Polymer-Bound Mo Complexes

Stepwise Solid-Phase Synthesis of Di- and Trinuclear Metal Complexes**

Katja Heinze* and Juan D. Bueno Toro

Monodisperse oligomers play a central role in understanding the chemistry and the physics of polymeric organic and inorganic materials.^[1] The synthesis of monodisperse oligomers can be achieved by self-organization processes, random synthesis followed by separation processes, or by a step-bystep synthesis. All these strategies present their own advantages and disadvantages. Full control over chain length, end groups, and building-block sequence can be achieved using a stepwise approach. While this strategy is conceptually straightforward, it becomes increasingly tedious for higher oligomers owing to the purification steps needed. A particular elegant method for a repeated stepwise synthesis is the solidphase synthesis methodology which allows the purification of all intermediates by simple filtration. This strategy has been successfully applied to the synthesis of organic oligomeric compounds^[2] while organometallic oligonuclear complexes have not been prepared in a stepwise manner by solid-phase synthesis. Mononuclear metal complexes have been prepared by solid-phase synthesis^[3-12] for example, for biolabeling purposes or oligonucleotide-DNA/RNA binding studies and a dinuclear complex^[13] has been synthesized by simultaneous double metalation of a peptide bound to a solid phase.

We have already designed a system (polystyrene (PS)/ divinyl benzene-silyl ether linker-bidentate Schiff base ligand; **1b** in Scheme 1) which allows standard reactions of coordination and organometallic chemistry to be performed under solid-phase reaction conditions and the release of the final products from the insoluble matrix by fluoridolysis of the silyl ether linker.^[14,15] The first application of this solid-phase reaction system to the synthesis of di- and trimetallic complexes is reported herein.

The molybdenum carbonyl complexes reported herein possess several properties which make them suitable for solid-phase synthesis approach, these are: 1) substitutionally inert metal–ligand bonds (molybdenum–carbonyl and molybde-num–isonitrile bonds), 2) carbonyl and isonitrile ligands which serve as sensitive analytical probes for IR spectroscopic analysis of the solid-phase system,^[16,17] 3) highly colored complexes which permits UV/Vis spectroscopic analysis of

[*]	Dr. K. Heinze, DiplChem. J. D. B. Toro
	Anorganisch-Chemisches Institut
	Universität Heidelberg
	Im Neuenheimer Feld 270, 69120 Heidelberg (Germany)
	Fax: (+49) 6221-545-707
	E-mail: katja.heinze@urz.uni-heidelberg.de
	This would be also be be for a been and the stars of the formation of the stars of

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

^[**] This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. The generous support of Prof. Dr. G. Huttner is gratefully acknowledged.

Communications



Scheme 1. Synthesis of oligonuclear molybdenum carbonyl complexes by solution phase (1a-5a; X=H) and solid-phase $(1b-5b; X=PS-Si(iPr)_2)$ methods. 1) $[(CH_3CN)_3Mo(CO)_3]; 2) CN-(N\cap N'); 3) [(CH_3CN)_2Mo(CO)_4].$

the solid-phase system), and 4) thermally releasable carbonyl ligands which can be detected by thermogravimetric (TG) analysis of the solid-phase system.

The reactions performed are summarized in Scheme 1. Stirring the functionalized resin $\mathbf{1b}^{[15]}$ with an excess of [(CH₃CN)₃Mo(CO)₃] yields a reactive, immobilized [(diimine)Mo(CO)₃(CH₃CN)] complex which, after filtration and washing, can then be treated with an excess of the bridging isonitrile Schiff base ligand $CN-(N\cap N')^{[18]}$ to give the green, immobilized tricarbonyl isonitrile complex 2b (Scheme 1) (the replacement of the CO ligands by CN- $(N \cap N')$ does not occur under these conditions^[15]). This complex possesses a potential chelating diimine moiety. To this diimine unit a $\{Mo(CO)_4\}$ end cap is attached by treating the resin with an excess of $[(CH_3CN)_2Mo(CO)_4]$ to give the black dinuclear complex 4b (Scheme 1). Alternatively, the chain-growth steps can be repeated by adding $[(CH_3CN)_3Mo(CO)_3]$ and $CN-(N\cap N')$ to form the green dinuclear complex **3b** (Scheme 1). End capping with [(CH₃CN)₂Mo(CO)₄] furnishes the immobilized trinuclear complex 5b.

Thermogravimetric analysis of the metal-complex-functionalized resins 2b-5b shows that upon heating to 200 °C carbon monoxide is released. This result is confirmed by IR spectroscopic analysis of the gas phase and by thermogravimetric analysis of the free complex 2a (see Supporting Information). The amount of CO released at 200 °C corresponds well to the expected CO loss.^[19] This finding indicates the expected number of molybdenum–carbonyl units are present in the polymers 2b-5b.

As IR and UV/Vis spectra of these oligonuclear complexes are superpositions of spectra of corresponding mononuclear complexes (see the Supporting Information and refs. [18,20,21]) the complex growth on the solid support can



Figure 1. IR spectra of resins 2b and 3b.

conveniently be observed by these methods. Figure 1 shows the IR spectra of polymers **2b** and **3b**. The relative intensities of the v_{CO} band ($\tilde{\nu} = 1923$, 1856, 1828 cm⁻¹) and v_{CN} band ($\tilde{\nu} = 2080$ cm⁻¹) approximately double when a second {Mo(CO)₃CN–(N∩N')} fragment is added to resin **2b** to give **3b** (compared to the v_{CH} bands of the polystyrene backbone as internal standard). The same observation holds for resins **4b** and **5b** which additionally display the characteristic v_{CO} absorption bands ($\tilde{\nu} = 2013$ cm⁻¹) of the {Mo(CO)₄} fragments (Figure 2).

The colors of the complex-functionalized resins arise from several absorption bands in the visible region: π - π * absorptions of the diimine chromophore at around 400 nm, metal-to-ligand charge transfer (MLCT) bands of the [(diimine)Mo-(CO)₃(CN-R)] chromophore at around 680 nm and MLCT bands of the [(diimine)Mo(CO)₄] chromophore at around 600 nm.^[15,18,20,21] Consequently, the UV/Vis spectra of the immobilized di- and trinuclear complexes display absorption bands corresponding to the presence of the incorporated



Figure 2. IR spectra of resins 4b and 5b.

chromophores: resins **2b** and **3b** exhibit absorption bands at 400 and 680 nm, while resins **4b** and **5b** additionally absorb at 600 nm. Thus resins **2b** and **3b** with only [(diimine)Mo-(CO)₃(CN-R)] chromophores appear green and resins **4b** and **5b** with additional [(diimine)Mo(CO)₄] chromophores appear black.

Cleavage of the immobilized complexes **2b**, **3b**, **4b**, and **5b** with tetra-*n*-butylammonium fluoride and protonation of the soluble anionic complexes with acetic acid (Scheme 2) is

2b, 3b, 4b, 5b
$$\frac{1}{2}$$
 $\stackrel{-}{\longrightarrow}$ 2a, 3a, 4a, 5a + PS-Si(*i*Pr)₂-F

Scheme 2. Cleavage of the complexes 2a-5a from the support.

easily monitored by IR spectroscopy of the solution. The appearance of v_{CO} absorption bands in the IR spectra of the solutions indicates the release of the carbonyl complexes from the solid support into solution, protonation of the anionic complexes shifts all the v_{CO} absorption bands to higher energy as expected (see Experimental Section). Removing the insoluble support by filtration gives complexes 2a, 3a, 4a, and trinuclear complex 5a, respectively (Scheme 2). The soluble complexes 2a-5a were characterized by standard spectroscopic techniques. The ¹H NMR spectra of solutions of 2a-5a display several resonance signals in the aromatic region. Significant shifts of signals arising from the protons of the dangling $CN - (N \cap N')$ ligand in **2a** and **3a** are observed upon coordination of the $\{Mo(CO)_4\}$ unit to give **4a** and **5a**, respectively: the signal of the α proton of the pyridine part of the dangling ligand is shifted downfield by 0.6 ppm, the signal of the δ proton is shifted to upfield by 0.3 ppm, and the signal of the imine proton is shifted to higher field by 0.1 ppm as a result of coordination to the metal and the transoid/cisoid rearrangement of the ligand (Scheme 1, see Supporting Information).

For comparison purposes all these complexes have also been prepared by standard solution synthesis (Scheme 1, X =H; see Supporting Information). In the solution-phase synthesis fewer synthetic steps are needed for the synthesis of oligonuclear complexes. However, purification of intermediates is much more difficult. Additionally, in solution, exact stoichiometric conditions have to be complied with to avoid tedious separations. In contrast the solid-phase approach enables the use of simple purification techniques that are identical for all intermediates and optimization of each step is not needed. Moreover, regents can be used in excess to drive the reactions to completion and thus avoiding premature chain truncation. These advantages outweigh the additional steps needed for solid-phase synthesis (functionalization of the polymer and cleavage) especially for higher oligomers.

Experimental Section

1a, **1b** and (4-isocyanophenyl)pyridine-2-ylmethylene amine CN– $(N \cap N')$ were prepared by published procedures.^[15,18] All the polystyrene resins used were cross-linked with 2% divinyl benzene. Ligand loading of resin **1b** was 0.50 mmol g⁻¹. All manipulations were carried out under argon. For the solid-phase reactions a flask with a nitrogen inlet and a coarse-porosity fritted glass filter that allows addition and removal of solvents and reagents without exposure to the atmosphere was used. Spectroscopic measurements were carried out as described elsewhere.^[15]

2b: [(CH₃CN)₃Mo(CO)₃] (115 mg, 0.38 mmol) dissolved in CH₃CN (4 mL) was added to resin 1b (500 mg, 0.25 mmol) swollen in toluene (5 mL). The suspension was stirred for 20 min and the resin turned from yellow to blue. The solvents were removed by filtration and the polymer was washed with toluene/CH3CN (1:1) until IR spectroscopy indicated complete removal of the excess $[(CH_3CN)_3Mo(CO)_3]$. Owing to the sensitivity of the immobilized complex, the resin swollen in toluene was immediately treated with the ligand CN-(N \cap N') (79 mg, 0.38 mmol) dissolved in THF (5 mL). The polymer turned green immediately and after 30 min the resin was washed with THF until IR spectroscopy indicated complete removal of the excess $CN(N \cap N')$. The resin **2b** was dried in vacuo giving a green powder or used directly for further reactions. No soluble $[(\text{diimine})Mo(CO)_x]$ complexes were detected by IR spectroscopy at any stage of the reaction. IR (CsI): $\tilde{\nu} = 2084$ (m, CN), 1921 (vs, CO), 1857 (s, CO), 1826 cm⁻¹ (s, CO). UV/Vis: $\lambda_{max} = 660$ nm. TG: $\Delta m/m =$ 4.4% at 200°C.

3b: prepared by the same procedure as **2b** but starting from **2b** IR (CsI): $\tilde{\nu} = 2083$ (m, CN), 1923 (vs, CO), 1856 (s, CO), 1830 cm⁻¹ (s, CO). UV/Vis: $\lambda_{max} = 660$ nm. TG: $\Delta m/m = 7.7$ % at 200 °C.

4b: $[(CH_3CN)_2Mo(CO)_4]$ (110 mg, 0.38 mmol) dissolved in THF (4 mL) was added to resin **2b** (obtained from 500 mg **1b**) swollen in toluene (5 mL). After stirring for 2 h the resin was washed with THF until IR spectroscopy indicated complete removal of the excess $[(CH_3CN)_2Mo(CO)_4]$. The resin **4b** was dried in vacuo giving a black powder. No soluble $[(diimine)Mo(CO)_3]$ complexes were observed by IR spectroscopy at any stage of the reaction. IR (CsI): $\tilde{\nu} = 2086$ (m, CN), 2013 (m, CO), 1919 (vs, CO), 1851 (s, CO), 1826 cm⁻¹ (s, CO). UV/Vis: $\lambda_{max} = 710$ nm. TG: $\Delta m/m = 8.7\%$ at 200 °C.

5b: was obtained by the same procedure as for **3b** but by starting from **3b**. IR (CsI): $\tilde{\nu} = 2084$ (m, CN), 2014 (m, CO), 1922 (vs, CO), 1853 (s, CO), 1833 cm⁻¹ (s, CO). UV/Vis: $\lambda_{max} = 720$ nm. TG: $\Delta m/m = 11.2$ % at 200 °C.

Cleavage of the resin bound complexes: tetra-*n*-butylammonium fluoride (TBAF·3H₂O; 158 mg, 0.5 mmol) in THF (5 mL) was added to the appropriate resin **2b–5b** (starting from 500 mg of **1b**; 0.25 mmol) swollen in THF (3 mL). The suspension was stirred slowly for 6 h. The colored solution was collected by filtration and the resin was washed thoroughly with THF until the washings were colorless. The combined filtrates were carefully acidified with degassed acetic acid (0.05 mL) to give intensely colored solutions of the respective complexes. Characteristic IR absorption bands before acidification: **2a**⁻: $\tilde{\nu} = 2093$ (m, CN), 1914 (vs, CO), 1840 (s, CO), 1810 cm⁻¹ (s, CO); **3a**⁻: $\tilde{\nu} = 2094$ (m, CN), 2009 (m, CO), 1912 (vs, CO), 1897 (vs, CO), 1835 (s, CO), 1808 cm⁻¹ (s, CO); **5a**⁻: $\tilde{\nu} = 2094$ (m, CN), 2009 (m, CO), 1911 (vs, CO), 1900 (vs, sh, CO), 1835 (s, CO), 1808 cm⁻¹ (s, CO). The complexes were precipitated by adding diethyl ether/ hexanes. Overall yields (solid-phase synthesis, cleavage, and acidification) based on the loading of **1b** were between 40 and 85% (depending on the solubility of the complex). After cleavage, mass spectrometry of the remaining silyl fluoride resins indicated the complete removal of the complexes.^[14,15] The complexes were characterized by IR, UV/Vis, and ¹H NMR spectroscopy and the obtained data correspond to those obtained from the solution-phase synthesized complexes **2a–5a** (see Supporting information).

Received: May 9, 2003 [Z51849]

Keywords: bridging ligands · molybdenum · polymer-bound complexes · polynuclear complexes · solid-phase synthesis

- Electronic Materials: The Oligomer Approach (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, 1998.
- [2] F. Zaragoza Dörwald, Organic Synthesis on Solid Phase, Wiley-VCH, Weinheim, 2000.
- [3] M. S. Robillard, A. R. P. M. Valentijn, N. J. Meeuwenoord, G. A. van der Marel, J. H. van Boom, J. Reedijk, *Angew. Chem.* 2000, 112, 3226–3229; *Angew. Chem. Int. Ed.* 2000, 39, 3096–3099.
- [4] K. S. Schmidt, M. Boudvillain, A. Schwartz, G. A. van der Marel, J. H. van Boom, J. Reedijk, B. Lippert, *Chem. Eur. J.* 2002, 8, 5566-5570.
- [5] M. S. Robillard, J. S. Leith, G. A. van der Marel, J. H. van Boom, J. Reedijk, *Eur. J. Inorg. Chem.* 2003, 1529–2532.
- [6] D. R. van Staveren, N. Metzler-Nolte, Chem. Commun. 2002, 1406-1407.
- [7] K. S. Schmidt, D. V. Filippov, N. J. Meeuwenoord, G. A. van der Marel, J. H. van Boom, B. Lippert, J. Reedijk, *Angew. Chem.* 2000, 112, 383–385; *Angew. Chem. Int. Ed.* 2000, 39, 375–377.
- [8] S. I. Khan, A. E. Beilstein, M. W. Grinstaff, *Inorg. Chem.* 1999, 38, 418–419.
- [9] S. I. Khan, A. E. Beilstein, M. Sykora, G. D. Smith, X. Hu, M. W. Grinstaff, *Inorg. Chem.* **1999**, *38*, 3922–3925.
- [10] A. E. Beilstein, M. W. Grinstaff, Chem. Commun. 2000, 509-510.
- [11] I. Vargas-Baca, D. Mitra, H. J. Zulyniak, J. Banerjee, H. F. Sleiman, Angew. Chem. 2001, 113, 4765-4768; Angew. Chem. Int. Ed. 2001, 40, 4629-4632.
- [12] J. F. Valliant, R. W. Riddoch, D. W. Hughes, D. G. Roe, T. K. Fauconnier, J. R. Thornback, *Inorg. Chim. Acta* 2001, 325, 155– 163.
- [13] S. van Zutphen, M. S. Robillard, G. A. van der Marel, H. S. Overkleeft, H. den Dulk, J. Brouwer, J. Reedijk, *Chem. Commun.* 2003, 634–635.
- [14] K. Heinze, U. Winterhalter, T. Jannack, Chem. Eur. J. 2000, 6, 4203-4210.
- [15] K. Heinze, Chem. Eur. J. 2001, 7, 2922-2932.
- [16] B. Yan, Acc. Chem. Res. 1998, 31, 621-630.
- [17] B. Yan, H.-U. Gremlich, S. Moss, G. M. Coppola, Q. Sun, L. Liu, J. Comb. Chem. 1999, 1, 46–54.
- [18] K. Heinze, V. Jacob, Eur. J. Inorg. Chem., accepted.
- [19] The theoretical amount of CO loss is calculated according to the following formula: $\Delta m/m = 100 (n_{\rm CO} \times M_{\rm CO})/(M_{\rm resin} + M_{\rm complex})$ with $n_{\rm CO} = 3$, 6, 7, 10, $M_{\rm CO} = 28 \text{ gmol}^{-1}$, $M_{\rm resin} = 1500 \text{ gmol}^{-1}$ (resin loading 0.5 mmol g⁻¹) and $M_{\rm complex} = 387$, 774, 595, 982 g mol⁻¹ for resins **2b**, **3b**, **4b**, and **5b**, respectively, giving $\Delta m/m = 4.45$, 7.39, 9.36, 11.28% for resins **2b**, **3b**, **4b**, and **5b**, respectively.
- [20] K. Heinze, J. Chem. Soc. Dalton Trans. 2002, 540-547.
- [21] K. Heinze, V. Jacob, J. Chem. Soc. Dalton Trans. 2002, 2379– 2385.