ORGANOMETALLICS

Volume 22, Number 21, October 13, 2003

Communications

Preparation of Resin-Bound Metal Carbonyl Reagents and Preliminary Demonstration of Their Use

Nicholas E. Leadbeater* and Emma L. Sharp

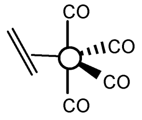
Department of Chemistry, King's College London, Strand, London, WC2R 2LS United Kingdom

Received July 28, 2003

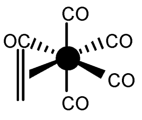
Summary: Polymer-supported ruthenium and molybdenum carbonyl fragments are prepared and their use is demonstrated in a ligand exchange reaction

Within the organic chemistry community, the past few years have seen a real burst of interest in the use of solid-supported catalysts and reagents.[1−3] There have been a number of reports of immobilization of organometallic complexes on functionalized polymer supports and their use as recoverable catalysts.[4,5] However, preparative inorganic and organometallic chemists do not seem to have taken advantage of using solid-supported synthesis in their chemistry, with only a few exceptions.[6−9] In this communication we report the preparation of polymer-supported metal olefin complexes and assess their use in ligand exchange reactions.

We have for some time been interested in the photochemical generation of transition metal carbonyl olefin complexes such as Ru(CO)$_4$(η^2-C$_2$H$_4$) (**1**) and Mo(CO)$_5$(η^2-C$_2$H$_4$) (**2**).[10] These complexes prove valuable synthetic intermediates for the preparation of a wide range of organometallic complexes since they are in essence sources of [RuCO)$_4$] and [Mo(CO)$_5$] fragments, the olefin ligands being very labile.[11,12]



Ru(CO)$_4$(η^2-C$_2$H$_4$) **1**



Mo(CO)$_5$(η^2-C$_2$H$_4$) **2**

---

* Corresponding author. E-mail: nicholas.leadbeater@kcl.ac.uk.

[1] Obrecht, D., Villagordo, J. M., Eds. *Combinatorial and Parallel Synthesis of Small-Molecular-Weight Compound Libraries*; Tetrahedron Organic Chemistry Series Vol. 17; Pergamon: London, 1998.

[2] Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; 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.

[3] Dörwald, F. Z. *Organic Synthesis on Solid Phase: Supports, Linkers, Reactions*; VCH: Weinheim, Chichester, 2000.

[4] For a review see: Leadbeater, N. E.; Marco, M. *Chem. Rev.* **2002**, *102*, 3217.

[5] For specific examples see: (a) Gibson, S. E.; Hales, N. J.; Peplow, M. A. *Tetrahedron Lett.* **1999**, *40*, 1417. (b) Comely, A. C.; Gibson, S. E.; Hales, N. J.; Peplow, M. A. *J. Chem. Soc., Perkin Trans. 1* **2001**, 2526. (c) Rigby, J. H.; Kondratenko, M. A.; Fiedler, C. *Org. Lett.* **2000**, *2*, 3917. (d) Rigby, J. H.; Kondratenko, M. A. *Org. Lett.* **2001**, *3*, 3683. (e) Maiorana, S.; Seneci, P.; Rossi, T.; Baldoli, C.; Ciraco, M.; de Magistris, E.; Licandro, E.; Papagni, A.; Provera, S. *Tetrahedron Lett.* **1999**, *40*, 3635. (f) Comely, A. C.; Gibson, S. E.; Hales, N. J. *Chem. Commun.* **2000**, 305. (g) Comely, A. C.; Gibson, S. E.; Hales, N. J. *Chem. Commun.* **1999**, 2075.

[6] Heinze, K. *Chem. Eur. J.* **2001**, *7*, 2922.

[7] Leadbeater, N. E.; van der Pol, C. *Chem. Commun.* **2001**, 599.

[8] (a) Beilstein A. E.; Grinstaff, M. W. *Chem. Commun.* **2000**, 50. (b) Schmidt, K. S.; Filippov, D. M.; Meeuwenoord, N. J.; van der Marel, G. A.; van Boom, J. H.; Lippert B.; Reedijk, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 375. (b) Robillard, M. S.; Valentjin, A. R. P. M.; Meeuwenoord, N. J.; van der Marel, G. A.; van Boom, J. H.; Lippert B.; Reedijk, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 3096.

[9] Tadesse, S.; Bhandari, A.; Gallop, M. A. *J. Comb. Chem.* **1999**, *1*, 184.

[10] (a) Leadbeater, N. E. *Inorg. Chem. Commun.* **2001**, *4*, 395. (b) Edwards, A. J.; Leadbeater, N. E.; Lewis J.; Raithby, P. R. *J. Organomet. Chem.* **1995**, *503*, 15. (c) Leadbeater, N. E.; Lewis, J.; Raithby, P. R. Edwards, A. J. *J. Organomet. Chem.* **1997**, *546*, 567.

[11] Leadbeater, N. E. *J. Chem. Soc., Dalton Trans.* **1995**, 2923.

[12] Leadbeater, N. E. *Organometallics* **1998**, *17*, 5913.

10.1021/om034072l CCC: $25.00 © 2003 American Chemical Society
Publication on Web 09/12/2003

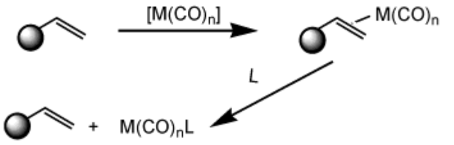
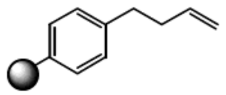


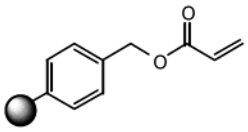
Figure 1. Concept for preparation and use of polymer-supported organometallic fragments.

One of the problems with the olefin complexes is that they have to be made just prior to use, and many are sensitive to air and moisture and decompose on removal of solvents. In solid-phase chemistry, the support can give increased stability to reactive intermediates by blocking bimolecular reaction steps.[6] As a result, we were interested in investigating the potential for the preparation of storable sources of $[RuCO)_4]$ and $[Mo(CO)_5]$ by immobilizing these fragments on olefin-functionalized polymer supports. We then wanted to see if it was possible to remove the metal fragments from the support in a simple ligand exchange reaction. The concept is shown in Figure 1.

We chose as supports butenyl polystyrene **3** and acryloyl polystyrene (so-called REM resin) **4**. The former is analogous to ethene and the latter to methyl acrylate, both of which have been used to prepare $Ru(CO)_4(\eta^2$-olefin) complexes previously. From solution-phase studies in our laboratories,[10] we would expect any complex formed with **3** to be less stable than that formed with **4** but, at the same time, less reactive in ligand transfer reactions. Both the olefin-functionalized polymer supports are commercially avaliable or else easily made from bromopolystyrene in the case of **3** or hydroxymethyl polystyrene in the case of **4**.

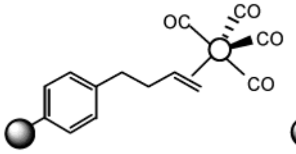


3

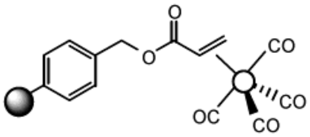


4

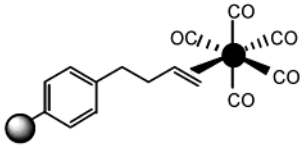
We initially focused attention on the ruthenium carbonyl complexes. The supported compounds were prepared by irradiating a dichloromethane solution containing the swollen support and $Ru_3(CO)_{12}$ using a broad-band UV source. After filtering off the beads and washing thoroughly, the supported metal complex was characterized using IR spectroscopy, comparing the spectum obtained with that of a sample of a homogeneous analogue (either **1** in the case of **5** or $Ru(CO)_4(\eta^2\text{-}H_2C{=}CHCO_2Me)$ in the case of **6**).[13] Metal loading was determined by measuring mass increase and also metal analysis by ICP-AA of the freshly prepared material, these methods for obtaining a good approximation of the metal loading being well accepted within the polymer-supported catalysis field. We also ran gel-phase ^{13}C NMR spectra on the supported alkene complexes to characterize them further. However, the alkene functionalities in the polymer backbone drown out any signals from the alkene moieties attached to the metal fragments. Using **3** and **4** with alkene functionality loadings of 3.9 and 1.1 mmol/g, respectively, we find that we can prepare **5** and **6** easily with metal loadings of 0.117 and 0.216 mmol/g, respectively. Molybdenum complexes **7** and **8** were prepared and characterized using an analogous methodology, $Mo(CO)_6$ being used as the starting metal carbonyl. Metal loadings of 0.65 and 0.85 mmol/g were obtained for **7** and **8**, respectively.



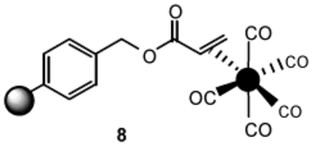
5



6



7



8

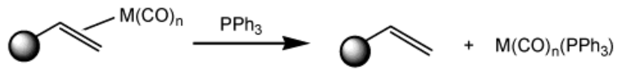
The ruthenium complexes are found to be more stable than their molybdenum conjeners. We find that **5** and **6** are stable in air at room temperature, no loss of activity being observed over the period of 2 days.[14] However, for storage longer than 2 days we keep the materials in a refrigerator (still in air) and find they last in excess of a month without any noticeable reduction in activity. We find that **7** and **8** are less stable, and we keep these stored in the refrigerator (again in air) prior to use. In line with our predictions, **7** is more stable than **8**, and **6** more than **5**.

Having prepared the supported complexes, we wanted to study their reactivity in simple ligand exchange reactions. Our idea was to be able to make the complexes and then use them as and when required rather than, in the case of the solution-phase analogues, preparing them every time prior to use. As a test reaction we have assessed the ligand exchange to a phosphine. Taking a solution of triphenylphosphine, we added 1 equiv of the supported complex and stirred the reaction mixture overnight.[15] As a control, we prepared solution-phase analogues and undertook similar ligand exchange reactions.

---

(13) Preparation of 5: To dichloromethane (100 mL) containing 3-butenyl polystyrene (100 mg, 0.388 mmol of alkene, resin loading of 3.9 mmol/g) was added $Ru_3(CO)_{12}$ (53 mg, 0.083 mmol). The mixture was irradiated using a broad-band UV source for 35 min while bubbling nitrogen through the reaction mixture to facilitate agitation. The beads were filtered, washed with dichloromethane and hexane (5 × 2 mL of each), and then dried under vacuum. A loading of $[RuCO)_4]$ of 0.117 mmol/g is obtained. **5**: IR $\nu_{(CO)}$: 2104(w), 2020(s), 1985(vs) [cf. **1**: IR $\nu_{(CO)}$: 2105(m), 2023(vs), 1995(s)]. Preparation of 6: The procedure was as with **5** but using REM resin (102 mg, 0.11 mmol of alkene, resin loading of 1.1 mmol/g) and $Ru_3(CO)_{12}$ (30 mg, 0.047 mmol). A loading of $[RuCO)_4]$ of 0.216 mmol/g is obtained. **6**: IR $\nu_{(CO)}$: 2121 (w), 2064(s), 2045(vs), 2006(m) [cf. $Ru(CO)_4(H_2C{=}CHCO_2Me)$: IR $\nu_{(CO)}$: 2121 (w), 2064(s), 2045(vs), 2006(m)]. Preparation of 7: The procedure was as with **5** but using 3-butenyl polystyrene (101 mg, 0.384 mmol of alkene) and $Mo(CO)_6$ (100 mg, 0.379 mmol) and an irradiation time of 25 min. A loading of $[MoCO)_5]$ of 0.65 mmol/g is obtained. **7**: IR $\nu_{(CO)}$: 2079 (m), 1984(vs), 1957(vs) [cf. $Mo(CO)_5(C_2H_4)$: IR $\nu_{(CO)}$: 2086 (m), 1976(vs), 1960(vs)]. Preparation of 8: The procedure was as with **6** but using REM resin (100 mg, 0.11 mmol of alkene) and $Mo(CO)_6$ (28 mg, 0.11 mmol) and an irradiation time of 25 min. A loading of $[MoCO)_5]$ of 0.85 mmol/g is obtained. **8**: IR $\nu_{(CO)}$: 2089 (m), 1976(vs, br) [cf. $Mo(CO)_5(H_2C{=}CHCO_2Me)$: IR $\nu_{(CO)}$: 2086 (m), 1976(vs), 1960(vs)].

(14) By "no loss of activity" we mean that the same amount of metal comes off the support and forms the desired metal phosphine complex when used in the ligand exchange reactions discussed later in this communication. Should the alkene complex decompose, then we would not expect it to form the phosphine complex, as the decomposition products would be expected to be either metal oxide or higher nuclearity metal complexes.



For the supported ruthenium complexes, we find that at room temperature the best ligand exchange results are obtained with **5**, 30% of the ruthenium coming off the support during the course of the time period giving $Ru(CO)_4(PPh)_3$ as compared to 25% with **6**. However, if these were to be used as transfer agents in synthesis, it would be necessary to obtain much greater quantities of the ruthenium coming off the support. We find that if the reaction mixtures are gently warmed (40 °C) overnight, much better results can be obtained. With **5**, we get 80% of the ruthenium coming off the support, and with **6** we get 75%. These results are also reflected in the case of **1** and $Ru(CO)_4(H_2C{=}CHCO_2Me)$, where better results were obtained after warming at 40 °C overnight with PPh_3 as opposed to performing the reaction at room temperature. The differences between **5** and **6** also mirror observations from solution-phase studies of olefin for phosphine ligand exchange reactions.[16]

We performed similar ligand exchange experiments with **7** and **8** and again find that the best results are obtained when warming the reaction mixture to 40 °C overnight. With **7**, only 45% of the metal comes off the support, this poor result being attributed at least in part to the low stability of **7** over time. With **8**, 85% of the metal comes off the support. The fact that the metal comes off the support is evident not only from the clear formation of product but also from the IR spectra of the beads after the reaction, which show the large reduction in intensity of the peaks attributed to the CO stretches of the metal carbonyl fragments.

In summary, we have prepared a number of polymer-supported metal carbonyl olefin complexes. They are easily made and are stable. We have shown in simple ligand exchange reactions that these supported complexes can be used as sources of metal carbonyl fragments. Work is now underway to expand the scope of the methodology and prepare other polymer-supported organometallic synthons.

Acknowledgment. The Royal Society is thanked for a University Research Fellowship (NEL), and the EPSRC is thanked for a DTA award (E.L.S.). Funding from King's College London is acknowledged.

OM034072L

---

(15) Representative example of the metal complexes in ligand exchange reactions: To dichloromethane (10 mL) containing **7** (26.8 mg, 0.018 mmol of metal complex assuming resin loading of 0.653 mmol/g) was added PPh_3 (4.7 mg, 0.018 mmol). The mixture was stirred overnight at 40 °C. The light brown beads were then filtered off and washed sequentially with dichloromethane and hexane (10 mL of each). The solvent was removed from the filtrate, leaving 5.9 mg of material, this corresponding to a mass increase of 1.8 mg. The ^{31}P NMR of the product mixture shows peaks for $Mo(CO)_5(PPh_3)$ [$\delta = 30$] and free PPh_3 [$\delta = -4$]. The presence of $Mo(CO)_5(PPh_3)$ is confirmed by the IR spectrum, which in the carbonyl region shows signals at 2072(s), 1945(vs), these corresponding to literature data for the complex [IR $\nu_{(CO)}$: 2072(s), 1947(vs), 1940(sh)]. This indicates that 45% of the $[Mo(CO)_5]$ complex has come off the support.

(16) Leadbeater, N. E. *J. Photochem. Photobiol., A* **1997**, *106*, 67.