

Stepwise Assembly of Mixed Metal Dinuclear Carbonyl Complexes

Katja Heinze*^[a] and Volker Jacob^[a]

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The one-pot/three-step solution synthesis of a library of nine directional, dinuclear mixed-metal complexes composed of different metal-carbonyl units ($M = \text{Cr}, \text{Mo}, \text{W}$) and a bifunctional bridging isocyanide Schiff-base ligand is described. The well-defined metal sequence in these complexes with

Cr, Mo, and W in two positions can be determined post-synthesis by a combination of spectroscopic methods.

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Introduction

One-dimensional materials are interesting with respect to their exceptional physical and chemical,^[1–3] such as photo-physical or electrochemical properties.^[4] However, the synthesis of metal-containing chain complexes with defined chain lengths is difficult to achieve. An elegant approach to overcome the problem of obtaining mixtures of complexes with different chain lengths is the design and synthesis of special ligands which allow for only one definite chain length. This approach has been used, for example, in the synthesis of oligo- α -pyridylamino ligands which form string complexes with two, three, four, five, and seven metal centres depending on the length of the ligand.^[5–8] The problem is thus transferred to organic synthesis of the ligand while metal incorporation is subject to self-organisation processes. A particular drawback of this approach is the need to synthesise special ligands for each chain length and the limited control over the metal sequence within the chain, as usually only homometallic complexes are obtained.

The construction of oligonuclear metal complexes may also be achieved by the stepwise connection of stable metal complexes through covalent bonds using a protection/deprotection strategy which has been successfully applied, for example, to defined ferrocene oligomers^[9,10] and oligo-porphyrin systems.^[11–14]

A similar, albeit more difficult, approach is the controlled stepwise assembly of building blocks through coordinative bonds. Such a procedure should allow the synthesis of complexes with any desired chain length controlled by the number of repetition cycles. Repeated complex activation and subsequent addition of a metal-bridging ligand fragment to a starting complex has been employed for the synthesis of

oligonuclear ruthenium–pyrazine complexes.^[15] Sequential protection/deprotection of a potential coordination site of a coordinated ligand has allowed a step-by-step synthesis of oligonuclear ruthenium and osmium polypyridine complexes.^[16] Redox activation has been used to construct oligomeric iron/platinum complexes by a stepwise procedure.^[17]

The repeated alternate addition of metal complex fragments and bridging ligands would be a procedure which allows full control over chain length, metal, and ligand sequence within the backbone. An important prerequisite for this method is the kinetic stability of the metal–ligand bonds within the chain so that undesired self-organisation processes, which would ultimately lead to the thermodynamically most stable species (e.g. scrambled metals, oligomer mixtures, or polymers), are suppressed.

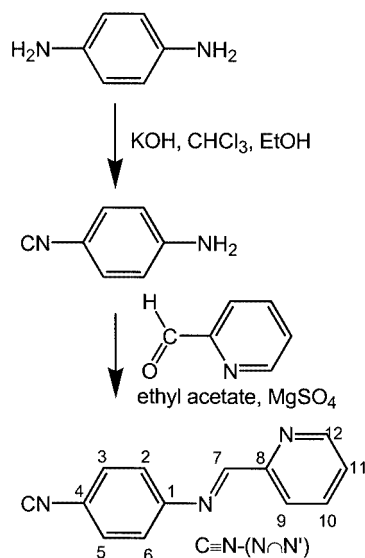
The stepwise solution synthesis and characterisation of nine dinuclear chain complexes composed of different metal–carbonyl units ($M = \text{Cr}, \text{Mo}, \text{W}$) and a bifunctional bridging isocyanide Schiff-base ligand is the subject of this contribution.

Results and Discussion

Inert metal–ligand bonds are required for the stepwise controlled synthesis of multinuclear metal chain complexes. The coordinative bond between isocyanides and M^0 carbonyl complexes ($M = \text{Cr}, \text{Mo}, \text{W}$) is kinetically stable so that ligand-exchange processes are prevented.^[18–20] Consequently, a suitable bridging ligand with an isocyano group is used in the assembly of dinuclear metal complexes.

The bridging Schiff-base ligand (4-isocyanophenyl)pyridine-2-ylmethylenamine $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ is accessible by a two-step procedure starting from 1,4-diaminobenzene (Scheme 1). Transformation of one amino group into the desired isocyano group gives 4-isocyanophenylamine in rather poor yields according to the literature.^[21] Optimis-

^[a] Anorganisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany
Fax.: (internat.) +49-(0)6221-545707
E-mail: katja.heinze@urz.uni-heidelberg.de

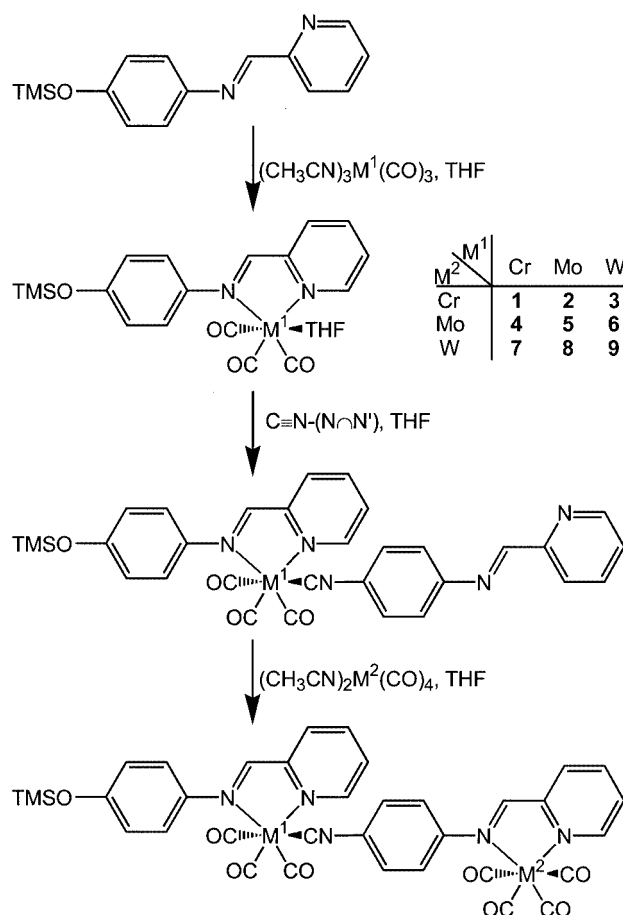


Scheme 1

ation of the purification increased the yield to 45% (see Exp. Sect.). Schiff-base condensation of the remaining amino group with pyridine-2-carbaldehyde affords the desired ligand $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ (Scheme 1). $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ can act as bridging ligand between two M^0 -carbonyl units through i) the chelating Schiff-base moiety, and ii) the isocyano group.

The trimethylsilyloxy-substituted analogous Schiff-base ligand $\text{TMSO}-(\text{N}\cap\text{N}')$ ^[18] was used as the starting point for the synthesis of dinuclear complexes. $\text{TMSO}-(\text{N}\cap\text{N}')$ reacts with one equivalent of $[(\text{CH}_3\text{CN})_3\text{M}^1(\text{CO})_3]$ ($\text{M}^1 = \text{Cr}, \text{Mo}, \text{W}$) in THF at ambient temperature to give the reactive intermediate complexes $[\text{TMSO}-(\text{N}\cap\text{N}')-\text{M}^1(\text{CO})_3\text{thf}]$ (Scheme 2).^[18] The labile solvent molecule can be displaced by the isocyanide ligand $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ to afford green stable intermediate isocyanide complexes $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')]$ (Scheme 2). The potentially chelating Schiff-base site of the coordinated $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ ligand is finally coordinated to an $\text{M}^2(\text{CO})_4$ fragment by reaction with $[(\text{CH}_3\text{CN})_2\text{M}^2(\text{CO})_4]$ ($\text{M}^1 = \text{Cr}, \text{Mo}, \text{W}$) yielding the dinuclear complexes $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{M}^2(\text{CO})_4]$ **1–9** with the metals Cr, Mo, and W in defined positions of M^1 and M^2 (Scheme 2). This reaction sequence may be performed as a one-pot procedure — isolation of the intermediate complexes is unnecessary — provided that exact stoichiometric conditions are fulfilled. Otherwise, side products such as $[\text{X}-(\text{N}\cap\text{N}')\text{M}^{1,2}(\text{CO})_4]$, $[\text{X}-(\text{N}\cap\text{N}')\text{M}^{1,2}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{V}]$ ($\text{X} = \text{OTMS}, \text{CN}$) are obtained in larger amounts which have to be removed by chromatography. The reactions can easily be monitored by IR spectroscopy due to the characteristic IR absorption bands of the intermediate complexes (Table 1).

Formation of the intermediate complexes $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3\text{thf}]$ is shown by the appearance of two absorption bands in the ν_{CO} region (Table 1). Coordination of the isocyanide ligand $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ replaces



Scheme 2

Table 1. IR and UV/Vis spectroscopic data of intermediate complexes $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}(\text{CO})_3\text{L}]$ in THF ($\tilde{\nu}$ in cm^{-1} ; λ_{max} in nm)

L	Cr	Mo	W	Assignment
$\tilde{\nu}$ THF	1805	1802	1808	CO
	1906	1910	1907	CO
$\tilde{\nu}$ $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$	1826	1827	1827	CO
	1860	1855	1849	CO
	1915	1919	1915	CO
	2074	2076	2072	CN
λ_{max} THF	766	685	705	
λ_{max} $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$	660	618	628	

these two bands with a new set of three ν_{CO} bands plus one ν_{CN} band (Table 1, cf.^[18,19,20]). A further proof for isocyanide coordination is the shift of the ν_{CN} signal by about 50 cm^{-1} to lower energy than the signal of the free ligand $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ ($\nu_{\text{CN}} = 2127 \text{ cm}^{-1}$). This shift is also observed in the IR spectra of the dinuclear complexes **1–9** (Table 2). Introduction of the $\text{M}^2(\text{CO})_4$ fragment causes additional ν_{CO} bands to appear (Table 2) so that the IR spectra of the dinuclear complexes **1–9** can be described as a superposition of the IR spectra of the corresponding mononuclear isocyanide tricarbonyl complex $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')]$ and the tetra-

carbonyl complex $[\text{HO}-(\text{N}\cap\text{N}')\text{M}^2(\text{CO})_4]^{[18,19,20]}$ as shown in Figure 1 for the Cr-W complex **7**.

Table 2. IR spectroscopic data of complexes **1–9** in THF ($\tilde{\nu}$ in cm^{-1})

M^2 / M^1	Cr	Mo	W
Cr	1829	1827	1829
	1850	1850	1849
	1906	1906	1911 br
	1913	1918	
	2006	2007	2006
	2073	2075	2072
Mo	1829	1828	1827
	1849	1850	1849
	1907	1909	1907
	1913 sh	1917	1911 sh
	2013	2012	2013
	2069	2079	2068
W	1830	1827	1829
	1849	1849	1849
	1896	1897	1896
	1915	1914	1913
	2006	2008	2006
	2072	2079	2073

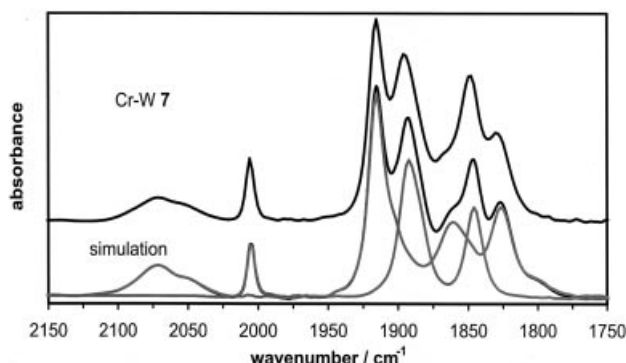


Figure 1. IR spectrum of dinuclear complex **7** and spectra of the corresponding mononuclear complexes $[\text{HO}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_4]^{[20]}$ and $[\text{TMSO}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')]^{[20]}$ in THF

The ^1H NMR spectra of the complexes **1–9** show broad and overlapping multiplets in the aromatic region (see Exp. Section) and are thus not particularly informative. Only the signals for the imine protons (chemical shift range $\delta = 8.4–8.9$ ppm) are clearly assignable (Table 3). A closer in-

Table 3. ^1H NMR chemical shifts of imine protons of complexes **1–9** in CD_2Cl_2

M^2 / M^1	Cr	Mo	W
Cr	8.48	8.62	8.90
	8.54	8.49	8.48
Mo	8.42	8.61	8.83
	8.47	8.58	8.51
W	8.54	8.51	8.90
	8.87	8.84	8.87

spection reveals that imine protons of the tungsten complexes resonate at $\delta \geq 8.84$ ppm while imine protons of the chromium and molybdenum complexes resonate at higher fields with $\delta \leq 8.62$ ppm in THF. ^{13}C NMR spectra could not be obtained due to the low solubility of the complexes.

In the UV/Vis spectra of complexes **1–9** one or two MLCT absorption bands are observed in the range 524–666 nm (Table 4). The low-energy absorption is due to the $(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3$ chromophore, while the high-energy absorption arises from the $(\text{N}\cap\text{N}')\text{M}^2(\text{CO})_4$ chromophore.^[18–20,22–24] Like the IR spectra the UV/Vis spectra can be interpreted as a superposition of spectra of the individual chromophores, as shown for the ditungsten complex **9** in Figure 2. These observations demonstrate that, in each case, the two metal fragments of the dinuclear system behave as mechanically (IR) and electronically (UV/Vis) independent units, which appears reasonable in view of the large metal–metal distance of around 10 Å (estimated on model calculations) and the flexible orientation of the $\text{M}^2(\text{CO})_4$ fragment with respect to the $\text{M}^1(\text{CO})_3$ moiety.

Table 4. UV/Vis spectroscopic data of complexes **1–9** in THF (λ_{max} in nm; ϵ in $\text{M}^{-1}\text{cm}^{-1}$)

M^2 / M^1	Cr	Mo	W
Cr	598 (15200)	594 (9730)	608 (11900)
Mo	557 (8210)	524 (9000)	556 (12210)
	666 (5780, sh)	615 (7250, sh)	609 (11650)
W	570 (6030)	562 (9180)	570 (8170)
	640 (4390, sh)	613 (8600, sh)	600 (7760, sh)

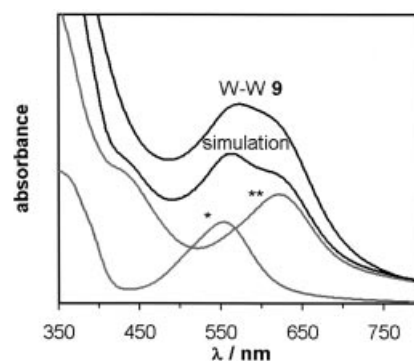


Figure 2. UV/Vis spectrum of the dinuclear complex **9** and spectra of the corresponding mononuclear complexes $[\text{HO}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_4]^{(*)[20]}$ and $[\text{TMSO}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')]^{(**)}$ in THF

As additional proof for the dinuclear nature of the complexes in solution, and to exclude a simple mixture of mononuclear complexes, the molecular masses of complexes **1–9** have been determined by osmometry (see Exp. Sect.). In all cases the results agree with the expected mass within experimental error. This also shows that the complexes remain stable in solution without dissociation, i.e. the metal–isocyanide bond remains intact.

The dinuclear species were further characterised by FAB mass spectroscopy (see Exp. Sect.). Peaks corresponding to

ions of the dinuclear complexes and to fragments with loss of one to seven carbon monoxide ligands but with an intact $\{\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{M}^2\}$ backbone substantiate the above findings.

The cyclic voltammograms of complexes **1–9** in $\text{CH}_2\text{Cl}_2/(\text{nBu}_4\text{N})(\text{PF}_6)$ show only irreversible and quasireversible oxidation waves, probably due to the loss of carbon monoxide upon oxidation. This behaviour has already been observed for the corresponding mononuclear complexes.^[18–20]

With all these spectroscopic data at hand we tried to answer the following question: Is it possible to determine (“read”) the metal sequence in these dinuclear complexes without any prior knowledge of the synthetic protocol used? In other words, can these nine complexes be distinguished with respect to their spectral properties? A closer inspection of the IR, ^1H NMR, and UV/Vis spectra of the complexes **1–9** reveals distinct differences between the individual complexes (Tables 2–4).

The IR spectra give three criteria:

- (i) $\tilde{\nu}_{\text{CN}} \geq 2075\text{ cm}^{-1}$ indicates $\text{M}^1 = \text{Mo}$ (complex **2** or **8**)
- (ii) $\tilde{\nu}_{\text{CO, tetra}} \geq 2012\text{ cm}^{-1}$ indicates $\text{M}^2 = \text{Mo}$ (complex **4** or **6**)

- (iii) both (i) and (ii) indicates $\text{M}^1 = \text{M}^2 = \text{Mo}$ (complex **5**)

The ^1H NMR spectra give two criteria:

- (iv) one $\delta_{\text{H}(\text{Imin})} \geq 8.84$ indicates $\text{M}^1 = \text{W}$ or $\text{M}^2 = \text{W}$ (**3**, **6**, **7**, or **8**)

- (v) two $\delta_{\text{H}(\text{Imin})} \geq 8.84$ indicates $\text{M}^1 = \text{M}^2 = \text{W}$ (complex **9**)

Criteria (iii) and (v) completely assign complexes **5** and **9**. Taking (i), (ii), and (iv) together complexes **2**, **8**, **4**, and **6** can be unambiguously assigned. For example, (i) and (iv) together indicates complex **8**. Combining IR and ^1H NMR spectroscopy all complexes except the isomeric pair **3/7** can be unambiguously assigned.

The Cr/W isomers **3** and **7** can be distinguished on the basis of their UV/Vis spectra: the difference of λ_{max} for the MLCT absorption maxima of the individual chromophores in the dinuclear species is almost twice as large for complex **7** as for complex **3** (estimated on the basis of the absorption bands of corresponding mononuclear complexes^[18–20]) so that for complex **7** a broad absorption with a low-energy shoulder is observed while complex **3** displays only one comparatively sharp band (Figure 3).

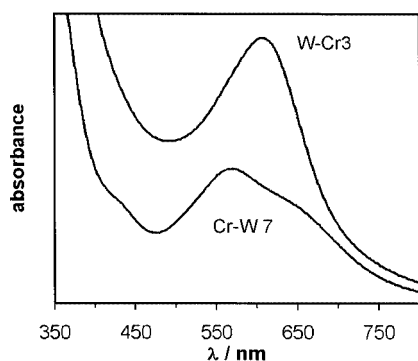


Figure 3. UV/Vis spectra of the dinuclear Cr/W complexes **3** and **7**

On the basis of IR (determination of molybdenum content and position), NMR (determination of tungsten content), and UV/Vis (discrimination between **3** and **7**) spectroscopy the metal positions in all nine dinuclear complexes **1–9** can be unambiguously determined.

Conclusion

Dinuclear directional complexes with well-defined metal sequences have been prepared in solution and characterised. However, low yields and lengthy purification renders this solution synthesis unsuitable for trinuclear and higher chain complexes which could be obtained by repeated chain growth cycles with $[(\text{CH}_3\text{CN})_3\text{M}(\text{CO})_3]$ and $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$. Currently a new method for the stepwise assembly of tri- and oligonuclear complexes on a solid phase is being developed.^[18,25,26]

The metal sequence of nine dinuclear complexes with Cr, Mo, and W in two possible positions can be determined using a combination of standard spectroscopic techniques. It should be possible to extend the sequence determination to “sequencing” or “readout” of oligonuclear complexes if the simulation technique based on spectra of mononuclear complexes is used in combination with chemometric methods such as, for example, principal component analysis (PCA) or partial least-squares (PLS).^[29] As the spectroscopic determination of the chromium content is rather indirect a two letter code with molybdenum and tungsten as the basis might be advisable in larger chain complexes. The preparation and characterisation of oligonuclear complexes built from molybdenum and tungsten fragments is currently underway.^[26]

Experimental Section

Unless noted otherwise, all manipulations were carried out under argon by means of standard Schlenk techniques. All solvents were dried by standard methods and distilled under argon prior to use. All other reagents were used as received from commercial sources. NMR: Bruker Avance DPX 200 at 200.15 MHz (^1H), 50.323 MHz (^{13}C) at 303 K; chemical shifts (δ) in ppm with respect to residual solvent peaks as internal standards: CDCl_3 (^1H : $\delta = 7.24$; ^{13}C : $\delta = 77.0$ ppm), $[\text{D}_8]\text{THF}$ (^1H : $\delta = 1.73, 3.58$; ^{13}C : $\delta = 25.5, 67.7$), CD_2Cl_2 (^1H : $\delta = 5.32$; ^{13}C : $\delta = 53.8$ ppm). IR spectra were recorded on a BioRad Excalibur FTS 3000 spectrometer using CaF_2 cells or CsI disks. UV/Vis/NIR spectra were recorded on a Perkin–Elmer Lambda 19, 0.2 cm cells (Hellma, suprasil). Mass spectra were recorded on a Finnigan MAT 8400 spectrometer. Elemental analyses were performed by the microanalytical laboratory of the Organic Chemistry Department, University of Heidelberg. Molecular weight determinations in THF: Knauer vapour-pressure osmometer No. 7311100000, calibration with benzil.

The ligand $\text{TMSO}-(\text{N}\cap\text{N}')$ was prepared according to the literature procedure.^[18] The acetonitrile complexes were prepared from $[(\text{cycloheptatriene})\text{M}(\text{CO})_3]$ and $[(\text{norbornadiene})\text{M}(\text{CO})_4]$,^[27,28] respectively, by reaction with CH_3CN ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).

4-Isocyanophenylamine:^[21] 1,4-Diaminobenzene (0.28 mol, 30 g) was suspended in ethanol (120 mL) and chloroform (400 mL). A

solution of KOH (200 g) in water (800 mL) was carefully added and the mixture was refluxed for 2.5 h. The organic layer was separated and the residue was extracted twice with dichloromethane. The combined organic phases were washed with water and dried with MgSO_4 . After evaporation of the solvent the residue was purified by flash chromatography (Alox, diethyl ether, R_f = 0.5) giving the product as yellow needles. Yield: 15 g (0.13 mol, 45%). $\text{C}_7\text{H}_6\text{N}_2$ (118.1): calcd. C 71.17, H 5.12, N 23.71; found C 71.11, H 5.12, N 23.52. MS (EI): m/z (intensity [%], fragment) = 118 (100) $[\text{M}^+]$, 91 (33) $[\text{M}^+ - \text{HCN}]$. IR (CHCl₃): $\tilde{\nu}$ = 2129 (s, CN), 3410 cm^{-1} (br., NH). IR (CsI): $\tilde{\nu}$ = 2129 (s, CN), 3460 cm^{-1} (s, NH). ^1H NMR (CDCl₃): δ = 3.79 (br., 2 H, NH_2), 6.62 (d, 2 H, $H^{2,6}$, $^3J_{\text{H,H}}$ = 8.5 Hz), 7.17 (d, 2 H, $H^{3,5}$, $^3J_{\text{H,H}}$ = 8.5 Hz) ppm. ^{13}C NMR (CDCl₃): δ = 115.2 (s, $\text{C}^{2,6}$), 128.0 (s, $\text{C}^{3,5}$), 147.8 (s, C^1), C^4 and CN not observed ppm.

(4-Isocyanophenyl)pyridine-2-ylmethyleneamine $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$: A mixture of 4-Isocyanophenylamine (34.6 mmol, 4.08 g), pyridine-2-carbaldehyde (52.3 mmol, 5 mL), MgSO_4 (5 g), and ethyl acetate (80 mL) was heated under reflux for 6 h. The resulting brown suspension was filtered and the orange solution was evaporated to dryness. After recrystallisation from acetone/diethyl ether the brown solid was dried in vacuo for 4 days. Yield 5.5 g (26.5 mmol, 77%). $\text{C}_{13}\text{H}_9\text{N}_3$ (210.7): calcd. C 73.74, H 4.52, N 19.85; found C 73.89, H 4.49, N 19.62. m.p. 84–85 °C. MS(EI): m/z (intensity [%], fragment) = 207 (31) $[\text{M}^+]$, 179 ($\text{M}^+ - \text{HCN}$, – H), 79 (100) $[\text{C}_5\text{H}_5\text{N}^+]$. HR-MS(EI): Calcd. for $\text{C}_{13}\text{H}_9\text{N}_3$: 207.07965; found 207.07663. IR (CH₂Cl₂): $\tilde{\nu}$ = 2127 cm^{-1} (s, CN). IR (CsI): $\tilde{\nu}$ = 2131 cm^{-1} (s, CN). ^1H NMR ([D₈]THF): δ = 7.39 (d, 2 H, $H^{2,6}$, $^3J_{\text{H,H}}$ = 8.6 Hz), 7.45–7.49 (m, 1 H, H^1), 7.55 (d, 2 H, $H^{3,5}$, $^3J_{\text{H,H}}$ = 8.6 Hz), 7.90 (dvt, 1 H, H^{10} , J = 7.8, J = 1.2 Hz), 8.26 (d, 1 H, H^9 , J = 7.8 Hz), 8.62 (s, 1 H, H^7), 8.72 (d, 1 H, H^{12} , J = 4.8 Hz) ppm. ^{13}C NMR ([D₈]THF): δ = 121.5 (s, C^9), 122.5 (s, $\text{C}^{2,6}$), 125.8 (s, C^{11}), 127.7 (s, $\text{C}^{3,5}$), 136.7 (s, C^{10}), 150.0 (s, C^1), 150.2 (s, C^{12}), 152.4 (s, C^4), 155.1 (s, C^8), 163.2 ppm (s, C^7), CN not observed. All signals were assigned on the basis of DEPT, CH-COSY, and NOESY experiments. The conformation in solution is *transoid* as no cross peak between H^7 and H^9 is observed in the NOESY spectrum.

Complexes 1–9: All glassware was passivated with $(\text{CH}_3)_3\text{SiCl}$ before use. $[(\text{CH}_3\text{CN})_3\text{M}^1(\text{CO})_3]$ (1 mmol) was treated with $\text{TMSO}-(\text{N}\cap\text{N}')$ (270 mg, 1 mmol) in 40 mL of THF and the solution was stirred until IR control (see Table 1) indicated complete formation of $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}(\text{CO})_3\text{thf}]$ (at least 15 min). $\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')$ (207 mg, 1 mmol) was added as a solid and the solution turned green immediately. IR control indicated complete formation of $[\text{TMSO}-(\text{N}\cap\text{N}')\text{M}^1(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')]$ after 10 min (see Table 1). A solution of $[(\text{CH}_3\text{CN})_2\text{M}^2(\text{CO})_4]$ (1 mmol) in THF (10 mL) was then added. The reaction mixture turned black and was stirred for 30 min. Celite was added and the solution was evaporated to dryness. The dark residue was chromatographed on silica gel (T = 0 °C; Et₂O, purple fraction; THF, dark-blue fraction, product complex). The THF fraction was concentrated and layered with petroleum ether (40/60). The black precipitate was collected and dried in vacuo. Yields: 20–55% (0.2–0.55 mmol).

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_4]$ (1): $\text{C}_{35}\text{H}_{27}\text{Cr}_2\text{N}_5\text{O}_8\text{Si}$ (777.7): calcd. C 54.05, H 3.50, N 9.01; found C 53.22, H 3.62, N 9.58. Molecular mass found: 765. MS(FAB): m/z (intensity [%], fragment) = 777 (17) $[\text{M}^+]$, 693 (100) $[\text{M}^+ - 3\text{CO}]$, 581 (94) $[\text{M}^+ - 7\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.38 (s, 9 H, SiCH_3), 7.0 (br. s, 2 H), 7.2–7.6 (m, 8 H), 7.9 (br. s, 4 H), 8.48 (s, 1 H), 8.54 (s, 1 H), 9.29 (br. s, 1 H), 9.39 (br. s, 1 H) ppm. IR (CsI): $\tilde{\nu}$ = 1832, 1908, 2009 (CO), 2082 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_4]$ (2): $\text{C}_{35}\text{H}_{27}\text{CrMoN}_5\text{O}_8\text{Si}$ (821.7): calcd. C 51.16, H 3.31, N 8.52; found C 50.74, H 3.38, N 8.97. Molecular mass found: 846. MS(FAB): m/z (intensity [%], fragment) = 823 (15) $[\text{M}^+]$, 711 (100) $[\text{M}^+ - 4\text{CO}]$, 683 (58) $[\text{M}^+ - 5\text{CO}]$, 627 (40) $[\text{M}^+ - 5\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.38 (s, 9 H, SiCH_3), 7.02 (d, J = 8.0 Hz, 2 H), 7.2–7.6 (m, 8 H), 7.8–8.0 (m, 4 H), 8.49 (s, 1 H), 8.62 (s, 1 H), 9.2–9.4 (br. s, 2 H) ppm. IR (CsI): $\tilde{\nu}$ = 1832, 1911, 2010 (CO), 2084 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_4]$ (3): $\text{C}_{35}\text{H}_{27}\text{CrN}_5\text{O}_8\text{SiW}$ (909.6): calcd. C 46.22, H 2.99, N 7.70; found C 46.32, H 3.47, N 8.02. Molecular mass found: 917. MS(FAB): m/z (intensity [%], fragment) = 908 (100) $[\text{M}^+]$, 797 (66) $[\text{M}^+ - 4\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.38 (s, 9 H, SiCH_3), 7.0 (m, 2 H), 7.3–7.5 (m, 8 H), 7.93 (br. s, 4 H), 8.48 (s, 1 H), 8.90 (s, 1 H), 9.27 (br. s, 1 H), 9.38 (br. s, 1 H) ppm. IR (CsI): $\tilde{\nu}$ = 1828, 1907, 2008 (CO), 2080 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_4]$ (4): $\text{C}_{35}\text{H}_{27}\text{CrMoN}_5\text{O}_8\text{Si}$ (821.7): calcd. C 51.16, H 3.31, N 8.52; found C 50.73, H 3.40, N 8.68. Molecular mass found: 806. MS(FAB): m/z (intensity [%], fragment) = 739 (36) $[\text{M}^+ - 3\text{CO}]$, 711 (94) $[\text{M}^+ - 4\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.31 (s, 9 H, SiCH_3), 6.94 (d, J = 8.0 Hz, 2 H), 7.3–7.6 (m, 8 H), 7.9–8.0 (m, 4 H), 8.42 (s, 1 H), 8.47 (s, 1 H), 9.1–9.3 (m, 2 H) ppm. IR (CsI): $\tilde{\nu}$ = 1837, 1912, 2012 (CO), 2082 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_4]$ (5): $\text{C}_{35}\text{H}_{27}\text{Mo}_2\text{N}_5\text{O}_8\text{Si}$ (865.6): calcd. C 48.57, H 3.14, N 8.09; found C 48.31, H 3.28, N 8.91. Molecular mass found: 841. MS(FAB): m/z (intensity [%], fragment) = 866 (67) $[\text{M}^+]$, 782 (67) $[\text{M}^+ - 3\text{CO}]$, 670 (100) $[\text{M}^+ - 7\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.38 (s, 9 H, SiCH_3), 7.0 (d, J = 8.4 Hz, 2 H), 7.34 (d, J = 8.4 Hz, 2 H), 7.5–7.7 (m, 6 H), 7.9–8.0 (m, 4 H), 8.58 (s, 1 H), 8.61 (s, 1 H), 9.22 (d, J = 3.7 Hz, 1 H), 9.28 (br. s, 1 H) ppm. IR (CsI): $\tilde{\nu}$ = 1830, 1911, 2016 (CO), 2084 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_4]$ (6): $\text{C}_{35}\text{H}_{27}\text{MoN}_5\text{O}_8\text{SiW}$ (953.5): calcd. C 44.09, H 2.85, N 7.35; found C 43.34, H 3.22, N 8.01. Molecular mass found: 967. MS(FAB): m/z (intensity [%], fragment) = 955 (17) $[\text{M}^+]$, 927 (71) $[\text{M}^+ - \text{CO}]$, 915 (100) $[\text{M}^+ - 5\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.31 (s, 9 H, SiCH_3), 6.95 (d, J = 8.0 Hz, 2 H), 7.22 (d, J = 8.0 Hz, 2 H), 7.5–7.7 (m, 6 H), 7.9–8.0 (m, 4 H), 8.51 (s, 1 H), 8.83 (s, 1 H), 9.12 (br. s, 1 H), 9.31 (br. s, 1 H) ppm. IR (CsI): $\tilde{\nu}$ = 1829, 1907, 2016 (CO), 2077 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Cr}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_4]$ (7): $\text{C}_{35}\text{H}_{27}\text{CrN}_5\text{O}_8\text{SiW}$ (909.6): calcd. C 46.22, H 2.99, N 7.70; found C 45.41, H 3.29, N 7.88. Molecular mass found: 937. MS(FAB): m/z (intensity [%], fragment) = 909 (33) $[\text{M}^+]$, 825 (100) $[\text{M}^+ - 3\text{CO}]$, 797 (91) $[\text{M}^+ - 4\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.37 (s, 9 H, SiCH_3), 6.99 (m, 2 H), 7.4–7.6 (m, 8 H), 7.9–8.0 (m, 4 H), 8.54 (s, 1 H), 8.87 (s, 1 H), 9.30 (br. s, 1 H), 9.39 (br. s, 1 H) ppm. IR (CsI): $\tilde{\nu}$ = 1830, 1907, 2008 (CO), 2080 (CN) cm^{-1} .

$[\text{TMSO}-(\text{N}\cap\text{N}')\text{Mo}(\text{CO})_3\text{C}\equiv\text{N}-(\text{N}\cap\text{N}')\text{W}(\text{CO})_4]$ (8): $\text{C}_{35}\text{H}_{27}\text{MoN}_5\text{O}_8\text{SiW}$ (953.5): calcd. C 44.09, H 2.85, N 7.35; found C 43.64, H 2.63, N 7.80. Molecular mass found: 945. MS(FAB): m/z (intensity [%], fragment) = 955 (50) $[\text{M}^+]$, 927 (100) $[\text{M}^+ - \text{CO}]$, 870 (50) $[\text{M}^+ - 3\text{CO}]$, 759 (86) $[\text{M}^+ - 7\text{CO}]$. ^1H NMR (CD₂Cl₂): δ = 0.31 (s, 9 H, SiCH_3), 6.94 (d, J = 8.2 Hz, 2 H), 7.3–7.5 (m, 8 H), 7.9–8.0 (m, 4 H), 8.51 (s, 1 H), 8.84 (s, 1 H), 9.2–9.3 (br. s, 2 H) ppm. IR (CsI): $\tilde{\nu}$ = 1823, 1912, 2010 (CO), 2083 (CN) cm^{-1} .

[TMSO-(N \cap N')W(CO)₃C \equiv N-(N \cap N')W(CO)₄] (9): C₃₅H₂₇N₅O₈SiW₂ (1041.4): calcd. C 40.37, H 2.61, N 6.73; found C 40.71, H 2.99, N 7.56. Molecular mass found: 1017. MS(FAB): *m/z* (intensity [%], fragment) = 1041 (100) [M⁺], 845 (78) [M⁺ - 7CO]. ¹H NMR (CD₂Cl₂): δ = 0.38 (s, 9 H, SiCH₃), 7.02 (d, *J* = 8.0 Hz, 2 H), 7.3–7.6 (m, 8 H), 7.9–8.0 (m, 4 H), 8.87 (s, 1 H), 8.90 (s, 1 H), 9.25–9.50 (m, 2 H) ppm. IR (CsI): $\tilde{\nu}$ = 1829, 1903, 2008 (CO), 2081 (CN) cm⁻¹.

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