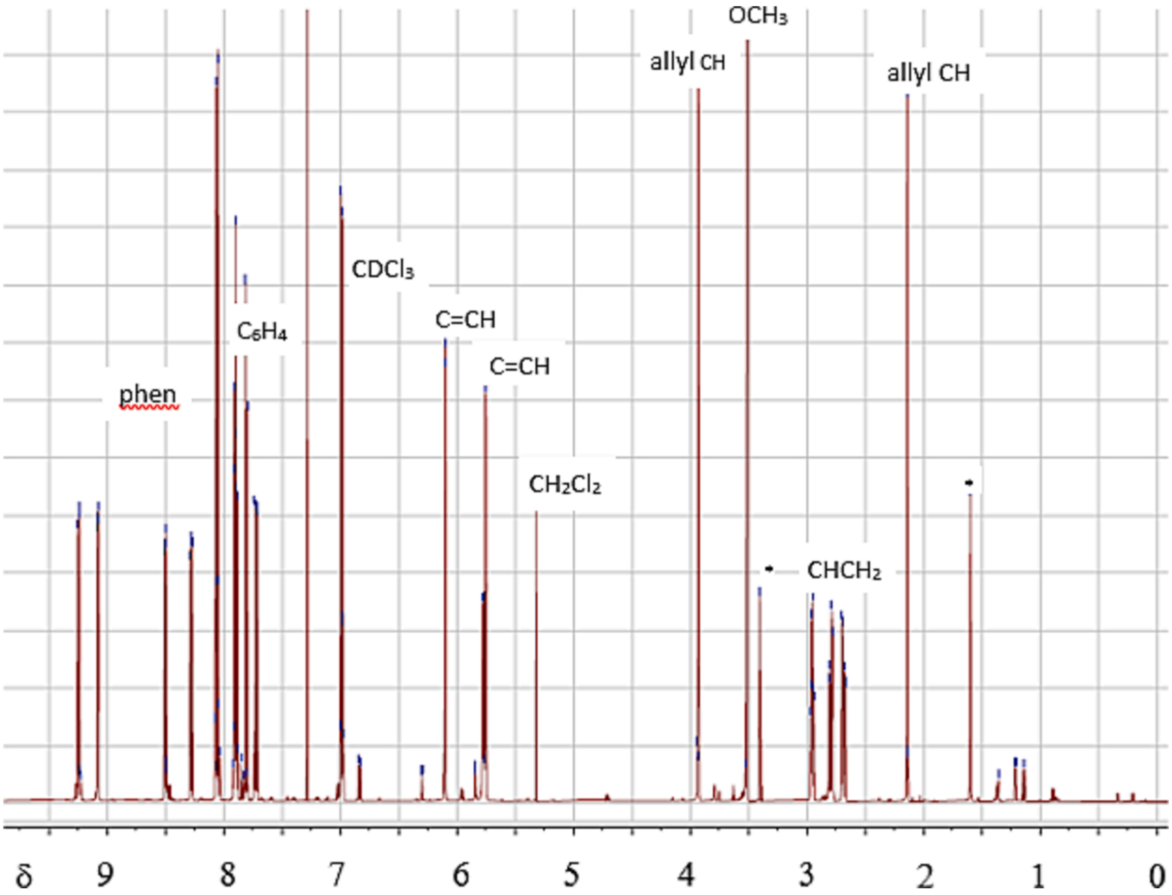


**Fig. 4.** The $^1$H NMR spectrum of one isomer of η$^3$-butadienyl complex **5** with assignments. (* represents impurity.).

anion on the alkyne, (b), is followed by migratory Mo-CO insertion, (c), and rearrangement, (d), to yield $\eta^3$-butadienyl **1**.

Addition of amine to the solutions of $[Mo(CO)_4L_2]$ and $XCH_2C{\equiv}CCH_2X$ in the presence of resin caused contraction of the beads and resulted in poor yields of **1**. However, adding the amine after filtration and removal of resin from the solution gave good yields of amide substituted $\eta^3$-butadienyl complexes **3**–**6** (Scheme 2). These were characterised by their elemental analysis and by IR and NMR spectroscopy, and data are given in the experimental section. All IR spectra exhibited two strong absorptions between 1890 and 1972 cm$^{-1}$ typical of a metal *cis*-dicarbonyl unit. The amide group at carbon 2 of the metal-bound $\eta^3$-butadienyl resulted in an absorption of medium intensity due to $C{=}O$ between 1635 and 1652 cm$^{-1}$, and a weak absorption near 3400 cm$^{-1}$ could be assigned to the amide NH stretch. Complexes **5** and **6** additionally gave an absorption in the range 1730–1745 cm$^{-1}$ for the ester group, and complex **5** gave rise to a pair of peaks at 1342 and 1519 cm$^{-1}$ due to the symmetric and asymmetric stretch of the $NO_2$ group, respectively. Reaction of the enantiomeric forms of **1** with an L-amino acid ester resulted in formation of two amide diastereomers of **5** or **6**. After careful fractional recrystallization of the mixed isomers, only the more insoluble isomer was isolated in sufficient purity and yield for NMR analysis. (The more soluble isomer retained impurities that could not be removed.) The $^1$H NMR spectrum of the less soluble isomer of complex **5** (with assignments) is shown in Fig. 4 as an example of the 2-substituted $\eta^3$-butadienyl complexes obtained and to aid further discussion. Other NMR spectra are given in the supporting information.

Complexes **3**–**6** all gave rise to two singlets near 2.0 and 3.9 ppm due to the allyl end of the butadienyl group, a pair of doublets near 5.7 and 6.2 ppm due to the double bond of this unit, and a triplet due to the amide proton occurred between 5.1 and 5.6 ppm. The propyl and hexyl protons of complexes **3** and **4** produced a series of multiplets in the range 0.45–2.12 ppm. The diastereotopic geminal protons $H_\beta$ and $H_{\beta'}$ were coupled to each other and to $H_\alpha$, giving rise to a typical AMX splitting pattern, as illustrated between 2.5 and 3 ppm in Fig. 4. Peak positions for the phen system and aromatic ring of amino acid complexes **5** and **6** were unexceptional, the phenyl ring ortho and meta protons of **6** showing typical coupling to the 4-fluoro substituent of 12 Hz and 6 Hz, respectively. The terminal allyl C(11) and central carbon C(12) of the metal-bound $\eta^3$-butadienyl unit gave rise to peaks near 48 and 57 ppm, respectively, and the terminal double bond C(13) = C(14) gave rise to peaks near 170 and 105 ppm, respectively. As expected, peaks for the metal-bonded carbonyls in all complexes appeared down field in the range 217–219 ppm. Attempts to grow crystals to confirm the differing isomeric structures of complexes **5** or **6** have been unsuccessful to date.

## 4. Conclusions

The synthetic route to 2-substituted $\eta^3$-butadienyl complexes has been significantly improved by incorporating a phosphonium halide functional group tethered to a resin. In addition to producing almost quantitative yield of the acyl chloride substituted complex **1**, use of a functionalised resin has combined two steps in the original synthetic method to reduce reaction time and temperature, and therefore energy consumption. The reaction can be conducted in a more sustainable and less toxic solvent, the resin is recyclable, and the waste produced is minimal. Table 2 gives the typical volumes of solvent required to make **1**, using either the two-step method of Scheme 1 or the resin process, and lists the hazards associated with each solvent. Use of the resin permits a 60 % reduction in total volume of solvents used in steps 2 and 3 of Scheme 1 and utilises a less hazardous and more sustainable medium for the reaction.

**Table 2**
Typical solvent volumes used in the two step and resin methods, and the solvent hazards associated with each solvent.

| Solvent and Method | Volume (cm$^3$)[a] | Solvent Hazards and Ranking[b] |
|---|---|---|
| Toluene, step 2 | 260 | H225, H304, H315, H336, H361, H373<br>Problematic and not sustainable. |
| Acetonitrile, step 2 | 17 | H225, H302,H312, H332, H319<br>Problematic and not sustainable. |
| Dichloromethane, step 3 | 25 | H315, H319, H336, H351<br>Problematic to hazardous. |
| Acetone, resin method | 50 | H225, H319, H336<br>Recommended to problematic, sourced sustainably. |

[a] A typical volume used to prepare 10 mmol of **1**.

[b] Reference [20].

Maximising conversion of $[Mo(CO)_4L_2]$ to **1** using the resins has made synthesis of amide derivatives **3**–**6** more efficient and four of the twelve principles of green chemistry have been successfully addressed: atom economy, prevention of waste, energy efficiency and use of catalysts. The synthetic versatility of **1** in formation of ester, thioester, selenoester and amide functionalised $\eta^3$-butadienyl complexes has been demonstrated previously, with typical overall yields based on $[Mo(CO)_4L_2]$ in steps 2 and 3 of Scheme 1 being in the range 45–60 % [18,19]. The new resin method, which combines these two steps, has improved this range for the amides to 69–84 %. Moving to the resin-based method of producing **1**, with its versatile acyl chloride group, will facilitate development of applications of this class of organometallic complex, whilst increasing the efficiency of the overall synthetic pathway. The use of functionalised polymeric resin as a packing in a continuous flow system to produce $\eta^3$-butadienyl complexes is being investigated.

## CRediT authorship contribution statement

**Annabelle G.W. Hodson:** Conceptualization, Methodology, Writing – original draft, Supervision, Investigation, Writing – review & editing. **Robert T. Mason:** .

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

The authors do not have permission to share data.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2023.116716.

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