Pergamon

Tetrahedron Letters 43 (2002) 691–693

TETRAHEDRON
LETTERS

Facile synthesis of polymer-supported cyclopentadienes

Nicholas E. Leadbeater*

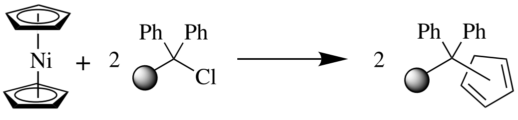
Department of Chemistry, King's College London, Strand, London WC2R 2LS, UK

Received 4 October 2001; revised 15 November 2001; accepted 21 November 2001

Abstract—A new route to polymer-supported cyclopentadienes using nickelocene as a source of cyclopentadiene is discussed. Nickelocene reacts directly with polymer-supported trityl chloride to yield the cyclopentadiene substituted analogue. With both Merrifield's resin and a PEG based bromo-functionalised resin the cyclopentadiene substituted analogues are formed on reaction of the iodide form of the resin with nickelocene in the presence of triphenylphosphine. © 2002 Elsevier Science Ltd. All rights reserved.

Catalysis using polymer-supported organometallics is continuing to gain interest within the chemical community.[1] Advantages of immobilizing metal complexes on derivitised polymer supports include ease of use and recyclability. One class of polymer-supported metal complex is those bearing a polymer-bound cyclopentadienyl unit. These complexes have found uses in, for example, hydroformylation,[2] hydrogenation[3] and olefin polymerisation catalysis.[4] In addition, there are many potential organic synthetic applications for supported cyclopentadiene complexes that have not been explored to date.

The conventional method for preparing polymer-supported cyclopentadiene ligands is by direct reaction of sodium cyclopentadienide (Na^+Cp^-) with a suitably derivitised support such as Merrifield's resin or other halogen terminated support. Problems of using this method are that purification of the resin at the end of the reaction can be difficult and time consuming; the sodium cyclopentadienide partaking in undesired side reactions leading to degradation of the polymer support or formation of intractable by-products coating the surface of the polymer spheres. This is especially the case when the polymer backbone contains polyglycol functionalities. In addition, loadings of cyclopentadiene on the support can vary greatly from one reaction to another meaning that the reaction is not always reliable.



1

2

Scheme 1.

Recent attention in our laboratory has been focused on the use of bis-cyclopentadienyl nickel (nickelocene) as a reagent for use in organic synthesis.[5] Nickelocene ($NiCp_2$) is commercially available or else readily prepared in high yield from cyclopentadiene and $NiCl_2$.[6] It is air and moisture stable although when stored for prolonged periods should be kept under a nitrogen atmosphere. The chemistry of nickelocene ($NiCp_2$) was explored in the 1960s by Werner and others,[7] but its potential use as a reagent for organic synthesis has only been exploited on a few occasions. It has however been shown that it is possible to alkylate the rings of nickelocene with the concomitant formation of the free substituted cyclopentadiene.[8–11] In this letter we show how this methodology can be used to prepare polymer-supported cyclopentadienes without the need to use the much more air and moisture sensitive ionic cyclopentadienide derivatives of alkaline metals such as Na^+Cp^-.

Our starting point was to study the reaction between polymer-supported trityl chloride **1** and nickelocene. Lemenovskii et al. have shown that, using the homogeneous analogue (i.e. triphenylmethyl chloride), it is possible to form triphenylmethylcyclopentadiene in good yield upon addition of half an equivalent of nickelocene.[9] We wanted to see if this was also possible using **1** and we are pleased to find that indeed it was. Addition of nickelocene to a THF solution containing **1** led, within 15 min, to the precipitation of $NiCl_2$, indicating that the reaction was taking place and that both

---

* Tel.: +0044 20 7848 1147; fax: +0044 20 7848 2810; e-mail: nicholas.leadbeater@kcl.ac.uk

0040-4039/02/$ - see front matter © 2002 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(01)02221-3

cyclopentadiene moieties on the nickelocene were being transferred to the polymer support (Scheme 1). Initially, a ratio of $NiCp_2$: supported trityl chloride of 1:1 based on the loading of the resin was used in order to maximise the formation of the polymer-bound cyclopentadiene **3**, but such a high ratio was found to be unnecessary. Equally good results were obtained using a ratio of $NiCp_2$: supported trityl chloride of 0.55:1 with a total reaction time of 30 min.[12] Using commercially available **1** with a loading of 1.27 mmol Cl/g resin, a loading of cyclopentadiene of 1.15 mmol/g was obtained.[13]

In an attempt to compare directly the nickelocene route to **2** with that using cyclopentadienide derivatives of alkaline metals, the reaction was performed using Na^+ Cp^-. This resulted in a lower loading of cyclopentadiene on the support and also led to decomposition products which were difficult to remove from the supported complex even after lengthy washing. This shows the advantage of the nickelocene route.

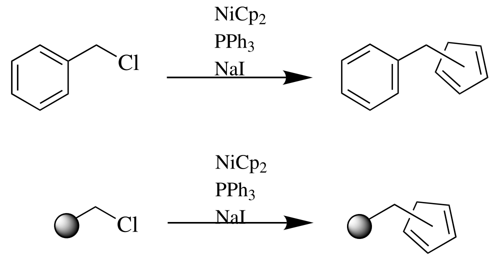
It is not unreasonable to suggest that attachment of a metal complex, especially one of a third row transition metal, to **2** may prove difficult due to the congestion around the cylopentadiene unit. As a result it would be desirable to attach the cyclopentadiene unit to a less hindered site on a polymer support such as, for example, on Merrifield's resin yielding **3**. However, attempts to prepare **3** by the direct reaction of Merrifield's resin with nickelocene were unsuccessful with only starting materials being detected even after agitating the reaction mixture for 1 week at room temperature. In an attempt to activate the Merrifield's resin, NaI was used as a halogen metathesis reagent (c.f. Finkelstein reaction) to yield polymer-supported benzyl iodide.[14,15] This was then reacted in situ with nickelocene but again with no success.

Hughes and Trujilo report that alkylation of cyclopentadienyl ligands of nickelocene can be greatly enhanced by addition of one equivalent of triphenylphosphine to the reaction mixture.[8] To investigate whether incorporating this modification into our reaction procedure would allow us to prepare **3**, we decided to look first at the reactivity of the homogeneous analogue, namely benzyl chloride. We found that if a DMF solution of benzyl chloride with one equivalent of nickelocene, one equivalent of triphenylphosphine and three equivalents of sodium iodide is stirred for 30 min the reaction mixture turns from green to purple (Scheme 2). Work-up of the reaction mixture allowed for the identification of the two products formed; namely the desired benzyl cyclopentadiene (characterised by comparison of NMR data with that in the literature[16]) in 89% yield and $NiCp(PPh_3)I$. This nickel complex is the same as that reported in the literature for the reaction of alkyl iodides with nickelocene. Adaptation of the reaction for use with Merrifield's resin was successful and **3** was formed in good yield (Scheme 2).[17]

Using commercially available Merrifield's resin with a loading of 1.8 mmol Cl/g resin, a loading of cyclopentadiene of 1.1 mmol/g was obtained. The reaction was found to take around 15 h to reach completion but monitoring is important because, at extended reaction times (>18 h) the desired product **3** was observed to undergo partial reaction with the $NiCp(PPh_3)I$ in solution giving a small quantity of a resin-bound nickel complex. In solution this is not a problem as contaminants can be removed in the work-up, but in the case of **3**, removal of nickel contaminants from the beads proves difficult.

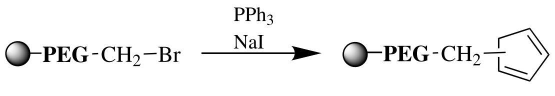
As discussed earlier, the problems of using sensitive ionic cyclopentadienide derivatives of alkaline metals as a source of cyclopentadiene are accentuated when the polymer backbone contains polyglycol functionalities. In an attempt to show the applicability of the nickelocene route to polymer-supported cyclopentadienes, we have prepared a cyclopentadiene derivitised PEG based resin. Reaction of NovaSyn® TG bromo resin[18] with nickelocene, PPh_3 and NaI in DMF leads to the desired substituted product **4** (Scheme 3).[19] Using NovaSyn® TG bromo resin with a loading of 0.35 mmol Br/g resin, a loading of cyclopentadiene of 0.28 mmol/g was obtained.[20] No decomposition or degradation of the PEG backbone occurs during the reaction and the supported complex can be easily obtained in pure form if the reaction is monitored and worked up after approximately 15 h (again prolonged reaction times lead to formation of small quantities of a resin-bound nickel complex).

In summary, a new route to polymer-supported cyclopentadienes has been developed using nickelocene as a source of cyclopentadiene, thereby overcoming the problems of using ionic cyclopentadienide derivatives of alkaline metals as a source of cyclopentadiene. Given the widespread use of cyclopentadienyl complexes in catalysis and as substrates for organic synthesis this route to the polymer-supported analogues may find uses as the starting point for a range of reactions.



3

Scheme 2.



4

Scheme 3.

Acknowledgements

The Royal Society is thanked for a University Research Fellowship. King's College London and Hoffmann La Roche are thanked for financial support. Dr M. M. Salter is thanked for useful discussions.

References

1. For recent reviews on polymer-supported catalysts and reagents, see: (a) Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. C.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815–4195; (b) Clapham, B.; Reger, T. S.; Janda, K. *Tetrahedron* **2001**, *57*, 4637–4662; (c) Shuttleworth, S. J.; Allin, S. M.; Wilson, R. D.; Nasturica, D. *Synthesis* **2000**, 1035–1074; (d) de Miguel, Y. R. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4213–4221.
2. See for example: (a) Dygutsch, D. P.; Eilbracht, P. *Tetrahedron* **1996**, *52*, 5461–5468; (b) Tung, H. S.; Brubaker, C. H. *J. Organomet. Chem.* **1981**, *216*, 129–137.
3. See for example: (a) Bhaduri, S.; Khwaja, H. *J. Chem. Soc., Dalton Trans.* **1983**, 419–423; (b) Grubbs, R. H.; Gibbons, C.; Kroll, L. C.; Bonds, W. D.; Brubaker, C. H. *J. Am. Chem. Soc.* **1973**, *95*, 2374.
4. Catalysts for olefin polymerisation have been immobilised on a number of cyclopentadiene derivitised supports. For examples, see: (a) Jezequel, M.; Dufaud, V.; Ruiz-Garcia, M. J.; Carrillo-Hermosilla, F.; Neugebauer, U.; Niccolai, G. P.; Lefebvre, F.; Bayard, F.; Corker, J.; Fiddy, S.; Evans, J.; Broyer, J. P.; Malinge, J.; Basset, J. M. *J. Am. Chem. Soc.* **2001**, *123*, 3520–3540; (b) Barrett, A. G. M.; de Miguel, Y. R. *Chem. Commun.* **1998**, 2079–2080.
5. Leadbeater, N. E. *J. Org. Chem.* **2001**, *66*, 7539.
6. Nickelocene can be purchased from a range of chemical manufacturers including Strem and Sigma-Aldrich. For a synthesis, see: Barnett, K. W. *J. Chem. Educ.* **1974**, *51*, 422.
7. For a discussion of early work on the chemistry of nickelocene, see: Werner, H. *J. Organomet. Chem.* **1980**, *200*, 335–348.
8. Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286.
9. Rufanov, K. A.; Kazennova, N. B.; Churakov, A. V.; Lemenovskii, D. A.; Kuz'mina, L. G. *J. Organomet. Chem.* **1995**, *485*, 173.
10. Mansson, J.-E.; Olsson, T.; Wennerstrom, O. *Acta Chem. Scand.* **1979**, *B33*, 307–308.
11. Moberg, C. *Acta Chem. Scand.* **1978**, *B32*, 149–151.
12. Polymer-supported trityl chloride (polymer matrix polystyrene crosslinked with 1% divinylbenzene) is commercially available from Nova-Biochem and Aldrich. In a typical reaction, nickelocene (130 mg, 0.7 mmol) was added to a Schlenk tube containing THF (20 ml) and **1** (0.5 g of a resin containing 1.27 mmol Cl/g support). After approximately 10 min, $NiCl_2$ was clearly seen to be precipitating in the form of a dark brown powder. After 30 min, the polymer beads were filtered together with the $NiCl_2$. Washing the beads thoroughly with THF, methanol, water, methanol and THF in this order removed the $NiCl_2$ leaving pure **2**.
13. Loading based on chloride microanalysis of **1** and **2**. Attempts were made to perform a chemical assay to determine loadings by reacting the resin bound cyclopentadiene with Cookson's reagent (4-phenyl-1,2,4-triazoline-3,5-dione) in a Diels–Alder reaction and then analysis of nitrogen content. However, we found that this gave anomalously high results for the loading because of competitive ene reactions between the resin backbone and the dione.
14. The Finkelstein reaction has been used previously for activation of Merrifield's resin with success. See for example: Lipshutz, B. H.; Blomgren, P. A. *Org. Lett.* **2001**, *3*, 1869–1871.
15. The reaction is performed using DMF as a solvent. This has the advantage over acetone as a solvent for the Finkelstein reaction in that the beads swell thereby opening more sites for reaction.
16. Licht, E. H.; Alt, H. G.; Karim, M. M. *J. Organomet. Chem.* **2000**, *599*, 275.
17. In a typical reaction, Merrifield's resin (250 mg of a resin containing 1.8 mmol Cl/g support) was added to a Schlenk tube containing a DMF (20 ml) solution of nickelocene (202 mg, 1.1 mmol), triphenylphosphine (290 mg, 1.1 mmol) and sodium iodide (495 mg, 3.3 mmol). After approximately 15 min the reaction mixture turned from deep green to purple–brown indicating that the reaction was taking place. The mixture was stirred for 15 h during which time the colour turned to a deep purple. After this time the polymer beads were filtered and washed thoroughly with THF, water, methanol and THF in this order, removing the excess NaI and leaving pure **3**.
18. The NovaSyn® TG bromo resin, commercially available from NovaBiochem, is a composite of low cross-linked polystyrene and 3000–4000 MW polyethylene glycol in which the ends of the PEG chains have been bromo functionalised.
19. In a typical reaction, NovaSyn® TG bromo resin (250 mg of a resin containing 0.35 mmol Br/g support) was added to a Schlenk tube containing an acetone (20 ml) solution of nickelocene (17 mg, 0.09 mmol), triphenylphosphine (23 mg, 0.09 mmol) and sodium iodide (14 mg, 0.27 mmol). After approximately 15 min the reaction mixture turned from green to purple–brown indicating that the reaction was taking place. The mixture was stirred for 15 h during which time the colour turned to a deep purple. After this time the polymer beads were filtered and washed thoroughly with THF, water, methanol and THF in this order, removing the excess NaI and leaving pure **5**. The ^1H MAS NMR spectrum of **5** shows evidence for the attachment of cyclopentadiene to the polymer-support, multiplets between 6.2 and 6.6 ppm being observed.
20. Loading based on bromide microanalysis of the NovaSyn® TG bromo resin and **4**.