ELSEVIER

Journal of Organometallic Chemistry 487 (1995) 131–137

Journal of Organometallic Chemistry

Modes of complexation of linear tri- and tetraamines with group 6 metal carbonyls

Nathalie Le Bris, Jean-Jacques Yaouanc, Jean-Claude Clément, Henri Handel, Hervé des Abbayes *

Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique (URA CNRS 322), UFR Sciences et Techniques, 6 Avenue Le Gorgeu, BP 809, 29285 Brest Cedex, France

Received 9 May 1994

Abstract

On reaction with Group 6 metal carbonyls $[M(CO)_6]$ (M = Cr, Mo or W), linear tri- and tetraamines act as bi- or tri-dentate ligands giving rise to complexes $[LM(CO)_4]$, $[L\{M(CO)_4\}_2]$ or $[LM(CO)_3]$ depending on the chain length and the metal M.

Keywords: Chromium; Molybdenum; Tungsten; Triamine complexes; Tetraamine complexes

---

1. Introduction

Until recently, the use of classical organic N-protecting groups was the only way to alkylate polyamines selectively. We recently showed in a preliminary communication [1] that some cyclic and linear tetraamines could be complexed by three nitrogen atoms to Group 6 metal carbonyls. Under these circumstances a selective ω-mono- [2] or ω,ω′-di-N-alkylation [3] could occur (Scheme 1).

The latter result opens a new route to ω,ω′-dialkylated analogues of spermine which are potent antineoplastic agents [4] or to lipopolyamines which proved to be efficient transfection agents for DNA delivery in the cell [5].

The first known examples of complexation by linear polyamines were those described by Wilkinson and co-workers in 1959 [6] who obtained *fac*-$[LM(CO)_3]$ type complexes after reaction of diethylenetriamine with $[M(CO)_6]$ (M = Cr, Mo or W). The same type of facial tricarbonyl complexes have been obtained by others with linear [7–9] or cyclic [10] triamines and cyclic tetraamines [11].

In order to investigate the scope and the limitations of our methodology, we undertook a study of the complexation modes of various linear tri- and tetraamines with Group 6 metal carbonyls.

2. Results and discussion

The complexation reactions of various linear polyamines with $[M(CO)_6]$ were undertaken under the same conditions, i.e. $[M(CO)_6]$ (1.1 mmol) and amine (1.0 mmol) in refluxing di-n-butyl ether.

2.1. Complexation of triamines

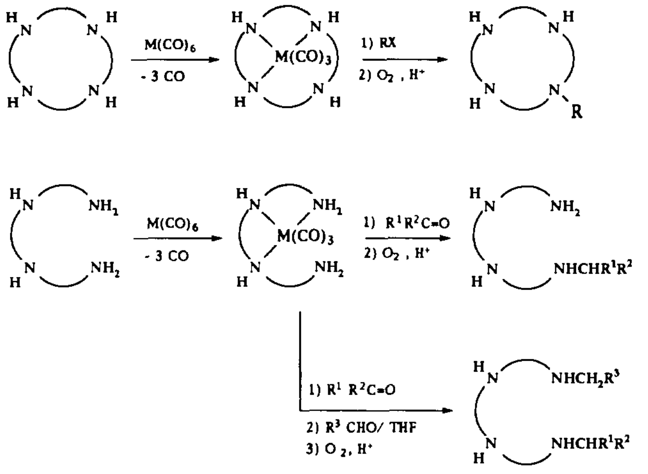
In order to settle the generality of the $[LM(CO)_3]$ complexation mode of diethylenetriamine described previously [6], we performed a series of reactions with triamine ligands L having longer carbon atom chains $[L = R^1NH(CH_2)_3NR^2(CH_2)_3NHR^3$; $R^1 = R^2 = R^3 = H$, CH_3; $R^1 = R^3 = H$, $R^2 = CH_3)$ to generate new complexes (Scheme 2). As shown by their elemental analysis, the L/M ratio in complexes **4** to **6** was 1:1 while their IR spectra exhibited the expected pattern for the three *fac* coordinated carbon monoxide of an $M(CO)_3$ group [~ 1885(s), 1760(vs) cm^{-1}].

When coordinated, a substituted nitrogen atom may become a stereocentre (Scheme 2). Furthermore, if rotation around the N–[M] bond is restricted as in complexes **4–6**, two positions *cis* or *trans* may be

---

* Corresponding author.

SSDI 0022-328X(94)05118-6

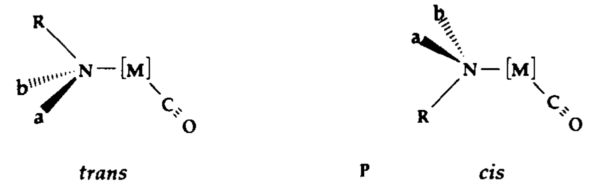


Scheme 1.

envisaged for an R group with respect to a coordinated carbon monoxide (Scheme 3). Complexes **4–6** may therefore exist as several stereoisomers.

Complexes **4** and **5** exhibit simple ^{13}C NMR spectra. Two signals (1 : 2 ratio) are observed near 230 ppm for the three carbon atoms of the M(CO)$_3$ group in which two CO are equivalent. Two kinds of signal are shown for the methylene groups bound to a nitrogen atom (N-CH$_2$, ~ 45 and ~ 50 ppm) and only one for the central methylene groups (N-CH$_2$$CH_2CH_2$N, ~ 26 ppm). It may be inferred from these observations that complexes **4** and **5** exist as a single stereoisomer with a plane of symmetry P as shown in Scheme 3. Since only one signal is observed for the carbon atom of the CH$_3$ group in complex **5** ($R^2 = CH_3$), it is inferred that only one position (*cis* or *trans*) is adopted (Scheme 4). The NMR data are unable to distinguish between them.

In contrast two different sets of signals are observed in the ^{13}C NMR spectrum of **6b**, clearly showing the presence of two stereoisomers **6b$_1$** and **6b$_2$** in a 40 : 60 ratio. Isomer **6b$_1$** shows two signals (2 : 1 ratio) for the M(CO)$_3$ group (227.9 and 227.4 ppm) which means that **6b$_1$** has the same geometry as complexes **4** and **5**;



Scheme 3.

6b$_2$ shows three distinct signals in the ratio 1 : 1 : 1 for the M(CO)$_3$ group (227.8, 226.1, 225.2 ppm) and nine distinct signals for the six methylene carbon atoms and the three non-equivalent *N*-methyl groups. This signal complexity may be ascribed reasonably to the same absolute configuration for the R^{1}HN[M] and the R^{3}HN[M] stereocentres. There is then no plane of symmetry.

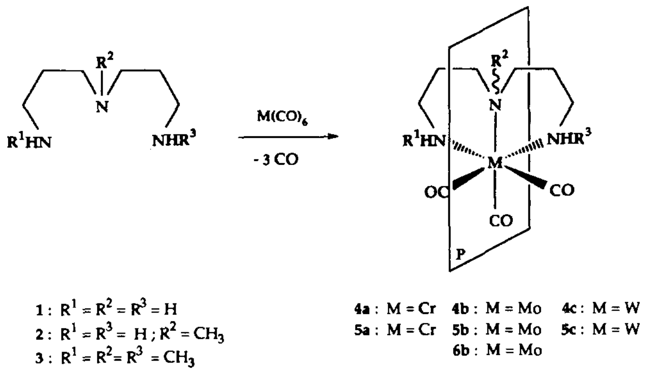
2.2. Complexation of tetraamines

Under the same experimental conditions the behaviour of five linear tetraamines was examined, i.e.

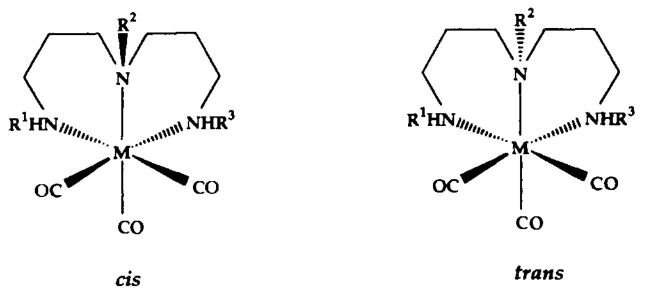
$NH_2(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$ (**7**) (2.2.2)
$NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$ (**8**) (3.2.3)
$NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$ (**9**) (2.3.2)
$NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$ (**10**) (3.3.3)
$NH_2(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$ (**11**) (3.4.3) (spermine)

For greater clarity they are designated by their hydrocarbon chains, for example (2.2.2) for 1,4,7,10-tetraazadecane (**7**), (2.3.2) for 1,4,8,11-tetraazaundecane (**9**), etc.

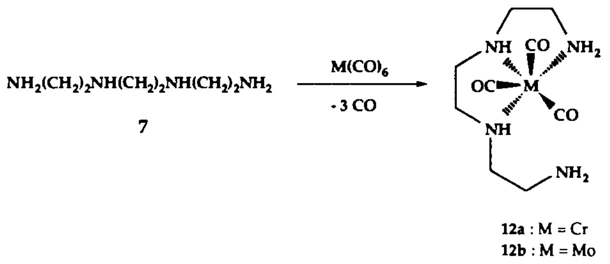
After reaction with [M(CO)$_6$] (M = Cr, Mo or W) the tetraamine (2.2.2) **7** affords complexes **12** showing the two expected IR ν_{CO} vibrations for *fac*-[LM(CO)$_3$] with C_{3v} local symmetry. This mode of coordination is evident from the ^{13}C NMR spectra which consist either of one set of signals (Mo) or two sets of signals (Cr and W) corresponding to diastereoisomeric mixtures. In the latter case NMR spectroscopy does not discriminate



Scheme 2.



Scheme 4.

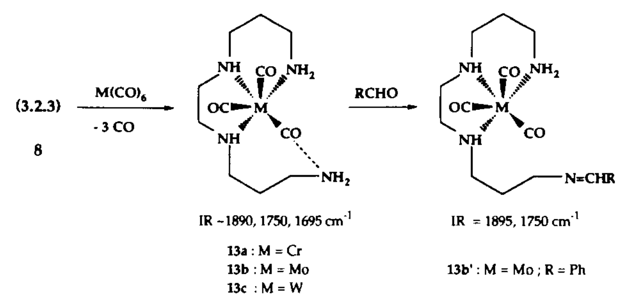


Scheme 5.

between the different possible diastereoisomers (in 20 : 80 and 25 : 75 ratios in DMSO-d_6 and DMF-d_7, respectively), for the chromium complex and in a 20 : 80 ratio in DMSO-d_6 for the tungsten complex. However, the common, significant feature in these spectra are three distinct signals in the ratio 1 : 1 : 1 near 220–230 ppm for three magnetically different carbonyls. This establishes the non-symmetrical tricoordination of this tetraamine (Table 1, entries 1, 2 and 3) with the three metals, leaving one of the terminal primary amino functions free (Scheme 5). Complete IR and NMR data are given under Experimental details.

The tetraamine (3.2.3) **8** reacts with [M(CO]$_6$] (M = Cr, Mo or W) to yield complexes **13** which exhibit a set of three vibrations of similar intensity in their IR spectra, instead of the two expected ν_{CO} bands. This could arise from a *mer*-[LM(CO)$_3$] structure having a C_{2v} local symmetry.

Nevertheless, the supplementary absorption band at ~ 1695 cm^{-1} totally disappears after reaction of the complexes with an aldehyde, yielding the normal IR pattern for a complex *fac*-[LM(CO)$_3$] [1]. The apparently 'abnormal' IR pattern is not a consequence of a different mode of coordination, but might result from an intramolecular interaction of the free amino group with the M(CO)$_3$ moiety (Scheme 6). The reaction with an aldehyde leads to a less basic imine derivative in which this interaction is suppressed and restoring the expected IR pattern for a complex *fac*-[LM(CO)$_3$]. In one case this derivative has been isolated and fully characterized [2] (complex **13b′**: M = Mo; R = Ph), confirming the tricoordination of **8**.



Scheme 6.

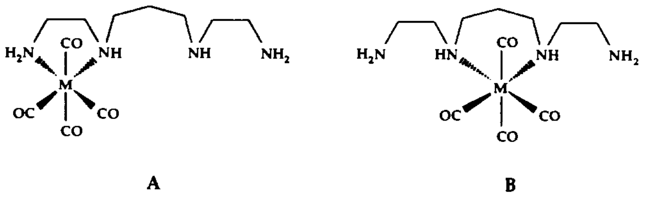
Furthermore, Wieghardt and co-workers describe the oxidation of *fac*-[LM(CO)$_3$] with cyclic triamines by halogens, leading to heptacoordinated cations [LM(CO)$_3$X]$^+$ which exhibit three characteristic ν_{CO} vibrations in their IR spectra. The presence of the halogen atom in the coordination sphere could explain this perturbation [9a].

By analogy, the interaction of the terminal aminopropyl group in complexes **13**, with the metal could create a similar perturbation so that the IR spectra show a supplementary band at 1695 cm^{-1}. A study of molecular models shows that the terminal aminopropyl chain can interact through the free nitrogen atom with three carbonyls. This 'abnormal' ν_{CO} band appears in all complexes containing a terminal aminopropyl chain (see complexes **16** and **18**). An aminoethyl group is too short and hence this kind of interaction is not observed (see complexes **12** and **14**).

The ^{13}C NMR spectra of (3.2.3) complexes **13** are fully consistent with the proposed structure (Table 1, entries 4, 5 and 6) and consist of three distinct signals for the M(CO)$_3$ tripod, five signals (plus one masked) for the carbon atoms α to nitrogen and two different signals for the carbon atoms β to nitrogen.

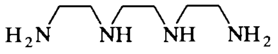
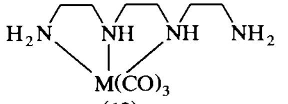
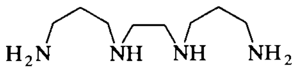
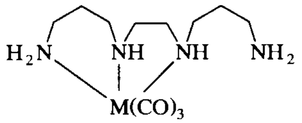
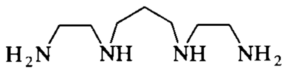
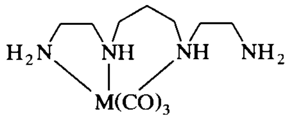
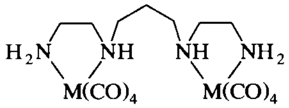
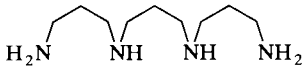
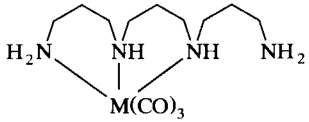
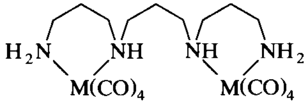
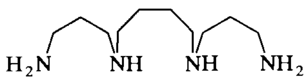
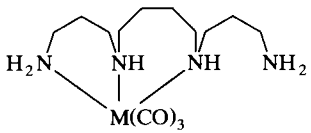
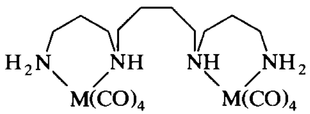
With the tetraamine (2.3.2) **9**, this specific mode of coordination is only observed after reaction with [W(CO)$_6$]: *fac*-[(2.3.2)W(CO)$_3$] is obtained and shows the expected IR and ^{13}C NMR data for such a structure (Table 1, entry 9). With [Cr(CO)$_6$] and [Mo(CO)$_6$] a dinuclear species [L{M(CO)$_4$}$_2$] appears along with the *fac*-[LM(CO)$_3$] (Table 1, entries 7 and 8). The presence of two M(CO)$_4$ moieties is clearly deducible from ^{13}C NMR data, since four distinct signals of equal intensity are noted for the carbonyl groups and there are only three signals for the carbon atoms α to nitrogen (noted α, α', α'' in Scheme 8). This multiplicity is incompatible with any of the two possible other mononuclear structures **A** or **B** (Scheme 7).

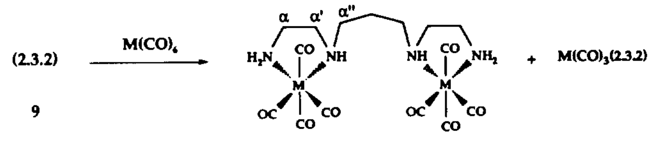
Structure **A** would show seven different resonances for the methylene carbon atoms and **B**, in which the two carbonyl groups *trans* to nitrogen are magnetically equivalent, would show three signals in the ratio 1 : 1 : 2 for the M(CO)$_4$ moiety.



Scheme 7.

Table 1
Complexes of linear tetraamines

Entry No.	Ligand	Complex		M	Yield (%)	$[LM(CO)_3]/[L\{M(CO)_4\}]$ ratio
1 2 3	 **(7)**	 **(12)**		Cr Mo W	84 90 46	– – –
4 5 6	 **(8)**	 **(13)**		Cr Mo W	90 95 57	– – –
7 8 9	 **(9)**	 **(14)**	 **(15)**	Cr Mo W	~ 80 ~ 80 46	55:45 90:10 100:0
10 11 12	 **(10)**	 **(16)**	 **(17)**	Cr Mo W	~ 80 ~ 80 37	80:20 90:10 100:0
13 14 15	 **(11)**	 **(18)**	 **(19)**	Cr Mo W	80 ~ 80 ~ 40	0:100 30:70 50:50



Scheme 8.

The IR spectrum is also consistent with this dinuclear structure, and shows the four ν_{CO} absorption bands predicted for complexes *cis*-[LM(CO)$_4$] having a local C_{2v} symmetry.

There is an evident tendency for [W(CO)$_6$] to favour [LM(CO)$_3$] formation whereas mixtures of [LM(CO)$_3$] and [L{M(CO)$_4$}$_2$] are obtained with [Mo(CO)$_6$] (90 : 10 ratio) and [Cr(CO)$_6$] (55 : 45 ratio). This may be due to the higher reactivity of a secondary compared to a primary amine and also to a greater ease of five-membered metallocycle formation with 'small' metal.

Similar results, only varying in the [L{M(CO)$_4$}$_2$]/[LM(CO)$_3$] ratio, are observed with the tetraamine (3.3.3) **10** (see Table 1, entries 10, 11 and 12), and again only *fac*-[LM(CO)$_3$] is obtained with [W(CO)$_6$].

Spermine (3.4.3) (**11**) is the only tetraamine in this series containing a four-carbon atom chain and we now pose the question as to whether a seven-membered metallocycle is possible. (To our knowledge, there is no precedent in the literature in the coordination of polyamines with metal carbonyls of Group 6.)

The stoichiometric reaction of spermine with [Cr(CO)$_6$] gives only the [L{M(CO)$_4$}$_2$] in medium yield (Table 1, entry 13). In contrast to (2.3.2) and (3.3.3) which can tricoordinate to some extent, seven-membered metallocycle formation is not observed with spermine and [Cr(CO)$_6$]. When two equivalents of [Cr(CO)$_6$] were used, a 80% yield of the dinuclear complex was obtained as shown by IR and ^{13}C NMR spectroscopies.

However, using [Mo(CO)$_6$] or [W(CO)$_6$] with spermine instead of [Cr(CO)$_6$] results in the formation of the *fac*-[LM(CO)$_3$] along with the dinuclear species. The formation of seven-membered metallocycles is not actually forbidden, but the formation depends strongly on the metal (Table 1, entries 14 and 15).

As summarized in Table 1, it appears that each tetraamine in this study is able to tricoordinate with Group 6 metal tricarbonyls, especially to [W(CO)$_6$].

The reactivity of these new complexes and their applications for the strict mono-N-functionalization of tetraamines has been studied [2,3]. The formation of a dinuclear complex in which all the four nitrogen atoms are deactivated is not a serious drawback for the ω-mono-N-functionalization since, in mixtures of *cis*-[L{M(CO)$_4$}$_2$]/*fac*-[LM(CO)$_3$], only the *fac*-[LM(CO)$_3$] can react.

3. Experimental details

3.1. General comments

All reactions were carried out under dinitrogen using standard Schlenk techniques. The solvents were freshly distilled from an appropriate desiccant (P_2O_5 for Bu_2O, CaH_2 for CH_2Cl_2 and hexane). Polyamines (triamines and tetraamines) were obtained from Aldrich or Fluka.

IR spectra were obtained using a Perkin-Elmer 1430 spectrometer. The ^{13}C NMR (75.47 MHz) data were recorded on a Bruker AC-300 spectrometer. Chemical shifts are given relative to the solvent DMSO-d_6, unless otherwise specified. Microanalyses were carried out either by the Centre de microanalyses du CNRS de Lyon or by the Analytische Laboratorien Drs. Malissa and Reuter, Germany.

3.2. General procedure

Sublimed [M(CO)$_6$] (M = Cr, Mo or W) (1.1 mmol) and polyamine (triamine or tetraamine) (1 mmol) were heated under reflux (142°C) in n-butyl ether (20 ml) for 2 h (M = Cr or Mo) or 6–7 h (M = W), while occasionally returning the sublimed [M(CO)$_6$] to the reaction solution by scraping the condenser walls.

A yellow precipitate formed during the reaction. After cooling to room temperature, the yellow solid was separated off, washed with hexane (3 × 20 ml) and then dried in vacuo at 50°C [1].

3.3. Spectroscopic data

fac-[{$H_2N(CH_2)_3NH(CH_2)_3NH_2$}Cr(CO)$_3$] (**4a**): Yield, 94%. ^{13}C NMR δ: 231.1, 230.1 (2C) (*C*O); 49.6, 41.9 (C_α–N); 25.7 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1880 (s), 1770 (vs, br) (ν_{CO}).

fac-[{$H_2N(CH_2)_3NH(CH_2)_3NH_2$}Mo(CO)$_3$] (**4b**): Yield, 96%. ^{13}C NMR δ: 227.0, 226.5 (2C) (*C*O); 49.9, 42.6 (C_α–N); 26.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1885 (s), 1770 (vs, br) (ν_{CO}).

fac-[{$H_2N(CH_2)_3NH(CH_2)_3NH_2$}W(CO)$_3$] (**4c**): Yield, 57%. ^{13}C NMR δ: 222.7 (J_{CW} = 185.0 Hz), 221.5 (2C) (J_{CW} = 185.2 Hz) (*C*O); 49.7, 42.6 (C_α–N); 26.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1865 (s), 1755 (vs, br) (ν_{CO}). Anal. Found: C, 26.82; H, 4.35; W, 44.70%. $C_9H_{17}N_3O_3W$. C, 27.06; H, 4.26; W, 46.11%.

fac-[{$H_2N(CH_2)_3NMe(CH_2)_3NH_2$}Cr(CO)$_3$] (**5a**): Yield, 90% ^{13}C NMR δ: 232.0, 230.2 (2C) (*C*O); 59.2, 53.4, 41.6 (C_α–N); 23.8 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1885 (s), 1760 (vs, br) (ν_{CO}).

fac-[{$H_2N(CH_2)_3NMe(CH_2)_3NH_2$}Mo(CO)$_3$] (**5b**): Yield, 95%. ^{13}C NMR δ: 227.0, 226.4 (2C) (*C*O); 59.8, 53.7, 42.2 (C_α–N); 24.5 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1890 (s), 1750 (vs, br) (ν_{CO}).

fac-[{$H_2N(CH_2)_3NMe(CH_2)_3NH_2$}$W(CO)_3$] (**5c**): Yield, 57%. ^{13}C NMR δ: 222.9 (J_{CW} = 186.8 Hz), 222.2 (2C) (J_{CW} = 189.6 Hz) (*C*O); 59.6, 54.9, 42.1 (C_α–N); 24.3 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1878 (s), 1745 (vs, br) (ν_{CO}). Anal. Found: C, 29.19; H, 4.63; W, 44.68%. $C_{10}H_{19}N_3O_3W$ Calc.: C, 29.07; H, 4.60; W, 44.53%.

fac-[{$MeHN(CH_2)_3NMe(CH_2)_3NHMe$}$Mo(CO)_3$] (**6b$_1$** + **6b$_2$**): Yield, 95%. ^{13}C NMR **6b$_1$** (40% vs. **6b$_2$**) δ: 227.9 (2C), 227.4 (*C*O); 58.7, 53.5, 53.4 (2C); 45.6 (C_α–N); 23.3 (C_β–N); **6b$_2$** (60% vs. **6b$_1$**) δ: 227.8, 226.1, 225.2 (*C*O); 64.3, 57.6, 56.9, 55.1, 52.8, 46.1, 42.6 (C_α–N); 24.7, 24.6 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1899 (s), 1760 (vs, br) (ν_{CO}).

fac-[(2.2.2)$Cr(CO)_3$] (**12a$_1$** + **12a$_2$**): Yield, 85%. ^{13}C NMR (DMSO-d_6) **12a$_1$** (80% vs. **12a$_2$**) δ: 233.9, 233.2, 232.4 (*C*O); 58.5, 50.0, 49.7, 46.4, masked peak, 37.5 (C_α–N); **12a$_2$** (20% vs. **12a$_1$**) δ: 234.1, 232.5, 230.8 (*C*O); 54.6, 50.6, 48.9, 45.9, 42.4, masked peak (C_α–N); (DMF-d_7) **12a$_1$** (75% vs. **12a$_2$**) δ: 234.6, 233.8, 233.2 (*C*O); 59.1, 50.9 (2C); 47.0, 40.7, 38.1 (C_α–N); **12a$_2$** (25% vs. **12a$_1$**) δ: 234.8, 233.1, 231.5 (*C*O); 55.3, 51.2 49.6, 47.0, 43.1, 40.2 (C_α–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1872 (s), 1752 (vs, br) (ν_{CO}).

fac-[(2.2.2)$Mo(CO)_3$] (**12b**): Yield, 90%. ^{13}C NMR δ: 229.4, 228.6, 227.5 (*C*O); 58.8, 50.9, 50.2, 46.2, masked peak, 37.9 (C_α–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1895 (s), 1755 (vs, br) (ν_{CO}).

fac-[(2.2.2)$W(CO)_3$] (**12c$_1$** + **12c$_2$**): Yield, 47%. ^{13}C NMR **12c$_1$** (80% vs. **12c$_2$**) δ: 225.6 (J_{CW} = 185.8 Hz), 224.0 (J_{CW} = 185.9 Hz), 223.8 (J_{CW} = 186.0 Hz) (*C*O); 59.9, 51.9, 51.4, 47.5, masked peak, 38.8 (C_α–N); **12c$_2$** (20% vs. **12c$_1$**) δ: 225.7 (J_{CW} = 186.0 Hz), 223.0 (J_{CW} = 186.7 Hz), 222.3 (J_{CW} = 184.2 Hz) (*C*O); 55.7, 52.2, 50.1, 47.8, 43.9, masked peak (C_α–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1875 (s), 1735 (vs, br) (ν_{CO}).

fac-[(3.2.3)$Cr(CO)_3$] (**13a**): Yield, 90%. ^{13}C NMR δ: 233.7, 231.6, 230.6 (*C*O); 53.5, 51.1, 50.3, 45.2, 44.9, masked peak (C_α–N); 32.5, 24.0 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1875 (vs), 1745 (vs), 1695 (vs) (ν_{CO}).

fac-[(3.2.3)$Mo(CO)_3$] (**13b**): Yield, 95%. ^{13}C NMR δ: 229.4, 228.1, 226.9 (*C*O); 53.6, 52.0, 50.8, 45.44, 45.37, masked peak (C_α–N); 32.5, 24.6 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1880 (vs), 1755 (vs), 1685 (vs) (ν_{CO}). Anal. Found: C, 37.36, H, 6.24; Mo, 27.55%. $C_{11}H_{22}N_4O_3Mo$ Calc.: C, 37.29, H, 6.21, Mo, 27.12%.

fac-[(3.2.3)$W(CO)_3$] (**13c**): Yield, 57%. ^{13}C NMR δ: 225.0 (J_{CW} = 185.8 Hz), 223.8 (J_{CW} = 184.4 Hz), 222.7 (J_{CW} = 185.3 Hz) (*C*O); 54.5, 52.9, 50.8, 46.1, 45.5, masked peak (C_α–N); 32.6, 24.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1885 (vs), 1750 (vs), 1690 (vs) (ν_{CO}).

fac-[(2.3.2)$Cr(CO)_3$] (**14a**): ^{13}C NMR δ: 232.20, 232.18, 231.8 (*C*O); 60.9, 53.6, 49.4, 45.4, 43.5, masked peak (C_α–N); 24.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1896 (s), 1754 (vs, br) (ν_{CO}) (55% vs. **15a**).

cis-[(2.3.2){$Cr(CO)_4$}$_2$] (**15a**): ^{13}C NMR δ: 228.0, 226.3, 216.4, 215.4 (*C*O); 54.8, 50.9, 42.3 (C_α–N); 28.0 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1995 (w), 1874 (s), 1859 (s, sh), 1816 (m) (ν_{CO}) (45% vs. **14a**).

fac-[(2.3.2)$Mo(CO)_3$] (**14b**): ^{13}C NMR δ: 228.4, 228.03, 227.98 (*C*O); 61.2, 54.1, 50.1, 45.8, 43.9, masked peak (C_α–N); 24.6 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1887 (s), 1752 (vs, br) (ν_{CO}) (90% vs. **15b**).

cis-[(2.3.2){$Mo(CO)_4$}$_2$] (**15b**): ^{13}C NMR δ: 222.0, 220.6, 208.0, 207.1 (*C*O); 55.1, 50.4, 41.4 (C_α–N); 28.7 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1994 (w), 1880 (s), 1855 (s, sh), 1812 (m) (ν_{CO}) (10% vs. **14b**).

fac-[(2.3.2)$W(CO)_3$] (**14c**): Yield, 46%. ^{13}C NMR δ: 224.3 (J_{CW} = 186.0 Hz), 223.3 (J_{CW} = 187.8 Hz), 223.0 (J_{CW} = 184.8 Hz); 62.0, 54.3, 49.9, 46.4, 44.8, 41.6 (C_α–N); 24.4 (C_β–N) ppm. IR (Nujol) (cm^{-1}): 1869 (s), 1750 (vs, br) (ν_{CO}) (100% vs. **15c**).

fac-[(3.3.3)$Cr(CO)_3$] (**16a**): ^{13}C NMR δ: 232.5, 230.7, 229.7 (*C*O); 56.0 50.9, 49.2, 49.0, 41.8, masked peak (C_α–N); 31.0, 25.7, 24.9 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1892 (s), 1750–1690 (vs, br) (ν_{CO}) (80% vs. **17a**).

cis-[(3.3.3){$Cr(CO)_4$}$_2$] (**17a**): ^{13}C NMR δ: 226.2, 225.6, 215.6, 215.1 (*C*O); 57.0, 54.7, 46.1 (C_α–N); 27.7, 26.6 (2C) (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1996 (w), 1870 (s), 1857 (vs, sh), 1814 (m) (ν_{CO}) (20% vs. **16a**).

fac-[(3.3.3)$Mo(CO)_3$] (**16b**): ^{13}C NMR δ: 228.4, 226.6, 226.3 (*C*O); 56.2, 52.0, 49.7, 49.1, 42.2, masked peak (C_α–N); 31.4, 26.5, 25.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1888 (s), 1750–1690 (vs, br) (ν_{CO}) (90% vs. **17b**).

cis-[(3.3.3){$Mo(CO)_4$}$_2$] (**17b**): ^{13}C NMR δ: 221.0, 219.7, 207.7, 207.0 (*C*O); 55.3, 51.9, 48.9 (C_α–N); 28.8, 26.4 (2C) (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1998 (w), 1876 (s), 1855 (vs, sh), 1808 (m) (ν_{CO}) (10% vs. **16b**).

fac-[(3.3.3)$W(CO)_3$] (**16c**): Yield, 37%. ^{13}C NMR δ: 223.4 (J_{CW} = 186.6 Hz), 222.5 (J_{CW} = 185.5 Hz), 221.9 (J_{CW} = 187.6 Hz) (*C*O); 57.2, 51.9, 49.3, 49.1, 42.4, masked peak (C_α–N); 31.3, 26.4, 25.4 (C_β–N) ppm. IR (Nujol) (cm^{-1}): 1875 (s), 1750–1690 (vs, br) (ν_{CO}) (100% vs. **17c**).

cis-[(3.4.3){$Cr(CO)_4$}$_2$] (**19a**): Yield, 80% (with 2 equiv. of [$Cr(CO)_6$]). ^{13}C NMR δ: 226.3, 224.8, 215.6, 215.1 (*C*O); 57.8, 54.7, 46.2 (C_α–N); 26.5, 25.4 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1995 (w), 1872 (s), 1859 (s, sh), 1815 (m) (ν_{CO}). Anal. Found: Cr, 19.70%. $C_{18}H_{26}N_4O_8Cr_2$ Calc.: Cr, 19.62% (100% vs. **18a**).

fac-[(3.4.3)$Mo(CO)_3$] (**18b**): ^{13}C NMR δ: 228.6, 227.5, 227.0 (*C*O); 57.8, 53.5, 49.4, 46.6, 46.3, 44.7 (C_α–N); 32.8, 28.8, 27.5, 27.1 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1890 (s), 1770–1700 (vs, br) (ν_{CO}) (30% vs. **19b**).

cis-(3.4.3){$Mo(CO)_4$}$_2$] (**19b**): ^{13}C NMR δ: 221.1, 219.6, 207.8, 207.0 (*C*O); 57.6 55.2, 47.3 (C_α–N); 27.1, 25.6 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 2000 (w), 1881 (s), 1864 (vs, sh), 1817 (m) (ν_{CO}) (70% vs. **18b**).

fac-[(3.4.3)$W(CO)_3$] (**18c**): ^{13}C NMR δ: 223.5 (2C)

(J_{CW} = 181.4 Hz), 223.1 (J_{CW} = 181.4 Hz) (*C*O); 58.9, 53.6, 49.8, 47.4, 47.3, 44.8 (C_α–N); 33.0, 32.9, 28.6, 27.5 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1875 (s) 1750–1690 (vs, br) (ν_{CO}) (50% vs. **19c**).

cis-[(3.4.3){W(CO)$_4$}$_2$ (**19c**): ^{13}C NMR δ: 212.7, 212.3, 206.2, 205.1 (J_{CW}, not measurable) (*C*O); 58.9, 56.0, 47.3 (C_α–N); 27.2, 25.5 (C_β–N) ppm. IR (CH_2Cl_2) (cm^{-1}): 1992 (w), 1875 (s), 1845 (vs, sh), 1805 (m) (ν_{CO}) (50% vs. **18c**).

Acknowledgements

This work was supported by the Région Bretagne and the Centre National de la recherche Scientifique (CNRS, URA 322). Dr. R. Pichon and N. Kervarec are gratefully acknowledged for NMR measurements.

References

[1] J.-J. Yaouanc, N. Le Bris, G. Le Gall, J.-C. Clément, H. Handel and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, (1991) 206.

[2] J.-J. Yaouanc, N. Le Bris, J.-C. Clément, H. Handel and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, (1993) 696.

[3] N. Le Bris, J.-J. Yaouanc, J.-C. Clément, H. Handel and H. des Abbayes, *Tetrahedron Lett., 34* (1993) 5429.

[4] R.J. Bergeron, A.H. Neims, J.S. McManis, T.R. Hawthorne, J.R.T. Vinson, R. Bortell and M. Ingeno, *J. Med. Chem., 31* (1988) 1183.

[5] (a) J.P. Behr, *Acc. Chem. Res., 26* (1993) 274; (b) J.P. Behr, *Methods Enzymol., 217* (1993) 599.

[6] E.W. Abel, M.A. Bennett and G. Wilkinson, *J. Chem. Soc.*, (1959) 2323.

[7] (a) C.S. Kraihanzel and F.A. Cotton, *Inorg. Chem., 2* (1963) 53; (b) F.A. Cotton, *Inorg. Chem., 3* (1964) 702; (c) F.A. Cotton and R.M. Wing, *Inorg. Chem., 4* (1965) 314; (d) F.A. Cotton and D.C. Richardson, *Inorg. Chem., 5* (1966) 1851.

[8] J.E. Ellis and G.L. Rochfort, *Organometallics, 1* (1982) 682.

[9] V. Zanotti, V. Rutar and R. Angelici, *J. Organomet. Chem., 414* (1991) 177.

[10] (a) P. Chaudhuri, K. Wieghardt, Y.H. Tsai and C. Krüeger, *Inorg. Chem., 23* (1984) 427; (b) G. Backes-Dahmann, W. Herrmann, K. Wieghardt and J. Weiss, *Inorg. Chem., 24* (1985) 485; (c) G. Backes-Dahmann and K. Wieghardt, *Inorg. Chem., 24* (1985) 4044.

[11] (a) R.W. Hay, I. Fraser and G. Ferguson, *J. Chem. Soc., Chem. Commun.*, (1987) 1715; (b) R.W. Hay and I. Fraser, *J. Chem. Soc., Dalton Trans.*, (1989) 2183.