

Solid- and Solution-Phase Synthesis of a Library of Mixed-Metal Complexes

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A solid-phase synthesis protocol has been developed for the stepwise assembly of mixed-metal dinuclear complexes built from chromium, molybdenum and tungsten and a directional bridging ligand. Complexes with all nine possible metal combinations have been prepared on polystyrene/divinylbenzene copolymer employing a metal-complex-compatible silyl ether linker. Release of the metal complexes from the polymeric support is accomplished by fluoridolysis under mild conditions. The metal sequence in these complexes is pre-

cisely determined by the reaction sequence and is retained under the applied reaction conditions as shown by IR, NMR and UV/Vis spectroscopic analysis of the cleaved soluble products. Additionally, the same complex library has been prepared by conventional solution-phase synthesis to allow evaluation of the advantages and disadvantages of the solid-phase synthesis method.

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Introduction

Monodisperse oligomers are essential for understanding the chemistry and the physics of polymeric organic and inorganic materials.^[1] Several synthetic strategies have been developed for their synthesis — self-organisation processes, random syntheses followed by separation processes or step-by-step syntheses — all of which have advantages and disadvantages. Full control over chain length, end groups and building-block sequence can be achieved using a stepwise assembly of building blocks.

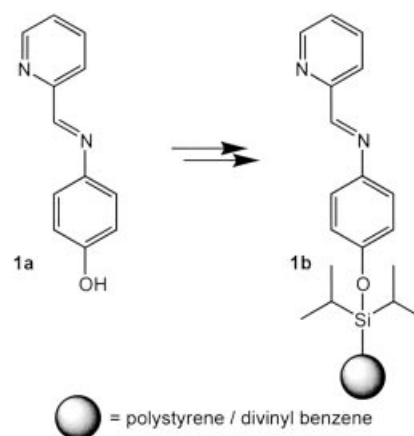
Although the step-by-step synthesis is straightforward, it becomes increasingly difficult for higher oligomers due to the purification steps needed. An elegant solution to this problem is synthesis on a solid support (solid-phase synthesis^[2]). This synthetic method, introduced by R. B. Merrifield for the synthesis of peptides,^[3] allows the purification of all intermediates by simple filtration. The development of new synthetic sequences which enable the (preferably combinatorial) solid-phase synthesis of non-natural, functionalised oligomeric compounds might aid the identification of synthetic oligomers with the capability of performing functions similar to those of peptides and proteins, for example catalysis, molecular recognition, signal transduction or conversion of chemical into mechanical energy.^[2]

Organometallic compounds, however, have only recently been synthesised by this method,^[4–17] and the solid-phase synthesis of organometallic complexes, in particular, remains a challenge.^[5,17] This is probably due to the fact that the

metal–ligand bonds of organometallic building blocks are much more labile than typical bonds of organic molecules, and thus the required orthogonal stability and reactivity of the polymer–molecule bond and the connections between the building blocks is much more difficult to achieve for organometallic complexes than for organic molecules.

A system satisfying the above criteria consists of a silyl ether linker between the molecule and the polymer support, which is cleavable by fluoride ions,^[18] and inert metal–isocyanide bonds between the organometallic building blocks.^[19]

The solution and solid-phase synthesis of homometallic di- and trinuclear complexes with carbonylmolybdenum complexes as building blocks has been reported recently.^[5] The extension of this synthetic strategy to assembling mixed-metal dinuclear complexes is reported in this contribution.



Scheme 1

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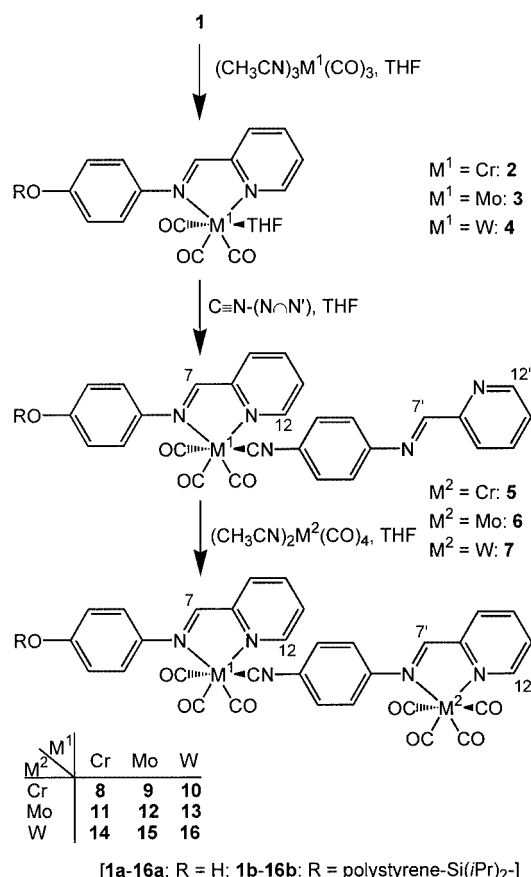
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Results and Discussion

General Solution- and Solid-Phase Synthesis

The hydroxy-functionalised Schiff-base ligand **1a** was used as starting point for the stepwise assembly of mixed-metal complexes. For the solid-phase synthesis approach **1a** was attached to polystyrene/divinylbenzene copolymer by a silyl ether linker to give the immobilised ligand **1b** (Scheme 1).^[4] The silyl ether allows the release of the final products of the solid-phase synthesis from the support by mild fluoridolysis.^[4,5,18]

Addition of a suitable $\{M^1(CO)_3\}$ source ($M^1 = \text{Cr}, \text{Mo}, \text{W}$) to **1a** or **1b** furnished the reactive soluble or polymer-bound complexes **2a–4a** and **2b–4b**,^[4] respectively (Scheme 2). These THF-containing complexes were subsequently treated with the bridging ligand (4-isocyanophenyl)(pyridin-2-ylmethylene)amine $\text{C}\equiv\text{N}-(\text{N}^{\cap}\text{N}')$ ^[19] to give the stable tricarbonyl isocyanide complexes **5a–7a** and **5b–7b**, respectively (Scheme 2). The potentially chelating diimine moiety of $\text{C}\equiv\text{N}-(\text{N}^{\cap}\text{N}')$ was finally coordinated to an $\{M^2(CO)_4\}$ fragment ($M^2 = \text{Cr}, \text{Mo}, \text{W}$) to give the dinuclear mixed-metal complexes **8a–16a** and **8b–16b**, respectively (Scheme 2). Each member of this “3 × 3 library” of mixed-metal complexes has been prepared by both solution- and solid-phase synthesis according to Scheme 2.



Scheme 2

All reactions in solution had to be performed under exact stoichiometric conditions to reduce the formation of side products such as $\text{X}-(\text{N}^{\cap}\text{N}')\text{M}(\text{CO})_4$ ($\text{X} = \text{CN}, \text{OH}$) or $\text{C}\equiv\text{N}-(\text{N}^{\cap}\text{N}')\text{M}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}^{\cap}\text{N}')$ which are difficult to remove after the synthesis of the dinuclear complexes (see Exp. Sect.).

Properties of the Soluble Complexes **5a–16a**

The two Schiff-base ligands present in the mononuclear complexes **5a–7a** give rise to several overlapping signals in the aromatic region of the ^1H NMR spectra (see Exp. Sect.). Pronounced chemical-shift differences are observed for the two imine protons $\text{H}^7/\text{H}^{7'}$ and the two protons α to the pyridine nitrogen atom ($\text{H}^{12}/\text{H}^{12'}$) due to the presence (H^7 : $\delta = 8.58$ – 8.89 ppm; H^{12} : $\delta = 9.30$ – 9.41 ppm) and absence ($\text{H}^{7'}$: $\delta = 8.73$ – 8.74 ppm; $\text{H}^{12'}$: $\delta = 8.53$ – 8.59 ppm) of a coordinated metal centre (see Scheme 2 and Exp. Sect. for atom numbering).

Complexes **5a–7a** display the typical ν_{CO} absorption pattern of a facially coordinated $\{M^1(\text{CO})_3\}$ fragment with disturbed local C_{3v} symmetry^[4,19–21] and an absorption band due to the coordinated isocyanide group of the $\text{C}\equiv\text{N}-(\text{N}^{\cap}\text{N}')$ ligand in their IR spectra (see Exp. Sect.). The absorption bands of **5a–7a** in the UV/Vis spectra between 613–655 nm can be assigned to a metal-to-ligand charge transfer transition of the $\{(\text{diimine})\text{M}^1(\text{CO})_3\}$ chromophore (see Exp. Sect.).^[4,19–21] The MLCT bands show negative solvatochromism as expected (see Supporting Information).^[22] A linear solvation-energy relationship analysis reveals that the most dominant term influencing the charge transfer is the polarity of the solvent, followed by the hydrogen-acceptor ability of the solvent (see Supporting Information).^[23]

The IR spectra of the dinuclear complexes are superpositions of the spectra of the corresponding tricarbonyl and tetracarbonyl complexes [disturbed local C_{3v} and C_{2v} symmetry of the $\text{M}(\text{CO})_n$ moieties, respectively];^[4,19–21] one ν_{CN} absorption and five ν_{CO} absorptions (two absorptions are not resolved) are observed in each case (Table 1). This finding was corroborated by DFT calculations of complexes **8a–16a** (see Supporting Information): the ν_{CO} and ν_{CN} absorptions of the $\text{M}^1(\text{CO})_3(\text{CNR})$ moieties are independent of the metal in the $\text{M}^2(\text{CO})_4$ fragment and vice versa (Figure 1; all standard deviations are below 2 cm^{-1}).

The ^1H NMR spectra of **8a–16a** consist of overlapping signals in the aromatic region. Particularly informative is the chemical shift of the two imine protons ($\text{H}^7/\text{H}^{7'}$: $\delta = 8.35$ – 8.90 ppm) and the two protons α to the pyridine nitrogen atom ($\text{H}^{12}/\text{H}^{12'}$: $\delta = 9.14$ – 9.40 ppm) which are influenced by metal coordination (cf. complexes **5a–7a**, Table 1, Exp. Sect.).

In the UV/Vis spectra of **8a–16a** two absorptions are observed in the visible region. These two absorptions arise from MLCT transitions of the $\{(\text{diimine})\text{M}^1(\text{CO})_3\}$ chromophore at lower energy and of the $\{(\text{diimine})\text{M}^2(\text{CO})_4\}$ chromophore at higher energy (Table 1).^[4,19–21]

A thorough examination of the spectroscopic data reveals that all dinuclear complexes exhibit similar but distinguish-

Table 1. Selected IR, UV/Vis and ^1H NMR spectroscopic data of **8a–16a** in THF

M^2/M^1	[a]	Cr	Mo	W
Cr	$\tilde{\nu}_{\text{CO}}^1$	1830	1826	1827
	$\tilde{\nu}_{\text{CO}}^2$	1849	1850	1849
	$\tilde{\nu}_{\text{CO}}^3$	1904	1906 (sh)	1903 (sh)
	$\tilde{\nu}_{\text{CO}}^4$	1912	1917	1911
	$\tilde{\nu}_{\text{CO}}^5$	2007	2007	2006
	$\tilde{\nu}_{\text{CN}}$	2073	2077	2073
	$\lambda_{\text{max}} (\epsilon)$	574 (4240)	585 (7480)	600 (6070)
Mo	$\delta_{\text{H}}(\text{imine})$	8.51 (2 H)	8.35, 8.47	8.49, 8.90
	$\tilde{\nu}_{\text{CO}}^1$	1827	1824	1827
	$\tilde{\nu}_{\text{CO}}^2$	1849	1848	1848
	$\tilde{\nu}_{\text{CO}}^3$	1910	1904	1909 (br)
	$\tilde{\nu}_{\text{CO}}^4$	1913	1917	
	$\tilde{\nu}_{\text{CO}}^5$	2013	2012	2013
	$\tilde{\nu}_{\text{CN}}$	2070	2078	2067
W	$\lambda_{\text{max}} (\epsilon)$	546 (6925)	536 (5575)	547 (5290)
		628 (5205)	600 (4545)	608 (4860)
	$\delta_{\text{H}}(\text{imine})$	8.54, 8.57	8.57, 8.61	8.57, 8.90
	$\tilde{\nu}_{\text{CO}}^1$	1825	1824	1826
	$\tilde{\nu}_{\text{CO}}^2$	1847	1849	1848
	$\tilde{\nu}_{\text{CO}}^3$	1894	1894	1895
	$\tilde{\nu}_{\text{CO}}^4$	1915	1918	1912
$\tilde{\nu}_{\text{CO}}^5$	$\tilde{\nu}_{\text{CO}}^5$	2006	2006	2006
	$\tilde{\nu}_{\text{CN}}$	2072	2075	2071
	$\lambda_{\text{max}} (\epsilon)$	551 (6000)	554 (7425)	561 (8580)
		643 (5210)	605 (5515)	606 (6860)
	$\delta_{\text{H}}(\text{imine})$	8.53, 8.87	8.57, 8.90	8.87, 8.90

[a] IR values given in cm^{-1} ; λ_{max} in nm, ϵ in $\text{M}^{-1}\cdot\text{cm}^{-1}$; δ in ppm.

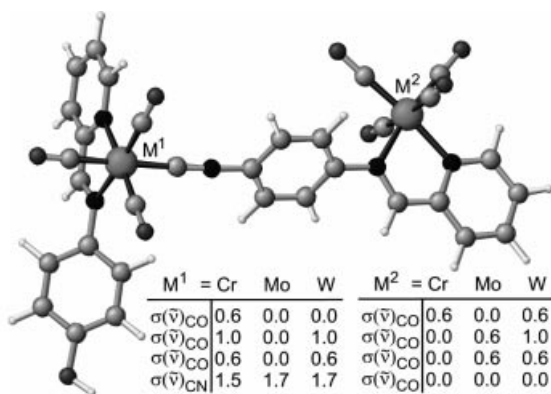


Figure 1. DFT (B3LYP, LANL2DZ) optimised geometry of complex **8a** ($\text{M}^1 = \text{M}^2 = \text{Cr}$) and standard deviations of the calculated average IR wavenumbers [cm^{-1}] of the $\text{M}(\text{CO})_n$ fragments of complexes **8a–16a**

able features. This allows the determination of the metal sequence of the complexes simply by a combination of IR (Figure 2), ^1H NMR and UV/Vis spectroscopic data (Table 1, Supporting Information).^[19]

There are five obvious criteria to distinguish complexes **8a–16a**:

- (i): $\tilde{\nu}_{\text{CN}} \geq 2075 \text{ cm}^{-1}$: $\text{M}^1 = \text{Mo}$ (**9a**, **12a**, **15a**) (Figure 2);
- (ii): $\tilde{\nu}_{\text{CO}}^5 \geq 2012 \text{ cm}^{-1}$: $\text{M}^2 = \text{Mo}$ (**11a**, **12a**, **13a**) (Figure 2);
- (iii): (i) and (ii): $\text{M}^1 = \text{M}^2 = \text{Mo}$ (**12a**) (Figure 2);

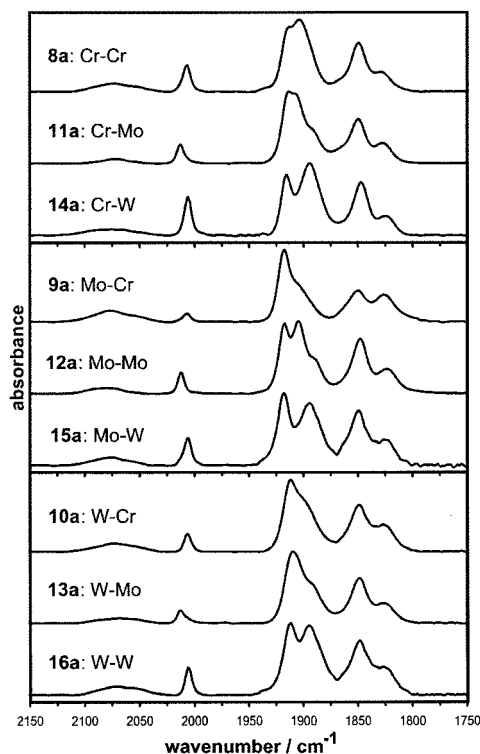


Figure 2. IR spectra of complexes **8a–16a** in THF

(iv): one $\delta_{\text{H}}(\text{imine}) \geq 8.87 \text{ ppm}$: M^1 or $\text{M}^2 = \text{W}$ (**10a**, **13a**, **14a**, **15a**);

(v): two $\delta_{\text{H}}(\text{imine}) \geq 8.87 \text{ ppm}$: $\text{M}^1 = \text{M}^2 = \text{W}$ (**16a**).

With these criteria the sequences of all complexes, except the Cr/W isomers **10a** and **14a**, can be unambiguously determined, for example (i) and (iv) describe complex **15a**. The two isomeric complexes **10a** and **14a** can be distinguished either by their IR spectroscopic pattern around 1900 cm^{-1} , as the difference between $\tilde{\nu}_{\text{CO}}^3$ and $\tilde{\nu}_{\text{CO}}^4$ amounts to 8 cm^{-1} for **10a** and 21 cm^{-1} for **14a** (Figure 2, Table 1), or by their MLCT absorptions in the UV/Vis spectra (Figure 3, Table 1). The energetic difference between the two MLCT absorptions is smaller for **10a** (2240 cm^{-1}) than for **14a** (3080 cm^{-1}) as expected from the MLCT absorptions of the corresponding mononuclear complexes (see Exp. Sect. and refs.^[4,21]).

Thus, all complexes can be distinguished by their spectroscopic signatures. These findings also imply that the complexes retain their metal sequence under the applied reaction conditions — there is no rearrangement, polymerisation or carbonyl scrambling.

In the solid state the IR data of **8a–16a** show that hydrogen bonds from the hydroxy group of the ligand **1a** are present ($\tilde{\nu}_{\text{OH}} = 3340\text{--}3469 \text{ cm}^{-1}$, see Exp. Sect.). These energies are compatible with the formation of $\text{OH}\cdots\text{O}$ hydrogen bonds between OH groups of different complexes or between the OH group and carbonyl ligands of different complexes.^[20,21]

For ligand **1a** and complexes **5a–7a** broad, structured absorption bands are observed in the region $3000\text{--}3455$

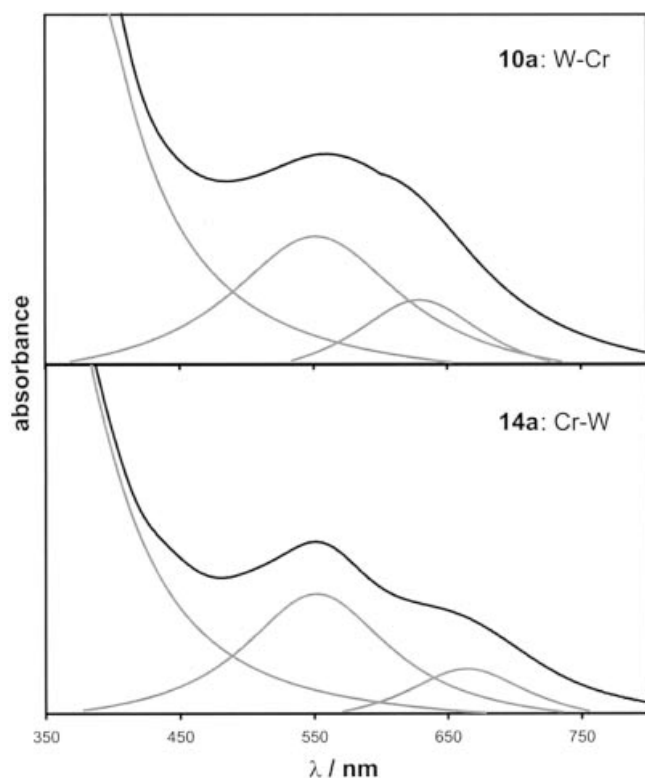


Figure 3. UV/Vis spectra of **10a** and **14a** in THF and deconvolution of the MLCT bands (Lorenz profiles)^[24]

cm^{-1} , which again suggests hydrogen-bonded structures. This has been confirmed by determination of the crystal structures of **1a** and **7a** (Figures 4 and 5). Intramolecular bond lengths and angles are unremarkable for both struc-

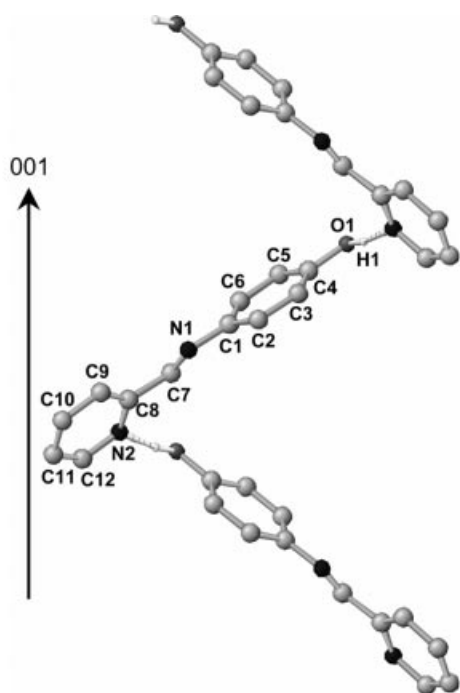


Figure 4. Structure of **1a** in the solid state

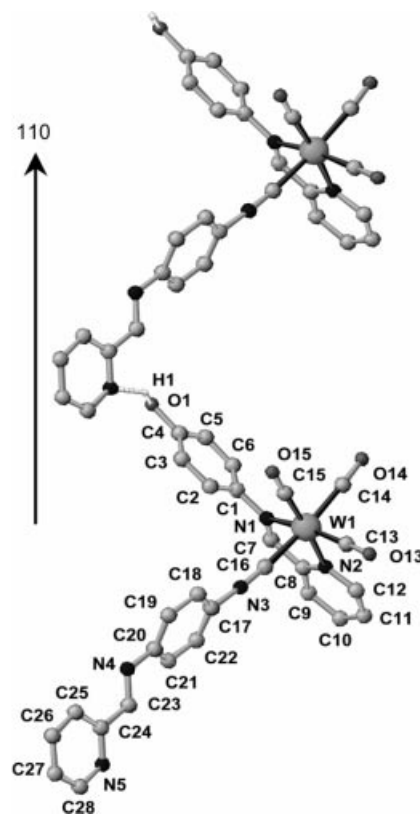


Figure 5. Structure of **7a** in the solid state

tures (Table 2), although the intermolecular connectivity is noticeable.

In both solid-state structures the OH group of the ligand forms hydrogen bonds to the nitrogen atom of a pyridine ring of a neighbouring molecule (**1a**: O1...N2; **7a**: O1...N5; Table 3, Figures 4 and 5). The molecules of **1a** form a zigzag chain along the 001 direction (a glide plane of the space group *Pbca*; repeat distance $c/2 = 6.8 \text{ \AA}$), while the molecules of **7a** form a linear chain along the 110 direction (repeat distance $13.9 \text{ \AA}$). The repeat distance for **7a** is more than twice as large as for **1a**. Thus, **7a** can be viewed as a higher homologue of **1a** with a $\text{W}(\text{CO})_3\text{-C}\equiv\text{N-(N}^\wedge\text{N}^\wedge)$ fragment inserted between the hydrogen donor and acceptor groups. In addition, this insertion introduces a directional change and thus straightens the zigzag chain of **1a** (angle between OH vectors of adjacent molecules $\pm 61^\circ$) to a linear chain of **7a** (angle between OH vectors of adjacent molecules 0°).

Properties of **5b–16b**

All polymer-bound complexes **5b–16b** were directly characterised on the solid support by IR and diffuse-reflectance UV/Vis spectroscopy, as well as thermogravimetric analyses (Table 4, Exp. Sect. and Supporting Information). The progress of the heterogeneous reactions can be monitored by IR spectroscopy due to the intense characteristic carbonyl and isocyanide absorption bands in this otherwise empty spectral region $1800\text{--}2100 \text{ cm}^{-1}$.^[5,25,26] These characteristic patterns allow the detection of $\{\text{M}(\text{CO})_3\}$ and

Table 2. Selected bond lengths [Å] and angles [°] for **1a** and **7a**

1a		7a	
		W1–N1	2.212(8)
		W1–N2	2.236(8)
		W1–C13	1.968(11)
		W1–C14	2.000(12)
		W1–C15	1.940(10)
		W1–C16	2.095(11)
		C13–O13	1.159(11)
		C14–O14	1.153(12)
		C15–O15	1.179(12)
		C16–N3	1.167(12)
		N1–C7	1.281(12)
		N2–C8	1.360(12)
		C7–C8	1.475(14)
C4–O1	1.3593(13)	C4–O1	1.376(12)
O1–H1	0.980(19)	O1–H1	1.12(11)
N1–C7	1.2743(14)	N4–C23	1.281(13)
N2–C8	1.3505(15)	N5–C24	1.322(13)
C7–C8	1.4709(16)	C23–C24	1.453(14)
		N1–W1–N2	72.2(3)
		N1–W1–C13	166.9(3)
		N1–W1–C14	94.0(4)
		N1–W1–C15	103.7(4)
		N1–W1–C16	87.0(3)
		N2–W1–C13	94.7(4)
		N2–W1–C14	96.8(4)
		N2–W1–C15	175.1(4)
		N2–W1–C16	89.8(3)
		C13–W1–C14	88.2(4)
		C13–W1–C15	89.3(4)
		C13–W1–C16	92.3(4)
		C14–W1–C15	86.2(4)
		C14–W1–C16	173.4(4)
		C15–W1–C16	87.3(4)
		N1–C7–C8–N2	–2.6(13)
N1–C7–C8–N2	–163.06(10)	N4–C23–C24–N5	174.8(11)
		C7–N1–C1–C2	131.3(11)
C7–N1–C1–C2	–148.66(11)	C23–N4–C20–C21	32.8(17)

Table 3. Hydrogen-bonding geometry (distances in Å, angles in °)

D–H...A	D–H	D...A	H...A	D–H...A
1a : O1–H1...N2 ^[a]	0.980(19)	2.7450(13)	1.772(20)	171.8(17)
7a : O1–H1...N5 ^[b]	1.12(11)	2.757(12)	1.74(11)	148(9)

^[a] Symmetry code $-x + 1/2, y, z + 1/2$. ^[b] Symmetry code $x + 1, y + 1, z$.

{M(CO)₄} fragments on the polymer support. The intensity of these absorption bands can be compared to the intensity of the ν_{CH} absorption bands of the polymer backbone as internal standard, thus allowing a semi-quantitative reaction control.^[5] The final immobilised dinuclear complexes display signals due to the {M(CO)₃} and {M(CO)₄} fragments and due to the isocyanide functional group (Table 4). The IR criteria (see above) for the different metal–metal sequences apply for the immobilised complexes as well, allowing the confirmation of the correct chain-growth even on a solid support:

Table 4. Analytical data of **8b–16b**

M ² /M ¹ [a]		Cr	Mo	W
Cr	$\tilde{\nu}_{\text{CO}}^1$ [b]	1846	1826 (sh)	1850
	$\tilde{\nu}_{\text{CO}}^2$ [b]	1890	1853	
	$\tilde{\nu}_{\text{CO}}^{3,4}$ [b]	1917	1922	1914
	$\tilde{\nu}_{\text{CO}}^5$ [b]	2008	2007	2008
	$\tilde{\nu}_{\text{CN}}$ [b]	2072	2081	2070
	λ_{max} [c]	420, 850	420, 730	420, 800
	$\Delta m/m_{\text{exp}}$ ($\Delta m/m_{\text{calcd.}}$ [d])	10.9 (11.7)	11.5 (11.5)	9.0 (10.9)
Mo	$\tilde{\nu}_{\text{CO}}^1$ [b]	1848	1822	1848
	$\tilde{\nu}_{\text{CO}}^2$ [b]	1888 (sh)	1851	1890 (sh)
	$\tilde{\nu}_{\text{CO}}^{3,4}$ [b]	1914	1921	1911
	$\tilde{\nu}_{\text{CO}}^5$ [b]	2015	2013	2013
	$\tilde{\nu}_{\text{CN}}$ [b]	2071	2086	2077
	λ_{max} [c]	420, 850	420, 800	420, 790
	$\Delta m/m_{\text{exp}}$ ($\Delta m/m_{\text{calcd.}}$ [d])	11.7 (11.5)	11.0 (11.2)	10.9 (10.6)
W	$\tilde{\nu}_{\text{CO}}^1$ [b]	1847	1824	1853
	$\tilde{\nu}_{\text{CO}}^2$ [b]	1904	1903	
	$\tilde{\nu}_{\text{CO}}^{3,4}$ [b]	1918 (sh)	1918	1918
	$\tilde{\nu}_{\text{CO}}^5$ [b]	2007	2007	2007
	$\tilde{\nu}_{\text{CN}}$ [b]	2073	2083	2075
	λ_{max} [c]	420, 890	420, 670	420, 940
	$\Delta m/m_{\text{exp}}$ ($\Delta m/m_{\text{calcd.}}$ [d])	11.2 (10.9)	11.5 (10.6)	10.4 (10.2)

^[a] IR values given in cm^{–1}; λ_{max} in nm, ϵ in M^{–1}·cm^{–1}; δ in ppm; $\Delta m/m$ in %. ^[b] In CsI. ^[c] In polytetrafluoroethylene. ^[d] $\Delta m/m_{\text{exp}}$ at 200 °C; $\Delta m/m_{\text{calcd.}} = 100 \times (7 \times M_{\text{CO}})/[M_{\text{resin}} + M_{\text{ligand}} + (7 \times M_{\text{CO}}) + M_{\text{M1}} + M_{\text{M2}}]$ with $M_{\text{CO}} = 28 \text{ g} \cdot \text{mol}^{-1}$, $M_{\text{resin}} = 1160 \text{ g} \cdot \text{mol}^{-1}$ (resin loading $0.9 \text{ mmol} \cdot \text{g}^{-1}$), $M_{\text{ligand}} = 207 \text{ g} \cdot \text{mol}^{-1}$, M_{M1} , $M_{\text{M2}} = 52$ (Cr), 96 (Mo), 184 (W) g·mol^{–1}.

(i): $\tilde{\nu}_{\text{CN}} \geq 2081 \text{ cm}^{-1}$: M¹ = Mo (**9b**, **12b**, **15b**) (Table 4);
(ii): $\tilde{\nu}_{\text{CO}}^5 \geq 2012 \text{ cm}^{-1}$: M² = Mo (**11b**, **12b**, **13b**) (Table 4);

(iii): (i) and (ii): M¹ = M² = Mo (**12b**) (Table 4).

The diffuse-reflectance spectra of the polymer-bound dinuclear complexes **8b–16b** show broad absorptions in the visible spectral region which can be assigned to the MLCT transitions of the two {(diimine)M(CO)_n} chromophores ($n = 3$ at lower energy; $n = 4$ at higher energy; Table 4).^[4,6]

These absorption bands are considerably shifted to lower energy relative to the MLCT bands of the soluble complexes as previously observed for similar immobilised complexes^[4–6] (Tables 1 and 4). As the energy of the MLCT absorptions is dominated by the solvent polarity (see above and ref.^[22]) the shift of the absorption bands of the immobilised complexes towards lower energy should be due to lower polarity of the polymer matrix. Even the degree of cross-linking influences the energy of the MLCT absorption bands. Resins with lower cross-linking (1% vs. 2% divinylbenzene) induce an even more pronounced bathochromic shift of the MLCT bands (Figure 6, Table 4 and ref.^[5]). Obviously, the resin polarity decreases with decreasing cross-linking. This lower polarity of the 1% cross-linked resin might be induced by the lower internal pressure due to the pressure dependence of the polarity.^[22] Thus, the MLCT absorption bands of the carbonyl complexes can be used to measure the resin polarity of different polymeric supports.

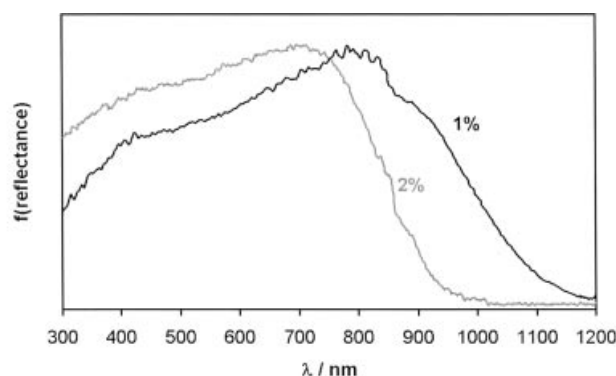


Figure 6. DRS UV/Vis spectra of **12b** (polystyrene with 1% and 2% divinylbenzene)

Thermogravimetric analyses of resins **8b–16b** show that carbon monoxide is released up to 200 °C, as detected from the IR spectrum of the gas above heated samples.^[5] The weight losses $\Delta m/m$ up to 200 °C of around 11% correspond well to the calculated weight losses (seven carbon monoxide molecules per immobilised complex) based on the initial ligand loading of the polymer (Figure 7, Table 4 and Supporting Information). This finding confirms the quantitative formation of the dinuclear complexes on the polymer, as the corresponding tricarbonyl complexes **5b–7b** show a weight loss, $\Delta m/m$, of around 6% (three carbon monoxide molecules per immobilised complex, Figure 7).

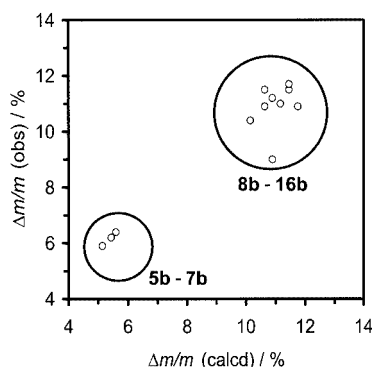
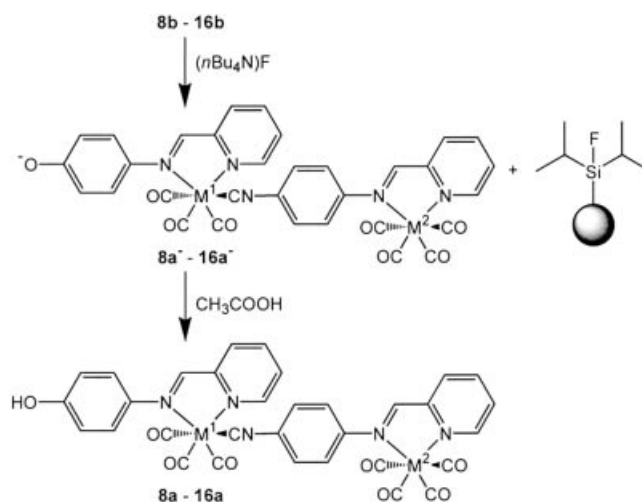


Figure 7. Correlation of experimental and calculated weight losses of resins **5b–16b**

In the final step of the solid-phase synthesis the dinuclear complexes were released from the support by cleavage of the Si–O bond with fluoride ions (Scheme 3).^[4,5,18] The soluble anionic complexes **8a[−]–16a[−]** can be detected in the IR and UV/Vis spectra of the cleavage solution (Table 5). All ν_{CO} absorption bands of **8a[−]–16a[−]** are shifted to lower energy, while the MLCT absorption bands are hypsochromically shifted, due to the negatively charged ligand, relative to the neutral parent complexes **8a–16a**.



Scheme 3

Protonation of **8a[−]–16a[−]** with acetic acid yields the neutral complexes **8a–16a**, which were characterised as above. In all cases no spectroscopic evidence was observed for the formation of side products, thus confirming the identity and stability of the polymer-bound complexes.

Advantages/Disadvantages of the Synthetic Methods

The obvious drawback of the solution synthesis is the difficulty of obtaining pure samples. The solution synthesis requires exact stoichiometric reaction conditions to avoid formation of side products (mainly monomeric tetracarbonyl complexes) and tedious purification procedures of the products.

In the solid-phase synthesis approach, however, excess reagents can be used, driving the reactions to completion and thus avoiding the formation of polymer-bound side products. The reaction progress on the solid phase can be monitored by IR spectroscopy.^[5,25,26] On the other hand the solid-phase synthesis requires adaptation of all reaction conditions and optimisation of the solid support. For the synthesis of the soluble complexes **8a–16a** identical reaction conditions can be applied irrespective of the metal centre to be incorporated (see Exp. Sect.). The synthesis of the polymer-bound complexes **8b–16b**, however, requires different reaction conditions depending on the metal fragment $\{\text{M}(\text{CO})_3\}$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) to be attached. The highly reactive chromium derivatives must be handled at low temperatures (−30 °C) to avoid formation of tetracarbonyl complexes, which seems to be promoted by the polymer support, while the less reactive carbonyl tungsten complexes must be activated at higher temperatures (60 °C); the solution reactions all proceed at room temperature (see Exp. Sect.). In addition, for reactions involving $\{\text{M}(\text{CO})_n\}$ ($\text{M} = \text{Cr}$ and W ; $n = 3, 4$) the properties of the polymer support have to be optimised. The degree of cross-linking (2% divinylbenzene in the initial experiments with molybdenum^[4,5]) has to be reduced to 1% divinylbenzene giving polymers

Table 5. IR and UV/Vis spectroscopic data of **8a**[−]–**16a**[−] in THF

M ² /M ¹	[a]	Cr	Mo	W
Cr	$\tilde{\nu}_{\text{CO}}^1$	1805	1805	1814
	$\tilde{\nu}_{\text{CO}}^2$	1830	1833	1841
	$\tilde{\nu}_{\text{CO}}^3$	1892	1894	
	$\tilde{\nu}_{\text{CO}}^4$	1905	1908	1897
	$\tilde{\nu}_{\text{CO}}^5$	2000	2002	2002
	$\tilde{\nu}_{\text{CN}}$	2088	2087	2084
	λ_{max}	460, 535, 600 (sh)	465, 540, 590 (sh)	433, 530, 600 (sh)
Mo	$\tilde{\nu}_{\text{CO}}^1$	1810	1808	1803
	$\tilde{\nu}_{\text{CO}}^2$	1832	1835	1832
	$\tilde{\nu}_{\text{CO}}^3$		1897	1880 (sh)
	$\tilde{\nu}_{\text{CO}}^4$	1897	1912	1897
	$\tilde{\nu}_{\text{CO}}^5$	2006	2009	2006
	$\tilde{\nu}_{\text{CN}}$	2071	2094	2084
	λ_{max}	470, 560, 600 (sh)	475, 544, 600 (sh)	468, 565, 600 (sh)
W	$\tilde{\nu}_{\text{CO}}^1$	1810	1804	1809
	$\tilde{\nu}_{\text{CO}}^2$	1830	1831	1831
	$\tilde{\nu}_{\text{CO}}^3$	1885	1884	1885
	$\tilde{\nu}_{\text{CO}}^4$	1905	1909	1903
	$\tilde{\nu}_{\text{CO}}^5$	2000	2000	2000
	$\tilde{\nu}_{\text{CN}}$	2084	2084	2079
	λ_{max}	468, 550, 600 (sh)	467, 550 (sh), 600 (sh)	450 (sh), 500 (sh), 600 (sh)

[a] IR values given in cm^{−1}; λ_{max} in nm.

with better swelling properties and larger effective pore-sizes. The better swelling properties of the low cross-linked resins impart a lower internal pressure (as shown by the “solvent” dependence of the MLCT absorption bands) and thus render the heterogeneous reactions faster and more selective.

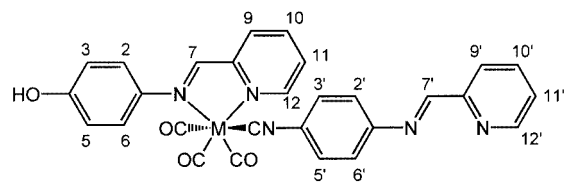
Conclusion

Dinuclear mixed-metal complexes with different metal centres at well-defined positions have been synthesised in solution and on a polymer support. The metal sequence of the soluble complexes can be determined by a combination of standard spectroscopic techniques and is retained under the applied reaction conditions. The solution synthesis is straightforward; however, the purification of the products is rather difficult, making this approach less suitable for longer-chain complexes. The solid-phase synthesis, although requiring more reaction steps (ligand immobilisation and product release) and differently optimised reaction conditions for each different reaction step, is much easier to accomplish. Furthermore, the solid-phase synthesis approach can easily be extended to longer-chain complexes by repeating the chain-growth reaction steps before the capping reaction without having to worry about solubility and purification of intermediates. This demonstrates the use of solid-phase synthesis methods in organometallic combinatorial chemistry.

Experimental Section

General: Unless noted otherwise, all manipulations were carried out under argon by means of standard Schlenk techniques. All sol-

vents were dried by standard methods and distilled under argon prior to use. **1a**^[4,5], **1b**^[4,5] and C≡N–(N[⊖]N')^[19] were prepared by literature methods. Polystyrene resins cross-linked with 1% divinylbenzene and with a ligand loading of 0.9 mmol·g^{−1} were used unless noted otherwise. The acetonitrile complexes were prepared from (cycloheptatriene)M(CO)₃ and (norbornadiene)M(CO)₄^[27,28] respectively, by reaction with CH₃CN (M = Cr, Mo, W). All other reagents were used as received from commercial sources. NMR spectra were recorded with a Bruker Avance DPX 200 at 200.15 MHz (¹H) at 303 K; chemical shifts are quoted in ppm with respect to residual solvent peaks as internal standards (CD₂Cl₂: δ = 5.32 ppm). IR spectra were recorded with a BioRad Excalibur FTS 3000 spectrometer using CaF₂ cells or CsI disks. UV/Vis/NIR spectra were recorded with a Perkin–Elmer Lambda 19, 0.2-cm cells (Hellma, Suprasil). DRS-UV/Vis spectra were measured with the same instrument using the Perkin–Elmer integrating sphere and poly(tetrafluoroethylene) as reference. Mass spectra were recorded with a Finnigan MAT 8400 spectrometer with a 4-nitrobenzyl alcohol matrix (FAB). Elemental analyses were performed by the microanalytical laboratory of the Organic Chemistry Department, University of Heidelberg. Thermogravimetric measurements were carried out with a Mettler TC 50, heating rate 10 K·min^{−1} under argon from 30–800 °C.



Solution Syntheses of 5a–7a: Freshly prepared [M(CO)₃(CH₃CN)₃] (M = Cr, Mo, W) was added to a solution of **1a** (198 mg, 1 mmol) in THF (40 mL). The blue solution was stirred until IR control indicated complete formation of the THF complexes **2a**, **3a** or **4a**. C≡N–(N[⊖]N') (207 mg, 1 mmol) was added as a solid and the

solution turned green immediately. The green solution was stirred until IR control indicated complete formation of the isocyanide complexes **5a**, **6a** or **7a**. The complexes were either isolated by addition of petroleum ether (boiling range 40–60 °C) and filtration of the precipitate or the solutions were used directly for the preparations of **8a–16a**.

5a: MS (FAB): m/z (%) = 541 (8) [M^+], 457 (48) [$M^+ - 3 CO$]. UV/Vis (THF): λ_{max} (ϵ) = 655 nm ($6330 M^{-1} \cdot cm^{-1}$). IR (THF): $\tilde{\nu}$ = 2071 (m, CN), 1915 (vs, CO), 1861 (s, CO), 1826 (s, CO) cm^{-1} . IR (CsI): $\tilde{\nu}$ = 3455 (br., OH), 2085 (m, CN), 1907 (vs, CO), 1838 (s, CO), 1811 (s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.0–7.6 (m, 10 H, $H^{2,6}$, $H^{2',6'}$, $H^{3,5}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.0 (m, 3 H, H^9 , H^{10} , $H^{10'}$), 8.23 (d, $^3J_{H,H}$ = 7.0 Hz, 1 H, H^9), 8.53 (br. s, 1 H, H^{12}), 8.58 (br. s, 1 H, H^7), 8.74 (br. s, 1 H, $H^{7'}$), 9.41 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, H^{12}) ppm. Satisfactory elemental analyses could not be obtained due to the inclusion of variable amounts of solvent molecules.

6a: MS (FAB): m/z (%) = 587 (31) [M^+], 559 (100) [$M^+ - CO$], 380 (95) [$M^+ - CN - (N^{\cap}N^{\cap})$]. UV/Vis (THF): λ_{max} (ϵ) = 613 nm ($3475 M^{-1} \cdot cm^{-1}$). IR (THF): $\tilde{\nu}$ = 2076 (m, CN), 1918 (vs, CO), 1855 (s, CO), 1824 (s, CO) cm^{-1} . IR (CsI): $\tilde{\nu}$ = 3388 (br., OH), 2089 (m, CN), 1911 (vs, CO), 1833 (s, CO), 1808 (s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.97 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, $H^{3,5}$), 7.3–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.0 (m, 3 H, H^9 , H^{10} , $H^{10'}$), 8.2–8.3 (m, 1 H, H^9), 8.59 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, H^{12}), 8.66 (s, 1 H, H^7), 8.73 (br. s, 1 H, $H^{7'}$), 9.30 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, H^{12}) ppm. Satisfactory elemental analyses could not be obtained due to the inclusion of variable amounts of solvent molecules.

7a: UV/Vis (THF): λ_{max} (ϵ) = 627 nm ($3225 M^{-1} \cdot cm^{-1}$). IR (THF): $\tilde{\nu}$ = 2071 (m, CN), 1913 (vs, CO), 1848 (s, CO), 1825 (s, CO) cm^{-1} . IR (CsI): $\tilde{\nu}$ = 3412 (br., OH), 2087 (m, CN), 1906 (vs, CO), 1831 (s, CO), 1807 (s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.01 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, $H^{3,5}$), 7.3–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.0 (m, 3 H, H^9 , H^{10} , $H^{10'}$), 8.2–8.3 (m, 1 H, H^9), 8.58 (br. s, 1 H, H^{12}), 8.74 (br. s, 1 H, $H^{7'}$), 8.89 (br. s, 1 H, H^7), 9.40 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, H^{12}) ppm. Satisfactory elemental analyses could not be obtained due to the inclusion of variable amounts of solvent molecules.

Solution Syntheses of 8a–16a: Freshly prepared $[(CH_3CN)_2M(CO)_4]$ ($M = Cr, Mo, W$) (1 mmol) was added to a solution of **5a**, **6a** or **7a** (1 mmol) in THF. The dark solution was stirred until IR control indicated complete formation of the dinuclear complex. Addition of petroleum ether (boiling range 40–60 °C) precipitated the product complexes, which were purified by repeated washings with diethyl ether (removal of mononuclear complexes) and recrystallisation from THF/diethyl ether.

8a: $C_{32}H_{19}Cr_2N_5O_8$ (705.5): calcd. C 54.48, H 2.71, N 9.93; found C 53.32, H 3.98, N 9.38. MS (FAB): m/z (%) = 705 (5) [M^+]. IR (CsI): $\tilde{\nu}$ = 3469 (br., OH), 2082 (m, CN), 2008 (m, CO), 1906 (vs, CO), 1833 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.1–7.7 (m, 10 H, $H^{2,6}$, $H^{2',6'}$, $H^{3,5}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.7–8.0 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.51 (br. s, 2 H, H^7 , $H^{7'}$), 9.29 (d, $^3J_{H,H}$ = 3.6 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 3.8 Hz, 1 H, $H^{12/12'}$) ppm.

9a: $C_{32}H_{19}CrMoN_5O_8$ (749.5): calcd. C 51.28, H 2.56, N 9.34; found C 51.46, H 3.49, N 9.36. IR (CsI): $\tilde{\nu}$ = 3449 (br., OH), 2091 (m, CN), 2009 (m, CO), 1910 (vs, CO), 1831 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.88 (br. d, 2 H, $H^{3,5}$), 7.1–7.5 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.7–7.9 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.35, 8.47 (s, 1 H, H^7 , $H^{7'}$), 9.14 (m, 2 H, $H^{12/12'}$) ppm.

10a: $C_{32}H_{19}CrN_5O_8W$ (837.4): calcd. C 45.90, H 2.29, N 8.36; found C 45.49, H 3.43, N 7.90. IR (CsI): $\tilde{\nu}$ = 3399 (br., OH), 2088 (m, CN), 2009 (m, CO), 1904 (vs, CO), 1831 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.9–7.1 (m, 2 H, $H^{3,5}$), 7.3–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.9–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.49 (s, 1 H, H^7), 8.90 (s, 1 H, $H^{7'}$), 9.29 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, $H^{12/12'}$) ppm.

11a: $C_{32}H_{19}CrMoN_5O_8$ (749.5): calcd. C 51.28, H 2.56, N 9.34; found C 51.43, H 3.53, N 9.62. MS (FAB): m/z (%) = 749 (5) [M^+], 665 (10) [$M^+ - 3 CO$]. IR (CsI): $\tilde{\nu}$ = 3449 (br., OH), 2091 (m, CN), 2014 (m, CO), 1909 (vs, CO), 1833 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.0–7.1 (m, 2 H, $H^{3,5}$), 7.2–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.54, 8.57 (s, 1 H, H^7 , $H^{7'}$), 9.20 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 5.0 Hz, 1 H, $H^{12/12'}$) ppm.

12a: $C_{32}H_{19}Mo_2N_5O_8$ (793.4): calcd. C 48.44, H 2.41, N 8.83; found C 48.17, H 3.55, N 8.47. MS (FAB): m/z = 792 (5) [$M^+ - H$], 380 (100) [$M^+ - CN - (N^{\cap}N^{\cap}) - Mo - 4 CO$]. IR (CsI): $\tilde{\nu}$ = 3340 (br., OH), 2088 (m, CN), 2013 (m, CO), 1913 (vs, CO), 1908 (vs, CO), 1833 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.99 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, $H^{3,5}$), 7.3–7.8 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.57 (s, 1 H, H^7), 8.61 (s, 1 H, $H^{7'}$), 9.20 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, $H^{12/12'}$), 9.30 (d, $^3J_{H,H}$ = 4.8 Hz, 1 H, $H^{12/12'}$) ppm.

13a: $C_{32}H_{19}MoN_5O_8W$ (881.3): calcd. C 43.61, H 2.17, N 7.95; found C 42.45, H 2.93, N 7.92. MS (FAB): m/z = 881 (30) [M^+], 853 (38) [$M^+ - CO$], 741 (45) [$M^+ - 5 CO$]. IR (CsI): $\tilde{\nu}$ = 3396 (br., OH), 2085 (m, CN), 2013 (m, CO), 1904 (vs, CO), 1830 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.9–7.1 (m, 2 H, $H^{3,5}$), 7.3–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.9–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.57 (s, 1 H, H^7), 8.90 (s, 1 H, $H^{7'}$), 9.20 (d, $^3J_{H,H}$ = 5.4 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 5.6 Hz, 1 H, $H^{12/12'}$) ppm.

14a: $C_{32}H_{19}CrN_5O_8W$ (837.4): calcd. C 45.90, H 2.29, N 8.36; found C 44.78, H 3.32, N 7.71. MS (FAB): m/z = 725 (15) [$M^+ - 4 CO$], 669 (8) [$M^+ - 6 CO$], 641 (10) [$M^+ - 7 CO$]. IR (CsI): $\tilde{\nu}$ = 3450 (br., OH), 2084 (m, CN), 2007 (m, CO), 1906 (vs, CO), 1831 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 6.9–7.1 (m, 2 H, $H^{3,5}$), 7.2–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.8–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.53 (s, 1 H, H^7), 8.87 (s, 1 H, $H^{7'}$), 9.31 (br. s, 1 H, $H^{12/12'}$), 9.40 (br. s, 1 H, $H^{12/12'}$) ppm.

15a: $C_{32}H_{19}MoN_5O_8W$ (881.3): calcd. C 43.61, H 2.17, N 7.95; found C 44.38, H 3.32, N 8.02. MS (FAB): m/z = 853 (5) [$M^+ - CO$], 797 (4) [$M^+ - 3 CO$], 685 (5) [$M^+ - 7 CO$]. IR (CsI): $\tilde{\nu}$ = 3393 (br., OH), 2093 (m, CN), 2009 (m, CO), 1910 (vs, CO), 1829 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.02 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, $H^{3,5}$), 7.2–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.7–8.0 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.57 (s, 1 H, H^7), 8.90 (s, 1 H, $H^{7'}$), 9.20 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, $H^{12/12'}$) ppm.

16a: $C_{32}H_{19}N_5O_8W_2$ (969.2): calcd. C 39.66, H 1.98, N 7.23; found C 40.77, H 2.69, N 7.98. MS (FAB): m/z = 969 (15) [M^+]. IR (CsI): $\tilde{\nu}$ = 3464 (br., OH), 2085 (m, CN), 2007 (m, CO), 1900 (vs, CO), 1831 (br., s, CO) cm^{-1} . 1H NMR (CD_2Cl_2): δ = 7.02 (m, 2 H, $H^{3,5}$, $^3J_{H,H}$ = 7.2 Hz), 7.2–7.7 (m, 8 H, $H^{2,6}$, $H^{2',6'}$, $H^{3',5'}$, H^{11} , $H^{11'}$), 7.9–8.1 (m, 4 H, H^9 , H^9 , H^{10} , $H^{10'}$), 8.87, 8.90 (s, 1 H, H^7 , $H^{7'}$), 9.32 (d, $^3J_{H,H}$ = 5.2 Hz, 1 H, $H^{12/12'}$), 9.40 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, $H^{12/12'}$) ppm.

Solid-Phase Synthesis of 5b–7b: Freshly prepared $[M(CO)_3(CH_3CN)_3]$ ($M = Cr, Mo, W$) (0.5 mmol), dissolved in

CH₃CN (15 mL), was added to resin **1b** (ca. 0.25 mmol), swollen in toluene (15 mL). The suspension was stirred (M = Cr: 20 min, –30 °C; M = Mo: 20 min, 20 °C; M = W: 60 min, 60 °C) and the resin turned from yellow to blue. The solvents were removed by filtration and the polymer was quickly washed with toluene/CH₃CN (1:1) until IR spectroscopy of the solution indicated complete removal of the excess [M(CO)₃(CH₃CN)₃]. Due to the sensitivity of the immobilised complex, the resin swollen in toluene was immediately treated with the ligand C≡N–(N[⊖]N[⊕]) (104 mg, 0.5 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 C≡N–(N[⊖]N[⊕]). The resin was dried under reduced pressure giving a dark green powder or used directly for further reactions. No soluble (diimine)Mo(CO)_x complexes were observed by IR spectroscopy at any stage of the reaction.

5b: IR (CsI): $\tilde{\nu}$ = 2074 (m, CN), 1919 (s, CO), 1863 (m, CO), 1833 (m, CO) cm^{–1}. UV/Vis: λ_{max} = 420 (sh), 880 (br.) nm. TG (200 °C): $\Delta m/m$ = 6.4% (calcd. 5.8%).

6b: IR (CsI): $\tilde{\nu}$ = 2084 (m, CN), 1922 (s, CO), 1857 (m, CO), 1826 (m, CO) cm^{–1}. UV/Vis: λ_{max} = 420 (sh), 810 (br.) nm. TG (200 °C): $\Delta m/m$ = 6.2% (calcd. 5.4%).

7b: IR (CsI): $\tilde{\nu}$ = 2072 (m, CN), 1913 (s, CO), 1850 (m, CO), 1822 (m, CO) cm^{–1}. UV/Vis: λ_{max} = 420 (sh), 830 (br.) nm. TG (200 °C): $\Delta m/m$ = 5.9% (calcd. 5.1%).

Solid-Phase Synthesis of 8b–16b: Freshly prepared [M(CO)₄–(CH₃CN)₂] (0.5 mmol) dissolved in THF (15 mL) was added to resin **5b**, **6b** or **7b** (ca. 0.25 mmol), swollen in THF (5 mL). After stirring at 20 °C for 2 h, the resin was washed with THF until IR spectroscopy indicated complete removal of the excess [M(CO)₄–(CH₃CN)₂]. The resin was dried under reduced pressure giving a black powder. No soluble (diimine)M(CO)_x complexes were observed by IR spectroscopy at any stage of the reaction.

Cleavage Procedure: A solution of tetra-*n*-butylammonium fluoride TBAF·3H₂O (2 equiv.) in THF was added to a suspension of the appropriate resin in THF (10 mL). The suspension was stirred at ambient temperature for 6 h. IR spectroscopy indicated the formation of the anionic complexes **8a[–]**–**16a[–]**. The polymer was filtered and washed with THF until the wash solutions were colourless. The combined filtrates were acidified with acetic acid, concentrated under reduced pressure and the complexes were precipitated by addition of diethyl ether. Recrystallisation as above yielded the complexes **8a**–**16a**. After cleavage, mass spectrometry of the remaining silyl fluoride polymer indicated complete removal of the complexes.^[18]

Crystallographic Structure Determinations: The measurements were carried out with an Enraf–Nonius Kappa CCD diffractometer using graphite monochromated Mo-*K*_α radiation. The data were processed using the standard Nonius software.^[29] All calculations were performed using the SHELXT PLUS software package. Structures were solved using direct or Patterson methods with the SHELXS-97 program and refined with the SHELXL-97 program.^[30] Graphical handling of the structural data during refinement was performed using XMPA^[31] and WinRay.^[32] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares calculations. Data relating to the structure determinations are collected in Table 6. CCDC-233938 (**1a**) and -233939 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Computational Methods: Density functional calculations were carried out with the Gaussian03/DFT^[33] program series. The B3LYP formulation of density functional theory was used employing the LanL2DZ basis set.^[33] Harmonic vibrational frequencies and IR

Table 6. X-ray crystallographic data of **1a** and **7a**

	1a	7a
Empirical formula	C ₁₂ H ₁₀ N ₂ O	C ₂₈ H ₁₉ WN ₅ O ₄ ·1.6THF
Formula mass	198.22	673.34·1.6THF
Crystal dimension [mm]	0.50 × 0.20 × 0.20	0.15 × 0.10 × 0.08
Crystal system	orthorhombic	triclinic
Space group (no.)	<i>Pbca</i> (61)	<i>P</i> $\bar{1}$ (2)
<i>a</i> [Å]	15.611(3)	9.2510(19)
<i>b</i> [Å]	9.285(2)	9.4420(19)
<i>c</i> [Å]	13.678(3)	21.324(4)
α [°]	90	84.46(3)
β [°]	90	87.01(3)
γ [°]	90	83.45(3)
Cell volume [Å ³]	1982.6(7)	1840.2(6)
Molecular units per cell	8	2
μ [mm ^{–1}]	0.087	3.184
Density (calcd.) [g cm ^{–3}]	1.328	1.420
<i>T</i> [K]	200	200
Scan range (2 θ) [°]	5.2–60.1	4.4–55.2
Scan speed [s·frame ^{–1}]	10	20
Measured reflections	22451	11662
Unique reflections	2902	8162
Obs. reflections [<i>I</i> ≥ 2 σ (<i>I</i>)]	2119	4691
Parameters refined	176	424
Max./min. of residual electron density [e·Å ^{–3}]	0.24/–0.19	3.00/–1.21
Agreement factors	<i>R</i> ₁ = 4.2%	<i>R</i> ₁ = 7.6%
(<i>F</i> ² refinement)	<i>R</i> _w = 10.9%	<i>R</i> _w = 18.1%

intensities were calculated by numerical second derivatives using analytically calculated first derivatives. Frequencies are not scaled.

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