

Preparation of resin-bound amine *N*-oxides and demonstration of their use in synthetic carbonyl cluster chemistry†

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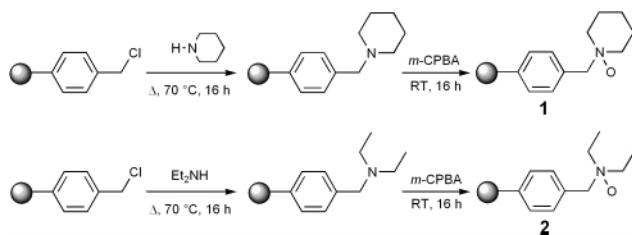
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The preparation of two polymer-supported amine *N*-oxides is presented and their application as an improved methodology for synthetic metal carbonyl cluster chemistry is illustrated.

Amine *N*-oxides are readily deoxygenated by metal carbonyls. This mild reaction offers a general method for the activation of the complexes towards the substitution of a carbonyl with another ligand, avoiding the extreme temperatures and pressures normally required for direct substitution of carbonyl groups.^{1,2} The main disadvantage of this route when applied to metal carbonyl clusters is that, in the case of unstable or highly-reactive complexes, it is often hard to remove all traces of amine *N*-oxide from the product. This has the drawback that, in subsequent reactions, a trace of *N*-oxide left in the starting material mixture can affect the reaction chemistry leading either to unwanted by-products or totally altering the course of the reaction.³

Within the organic chemistry community there is increasing interest in the development of polymer-supported catalysts and reagents for use in the synthesis of target molecules.⁴ One of the key advantages of immobilizing a catalyst or reagent on a polymer support is the ease of separation from the product mixture at the end of a reaction and hence the greatly simplified work-up needed. To date, synthetic inorganic and organometallic chemists do not seem to have taken advantage of using supported complexes in their chemistry. Here, we report the simple synthesis of two polymer-bound amine *N*-oxides and demonstrate their use and applicability in organometallic cluster chemistry through the synthesis of the ruthenium and osmium trinuclear cluster complexes $M_3(\text{CO})_{12-n}(\text{MeCN})_n$ ($M = \text{Ru}, \text{Os}; n = 1, 2$).⁵ The use of a supported *N*-oxide, as reported here, is significant since the cluster complexes can be prepared and purified very easily. These complexes have proven very useful as starting materials for a range of interesting cluster chemistry studies since their first reports in the early 1980s.^{6,7}

The desired polymer-supported amine *N*-oxides were prepared in two steps from Merrifield's resin using modified literature procedures (Scheme 1).^{8,9} Attention was focused on polymer-supported 'benzylpiperidine *N*-oxide' **1** and polymer-supported 'diethylbenzylamine *N*-oxide' **2**.[§] The final loading of *N*-oxide on the polymer support was calculated at ca. 0.9–1.0 mmol g resin⁻¹. Like their homogeneous analogues, **1** and **2** are



Scheme 1 The synthesis of polymer-supported *N*-oxides **1** and **2**.

† Electronic supplementary information (ESI) available: experimental details. See <http://www.rsc.org/suppdata/cc/b1/b100494h/>

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hygroscopic and are best stored under a blanket of dry nitrogen. Before use, water was removed by warming the beads gently (to no more than 35 °C) under vacuum.

The applicability and activity of the resin-bound amine *N*-oxides **1** and **2** were assessed initially by using them in the synthesis of the mono- and bis-acetonitrile-substituted clusters $\text{Ru}_3(\text{CO})_{11}(\text{MeCN})$ **3a** and $\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2$ **4a** following the method of Johnson and Lewis (Scheme 2).^{10¶} Product yields are shown in Table 1.

The selectivity for **3a** or **4a** depends primarily upon the acetonitrile: $\text{Ru}_3(\text{CO})_{12}$ ratio and upon the amine *N*-oxide: $\text{Ru}_3(\text{CO})_{12}$ ratio but it is almost impossible to obtain 100% pure **3a** via any amine *N*-oxide route. In polymer-supported reagent chemistry it is often the case that a slight excess of the resin-bound species is required since not all the active sites on the polymer are readily accessible. However, in order to form the monosubstituted complex **3a** we prefer to use exactly one equivalent of **1** or **2**. Although traces of $\text{Ru}_3(\text{CO})_{12}$ may then be present in the product, this compound is much less reactive and therefore less likely to perturb subsequent reactions than is **4a**, the impurity found if excess amine *N*-oxide is used.

The bis-substituted cluster is prepared in good yield using 2.5 equivalents of **1** or **2**. Again, the product can be easily separated from the amine *N*-oxide by filtering off the supported reagent.

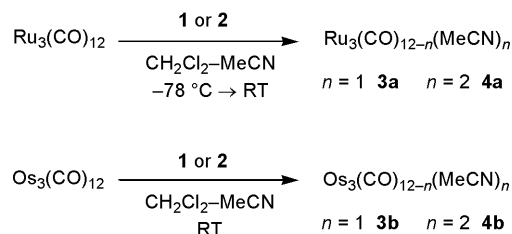
We studied the effect of temperature on the synthesis of **3a** and **4a** using **1** and **2** and found that it is essential to perform the addition of the amine *N*-oxide at or below 0 °C. This is of interest when compared with other reports of resin-bound reagents which suggest that reactions that need low temperatures when using homogeneous reagents can often be performed at room temperature using heterogeneous analogues because of the rate retarding effects of immobilization.

We find that a small quantity of a ruthenium complex remains attached to the beads, even after thorough washing. One possibility is that a small proportion of the $\text{Ru}_3(\text{CO})_{12}$ becomes tethered to the resin through more than one point of attachment. This is certainly possible given the close proximity of the amine *N*-oxide sites on the supported complex and the flexibility of the resin backbone. Once attached in this way, it may be difficult for the ruthenium complex formed to be removed from the support. This impacts on the recyclability of the resins but work is currently underway to alleviate this problem by removal of the trace metal before re-loading the resin with *N*-oxide.

As a continuation of our studies, we used the resin-bound *N*-oxides for the synthesis of $\text{Os}_3(\text{CO})_{11}(\text{MeCN})$ **3b** and $\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ **4b** (Scheme 2).¹¹ The mono-substituted complex was prepared by adding one equivalent of **1** or **2** to a dichloromethane–acetonitrile solution of $\text{Os}_3(\text{CO})_{12}$. Yields are shown in Table 1. Again, although traces of $\text{Os}_3(\text{CO})_{12}$ are

Table 1 Product yields

Product	Yield using 1 (%)	Yield using 2 (%)
$\text{Ru}_3(\text{CO})_{11}(\text{MeCN})$ 3a	83	84
$\text{Ru}_3(\text{CO})_{10}(\text{MeCN})_2$ 4a	85	92
$\text{Os}_3(\text{CO})_{11}(\text{MeCN})$ 3b	80	85
$\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2$ 4b	73	86



Scheme 2 The use of **1** and **2** in synthetic cluster chemistry.

present in the product, this is less likely to be problematic in subsequent reactions than is **4b**. The bis-substituted cluster is formed in good yield when three equivalents of **1** or **2** are added to a dichloromethane–acetonitrile solution of $\text{Os}_3(\text{CO})_{12}$.

With both the ruthenium and osmium clusters we find that **2** is a better reagent than **1**, giving higher yields and a more selective reaction. This could be due to the difference in steric bulk of the two amine oxides, the environment around the active centres in **2** being less crowded as compared with that around **1**. This is of key importance when considering the need for close encounter in the reaction between the clusters and the amine *N*-oxide.

In conclusion, the results presented here illustrate the applicability of **1** and **2** as reagents for the synthesis of substituted carbonyl clusters. They are particularly useful in the case of **3a** and **4a**, both of which are easily decomposed and where removal of the amine *N*-oxide from the reaction mixture is essential before performing further reactions.

We believe that it will be possible to use **1** and **2** as reagents for further chemistry and work is currently under way to confirm this assertion.

Experimental methods and spectroscopic data are presented as ESI.†

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Notes and references

§ Addition of an excess of amine (piperidine or diethylamine) to Merrifield's solid-phase resin (polystyrene crosslinked with 2% divinylbenzene; ca. 4.3 mmol Cl g resin⁻¹) in dioxane followed by heating overnight gives the resin-bound amine equivalent. Treatment of the resin-bound amines in chloroform with *m*-chloroperbenzoic acid at 0–25 °C gave the desired amine *N*-oxide.

¶ A dichloromethane–acetonitrile solution of $\text{Ru}_3(\text{CO})_{12}$ was cooled to –78 °C before adding the resin-bound amine *N*-oxide. The reaction mixture was then allowed to warm up to room temperature. Filtration of the solution to remove the resin-bound reagent followed by removal of the solvent leads to isolation of the product. The exploratory reactions were performed using ca. 20 mg $\text{M}_3(\text{CO})_{12}$ but can easily be scaled up to prepare larger quantities of product.

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