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Modes of complexation of non-substituted and substituted tetraazamacrocycles with Group 6 metal carbonyls. X-ray structure of [(permethylcyclam)Mo(CO)$_4$]

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Abstract

Reactions of complexation of tetraazamacrocycles L with Group 6 metal carbonyls [M(CO)$_6$](M = Cr, Mo, or W) lead to [LM(CO)$_4$], [LM(CO)$_3$] or [LM(CO)$_2$] entities, depending both on the size of the macrocycle and on the metal M. The structure of one representative complex [(permethylcyclam)Mo(CO)$_4$] has been determined by X-ray diffraction (permethylcyclam: 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane).

Keywords: *N*-functionalization; Chromium; Molybdenum; Tungsten; Macrocyclic complexes; X-ray structures

1. Introduction

Macrocyclic polyamines are intensively studied because of their numerous applications, which often require selective functionalization [1]. In a preliminary report, we have shown that after terdentate complexation with Group 6 metal carbonyls some tetraazamacrocycles can be mono-alkylated readily at the free nitrogen atom [2]. In order to define the scope and the limitations of this new approach, we undertook a study of the modes of complexation of various tetraazamacrocycles **1–8** (Scheme 1) with Group 6 metal carbonyls. (Tetraamines not commercially available were synthesised by a new method [3].)

Prior to our work, and with the few tetraamines studied, the generally observed coordination mode was *fac*-[LM(CO)$_3$] [4]. We show in this study that, depending on the metal and on the ligand, several coordination modes are observed (Eq. 1) under the standard conditions of complexation adopted here (stoichiometric amounts of **1–8** and metal carbonyl in refluxing di-*n*-butylether). We have also examined the effect on the complexation of permethylation of the four nitrogen atoms (ligands **6–8**).

$$\mathrm{L} + [\mathrm{M(CO)_6}] \xrightarrow[\Delta]{{}^n\mathrm{Bu_2O}} [\mathrm{LM(CO)}_{6-x}] + x\mathrm{CO}\uparrow \qquad (1)$$

2. Results and discussion

Coordination modes of cyclic tetraamines **1–8** with Group 6 metal carbonyls were established by IR (Table 1) and NMR spectroscopies (see Experimental details).

2.1. IR study of the coordination mode of cyclic tetraamines 1–8 with Group 6 metal carbonyls

2.1.1. Non-substituted ligands (Tables 1 and 2)

IR spectroscopy proved to be most helpful for the identification of the complexes [5]. IR data for complexes of **1** (cyclen), **2** (cyclam) and **3** (2333) with [Cr(CO)$_6$], [Mo(CO)$_6$] or [W(CO)$_6$] are consistent with

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Table 1
IR spectral data for new complexes

Macrocycle	Metal	Complex	IR bands (cm^{-1})
1	Cr	**11a**	1895 (s) 1755 (vs)
	Mo	**11b**	1885 (s) 1745 (vs)
	W	**11c**	1875 (s) 1725 (vs)
2	Cr	**12a**	1890 (s) 1755 (vs)
	Mo	**12b**	1895 (s) 1765 (vs)
	W	**12c**	1875 (s) 1740 (vs)
3	Cr	**13a**	1890 (s) 1750 (vs)
	Mo	**13b**	1885 (s) 1755 (vs)
	W	**13c**	1880 (s) 1865 (s) 1750 (vs) 1710 (vs)
4	Cr	**14a**	1995 (w) 1870 (vs) 1855 (s) 1810 (s)
	Mo	**14b**	1995 (w) 1865 (vs) 1845 (s) 1810 (s) 1890 (s) 1755 (vs)
	W	**14c**	1870 (s) 1740 (vs)
5	Cr	**15a**	1923 (s) 1903 (m)
	Mo	**15b**	2004 (w) 1860 (vs) 1844 (s) 1804 (s)
	W	**15c**	1998 (w) 1864 (vs) 1846 (s) 1810 (s)
6	Cr	**16a**	1892 (s) 1765 (vs) 1735 (vs)
	Mo	**16b**	1897 (s) 1970 (vs) 1742 (vs)
	W	**16c**	1884 (s) 1758 (vs) 1727 (vs)
7	Cr	**17a**	1999 (w) 1871 (vs) 1860 (s) 1835 (s)
	Mo	**17b**	1998 (w) 1872 (vs) 1865 (s) 1833 (s)
	W	**17c**	1998 (w) 1861 (vs) 1846 (s) 1813 (s)
8	Cr	**18a**	2000 (w) 1875 (vs) 1870 (s) 1820 (s)
	Mo	**18b**	2005 (w) 1885 (vs) 1870 (s) 1830 (s)
	W	**18c**	2001 (w) 1875 (vs) 1855 (s) 1825 (s)

a formulation *fac*-[LM(CO)$_3$]. The two ν(CO) bands in the region 1740–1895 cm^{-1} are consistent with local C_{3v} symmetry for the M(CO)$_3$ group (M = Cr, Mo, or W) which produces $A_1 + E$ stretching modes.

Complexes of **4** (3333) and **5** (3434) exhibit different IR patterns, depending on the metal. **4** reacts with [Cr(CO)$_6$] to give [LM(CO)$_4$] (M = Cr) with C_{2v} local symmetry judged by the four ν(CO) ligands ($2A_1 + B_1 + B_2$) [6]. With [W(CO)$_6$] **4** gives *fac*-[LM(CO)$_3$] (M = W), whereas with [Mo(CO)$_6$] an inseparable mixture of both types of complex were formed. The reactions of **5** (3434) with [Mo(CO)$_6$] and [W(CO)$_6$] lead exclusively to [LM(CO)$_4$] whereas with [Cr(CO)$_6$] it produces a complex of a new type. The two ν(CO) bands at 1923(s) cm^{-1} and 1903(m) cm^{-1} are not consistent with either [LM(CO)$_3$] or [LM(CO)$_4$] though NMR data suggest the structure indicated in Scheme 2.

2.1.2. Permethylated macrocycles ($R = R' = CH_3$) (Tables 1 and 3)

Compounds **7** and **8** react with [Cr(CO)$_6$], [Mo(CO)$_6$] or W(CO)$_6$ to yield [LM(CO)$_4$]. Tetraamine **6** behaves differently and gives [LM(CO)$_3$] entities. Their IR spectra exhibit three bands, which could arise from a *mer*-[LM(CO)$_3$] species with C_{2v} local symmetry. However, to our knowledge, the *mer* isomers have never been observed in [LM(CO)$_3$] complexes of strong σ-donor ligands. We believe that the actual isomeric form of complexes with substituted ligands is *fac* like those of non-substituted ligands. The three IR bands, rather than the two expected for ideal C_{3v} symmetry, may be explained easily by the deformation of the coordination polyhedron (lowering of symmetry) and the lifting of degeneracy of the E mode. In fact, **6** is more strained than **7** and **8**. Such a behaviour has already been reported for *fac*-[LM(CO)$_3$] compounds of 1,1,4,7,7-pentamethyldiethylenetriamine [7].

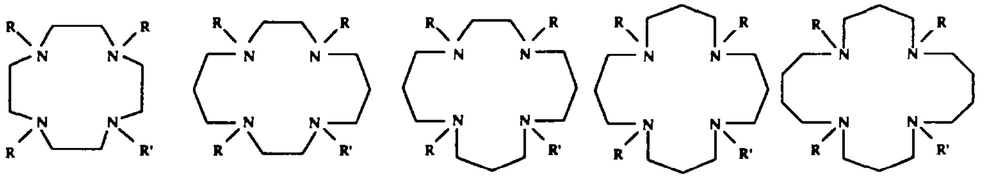
2.2. ^{13}C NMR study

2.2.1. Non-substituted ligands (Table 2)

Further information on the structures of these complexes was obtained from their ^{13}C NMR data. Spectra of derivatives of **1** (cyclen) exhibit two peaks at room temperature, well resolved with molybdenum and tungsten, but broadened with chromium, suggesting rapid exchange of the coordinated nitrogen atoms in this case, as shown in Scheme 3. Complexes of **2** (cyclam) and **3** (2333) show the expected signals for an unsymmetrical tridentate coordination of the *fac*-[LM(CO)$_3$] type.

If $n = 0$ (Scheme 4), only one regioisomer for compound [LM(CO)$_3$] is possible. If $n = 1$, two regioisomers are conceivable. They have been effectively observed with **3**, although separation of the two derivatives has not been realisable. In all cases, the asymmetry of the complexes renders all the atoms magnetically non-equivalent. Three signals in the 1 : 1 : 1 ratio are observed for the three carbon atoms of the M(CO)$_3$ group.

Compound **4** (3333) gives insoluble complexes with chromium and molybdenum. Hence the inferences from the IR data of LCr(CO)$_4$ (**14a**) or LMo(CO)$_x$ (**14b**)



1 : R = R' = H **2** : R = R' = H **3** : R = R' = H **4** : R = R' = H **5** : R = R' = H

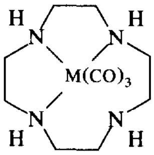
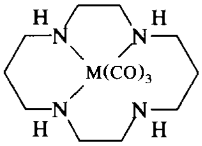
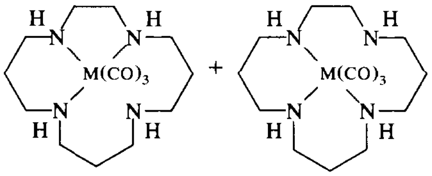
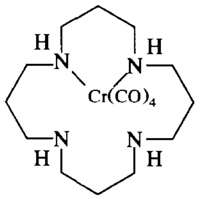
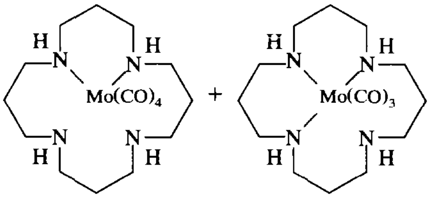
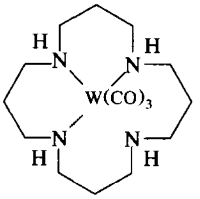
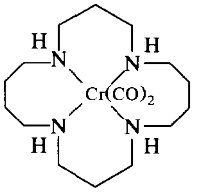
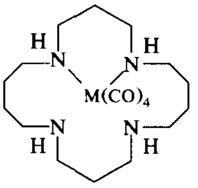
6 : R = R' = CH_3 **7** : R = R' = CH_3 **8** : R = R' = CH_3

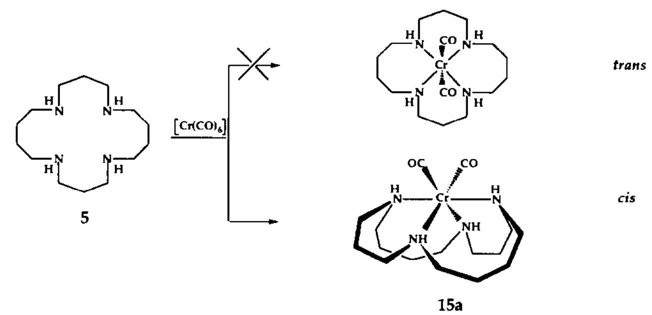
Scheme 1. Tetraazamacrocycles.

could not be confirmed by NMR measurements. Reaction of **4** with $[W(CO)_6]$ gives $[LW(CO)_3]$ (**14c**). Because of the symmetry of the macrocycle, the carbonyl ligands of the $W(CO)_3$ group (Scheme 5), generates two signals in the ratio 2 : 1.

As first inferred from IR data, tetraamine **5** (3434)

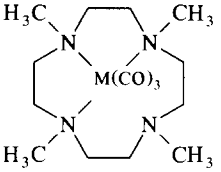
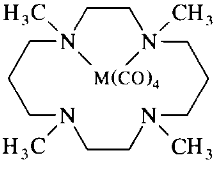
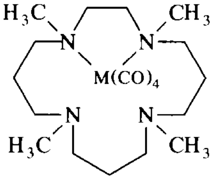
Table 2
Complexes with cyclic tetraamines

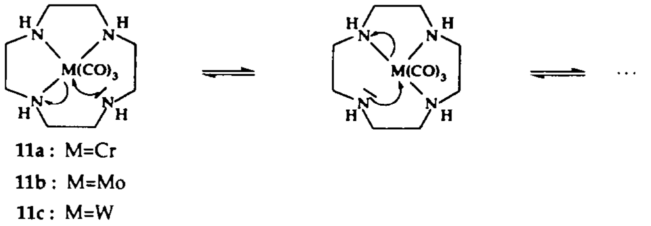
Macrocycle	Metal	Complexes		Yield (%)
1 (cyclen)	Cr Mo W		**11a** **11b** **11c**	80 80 55
2 (cyclam)	Cr Mo W		**12a** **12b** **12c**	80 87 60
3 (2333)	Cr Mo W		**13a** **13b** **13c**	80 75 60
4 (3333)	Cr Mo W	  	**14a** **14b** **14c**	67 70–75 55
5 (3434)	Cr Mo W	 	**15a** **15b** **15c**	62 82 64



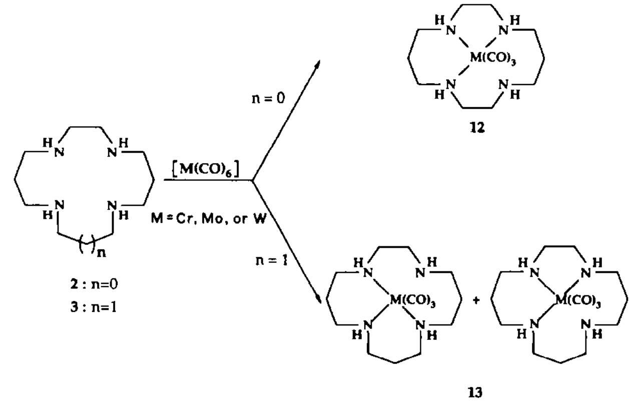
Scheme 2.

Table 3
Complexes with permethylated ligands

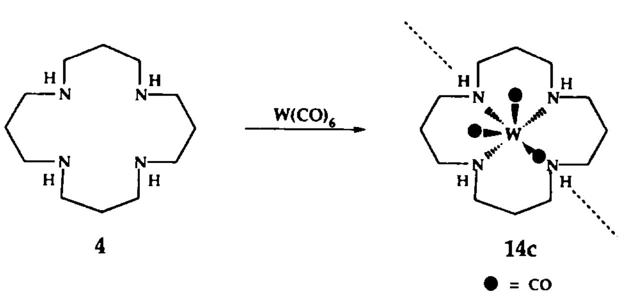
Macrocycle	Metal	Complexes		Yield (%)
6 Me_4cyclen	Cr Mo W		16a 16b 16c	77 81 55
7 Me_4cyclam	Cr Mo W		17a 17b 17c	< 5 82 47
8 Me_4(2333)	Cr Mo W		18a 18b 18c	75 75 60



Scheme 3.



Scheme 4.



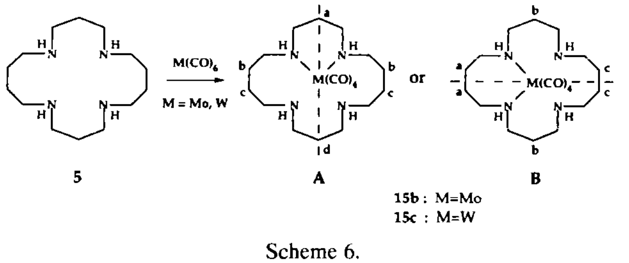
Scheme 5.

does not lead to [$LM(CO)_3$], but with [$Mo(CO)_6$] and [$W(CO)_6$] it yields $LM(CO)_4$ **15b** and **15c** respectively because the four CO ligands give three signals in a 2/1/1 ratio, as expected for local C_{2v} symmetry.

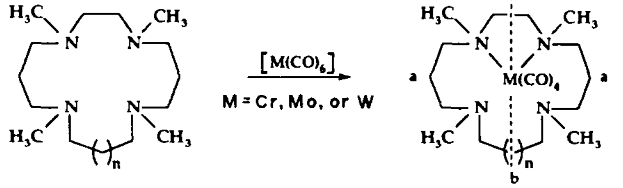
Of the two possible regioisomers **A** or **B** (Scheme 6), only **A** accounts for the NMR data because four distinct upfield signals are observed for the carbon atoms (a, b, c, d)β to nitrogen. **B** would have given only three (a, b, c).

With [$Cr(CO)_6$] **5** gives a complex which possesses a high symmetry because only one signal at 215.3 ppm for the CO ligands, and four sharp signals at 50.9, 50.0 (Cα–N), 29.5 and 28.2 ppm (Cβ–N) for the carbon atoms of the macrocycle are observed. Moreover, whereas the ^{15}N NMR spectrum of [$LW(CO)_4$](**A**) (L = **5**) (Scheme 6) shows two signals (−336.4 and −354.3 ppm) for the two types of nitrogen atom, that of the new complex exhibits only one peak (−338 ppm) for the four nitrogen atoms, [8]. This is consistent with a highly symmetric structure *trans*-[$LM(CO)_2$](D_{4h}). However, this structure must be ruled out because the IR spectrum recorded in hexane or dichloromethane shows two IR active bands, which suggest *cis*-[$LM(CO)_2$] structure with a C_{2v} local symmetry (rather than D_{4h} local symmetry for *trans*-[$LM(CO)_2$] which would be characterised by a single IR band). The very simple NMR spectra described above may be a result of the fluxionality of the [$M(CO)_2$] moiety on the NMR time scale. Considering these conflicting spectroscopic data, we propose *cis* symmetry for **15a** (Scheme 2).

No further information concerning the differences of reactivity of **5** with [$Cr(CO)_6$] and [$M(CO)_6$] (M = Mo



Scheme 6.



7: n=0
8: n=1

17: n=0
18: n=1

Scheme 7.

or W) is available at the moment. Compound (**15a**) may constitute, to our knowledge, the unique example of a tetradentate σ-donor complex derived from a Group 6 hexacarbonyl.

2.2.2. *Substituted ligands (Table 3)*

(a) Permethylated ligands. The permethylated cyclen **6** (Me_4cyclen) reacts with the three metal carbonyls to give complexes in which the $M(CO)_3$ moiety is in rapid exchange. At ambient temperature the NMR spectra show sharp single signals for the CO (ca. 230 ppm) and the methyl groups (ca. 51 ppm), and also a weak broadened signal (ca. 54 ppm) for the methylene groups, which becomes well resolved at higher temperatures. The ^{13}C NMR data yield no further information concerning the *fac* or *mer* geometry of the compounds (see section 2.1.2). Compounds **7** (Me_4cyclam) and **8** (Me_4(2333)) react with the three metal carbonyls to give $[LM(CO)_4]$ regularly with IR spectroscopy, and the three NMR signals (for example at 222.7, 207.9 and 206.9 for the complex $[Mo(CO)_4(Me_4cyclam)]$ **17b**) in the ratio 2 : 1 : 1 for the $M(CO)_4$ moiety.

Complexes derived from **7** ($n = 0$, Scheme 7) show only one signal for the carbon atoms β to nitrogen. In one case, (complex **17b**, M = Mo, $n = 0$), a single crystal suitable for an X-ray analysis was grown from a solution in dibutyl ether. The structure analysis confirms the proposed mode of coordination and the presence of a five-membered metallacycle (see Section 2.2.2 b).

It is likely that **8** coordinates similarly because only two types of carbon β to nitrogen (a and b) are entered in the NMR spectra (Scheme 7).

(b) The structure of **17b**. The crystal structure of **17b** is built of discrete $[(permethylcyclam)Mo(CO)_4]$ molecules. The bidentate permethylcyclam completes the octahedral coordination of the metal (Fig. 1). Selected bond lengths and angles are in Table 4. The mutually *trans* carbonyls CO(2) and CO(3) are bent away from the permethylcyclam. The N1–Mo–N4 angle is acute, as observed in other tetracarbonylmolybdenum complexes with chelating diamines or diphosphines [9–11]. The strong electron donor nature of the permethylcyclam is clearly indicated by the short molybdenum–carbon (carbonyl) bonds *trans* to the nitrogen atoms (π-back-bonding). The Mo–N distances are essentially the same as the corresponding bond lengths in other complexes with saturated amines [9,12,13]. The geometrical parameters in the permethylcyclam are normal.

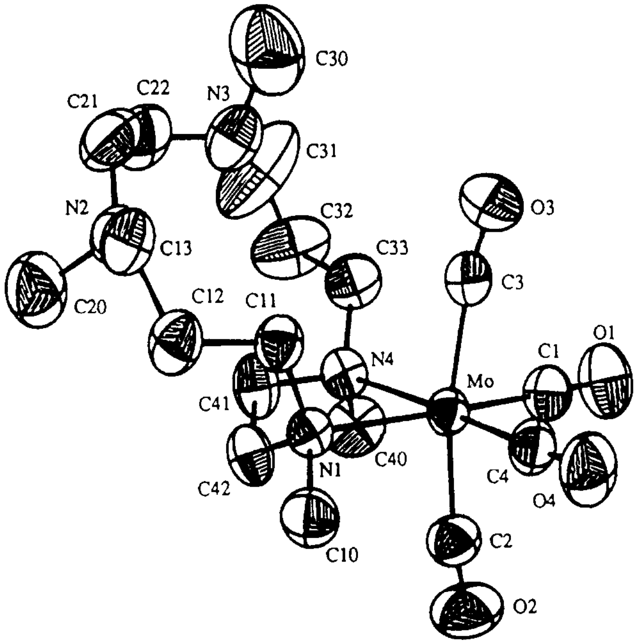


Fig. 1. ORTEP plot (50% probability level) of the molecular structure of $[(permethylcyclam)Mo(CO)_4]$ (**17b**).

3. Experimental details

$[M(CO)_6]$ (M = Cr, Mo, or W) were obtained from Aldrich chemicals; tetraazamacrocycles **1–3** were also obtained from Aldrich Chemicals, and **4** and **5** were prepared according to a published method from this laboratory [3] and permethyl ligands were prepared according to a method of Barefield and Wagner [14].

Table 4
Selected interatomic distances (Å) and angles (°) for $[(permethylcyclam)Mo(CO)_4]$ (**17b**)

Mo–N1	2.335(4)	Mo–C4	1.932(5)
Mo–N4	2.367(3)	C1–O1	1.170(5)
Mo–C1	1.926(4)	C2–O2	1.148(6)
Mo–C2	2.020(5)	C3–O3	1.145(6)
Mo–C3	2.007(5)	C4–O4	1.164(6)
N1–Mo–N4	76.8(1)	N4–Mo–C4	174.7(1)
N1–Mo–C1	174.8(2)	C1–Mo–C2	86.2(2)
N1–Mo–C2	93.7(2)	C1–Mo–C3	84.5(2)
N1–Mo–C3	96.2(2)	C1–Mo–C4	87.2(2)
N1–Mo–C4	97.9(1)	C2–Mo–C3	168.6(2)
N4–Mo–C1	98.1(2)	C2–Mo–C4	87.0(2)
N4–Mo–C2	93.8(2)	C3–Mo–C4	86.0(2)
N4–Mo–C3	94.1(2)		

Elemental analysis were performed by Laboratoire Central de Microanalyse du CNRS, Lyon, France. ^{13}C NMR (75.47 MHz), ^{15}N NMR (30.42 MHz) spectra were measured on a Bruker AC 300 instrument. IR spectra were measured on a Perkin-Elmer 1430 spectrometer.

All manipulations were carried out under purified N_2 with standard Schlenk techniques. Solvents were dried and distilled prior to use.

3.1. General procedure

Sublimed $[M(CO)_6]$ (M = Cr, Mo, or W) (1.1 mmol) and the cyclic tetraamine (1 mmol) were heated at reflux (142°C) in di-*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, and after cooling to room temperature, the yellow solid was separated off, washed with hexanes (3 × 20 ml) and then dried in vacuo at 50°C.

Yields are in Tables 2 and 3.

3.2. X-ray structure analysis of 17b

A yellow crystal suitable for X-ray analysis of dimensions 0.40 × 0.22 × 0.15 mm was grown from dibutyl ether and mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell was determined from 25 randomly selected reflections (CAD4 routines). The crystal and refinement data are given in Table 5. All calculations were carried out using the Enraf-Nonius SDP library [15]. Neutral atom scattering factors and anomalous dispersion corrections were those given by Cromer and Waber [16]. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (ψ scan) was made. The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. An absorption correction (DIFABS [17]) was applied after isotropic refinement of all atoms. All non-hydrogen atoms were further refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions (HYDRO program of SDP) riding on the carbon atoms bearing them. The final residuals were $R = 0.031$, GOF = 1.241, unit weights. The atomic coordinates of non-hydrogen atoms are given in Table 6.

3.3. Supplementary material

Anisotropic temperature factors, hydrogen atom positions, full bond distances and angles, least-squares planes, and a listing of structure factors are available from the authors. All data except the last have been deposited at the Cambridge Crystallographic Data Centre.

Table 5
Crystallographic data for [(permethylcyclam)Mo(CO)$_4$] (**17b**)

Molecular formula	$C_{18}H_{32}MoN_4O_4$
Formula weight, g	464.42
Crystal system	monoclinic
Space group	$P2_1/n$ (No. 14)
Cell dimensions:	
a, Å	9.187(8)
b, Å	20.455(8)
c, Å	12.024(9)
β, deg	94.03(7)
V, Å^3	2254.1
Z	4
ρ_{calc}, g·cm^{-3}	1.368
$F(000)$	968
Radiation, Å	λ (Mo-Kα) 0.71073
T,°C	18
Scan type	$\omega-2\theta$
Scan speed, deg·min^{-1}	1.5–8.3
Scan width, deg.	$\Delta\omega = 0.9 + 0.347 \tan\theta$
Reflections measured	$h, k, \pm l$
θ range, deg.	2–23
Linear abs., μ, cm^{-1}	5.935
No. of reflections measd.	5368
Decay, %	−3.1, corrected
Absorption corrections	
empirical, EAC, min-max	0.9116–0.9970
empirical, DIFABS, min-max	0.8359–1.1720
Cut off for obsd. data	$I > 3\sigma(I)$
No. of unique obsd. data (NO)	2600
No. of variables (NV)	244
$R(F)$	0.031
$Rw(F)$	0.031
weighting scheme	1
GOF	1.241
Max Δ/σ for last cycle	0.04

3.4. Spectroscopic data, elemental analysis

3.4.1. *fac-[cyclenCr(CO)$_3$] (11a)*

Yield: 80%. ^{13}C NMR (DMF-d$_7$): δ 231.8 (*C*O), 49.0 (*C*α-N). IR (CH_2Cl_2): ν_{CO} 1895 (s), 1755 (vs, br).

3.4.2. *fac-[cyclenMo(CO)$_3$] (11b)*

Yield: 80%. ^{13}C NMR (DMF-d$_7$): δ 227.1 (*C*O), 48.2 (*C*α-N). IR (CH_2Cl_2): ν_{CO} 1885 (s), 1745 (vs, br).

3.4.3. *fac-[cyclenW(CO)$_3$] (11c)*

Yield: 55%. ^{13}C NMR (DMF-d$_7$): δ 222.4 (*C*O), 46.4 (*C*α-N). IR (CH_2Cl_2): ν_{CO} 1875 (s), 1725 (vs, br).

3.4.4. *fac-[cyclamCr(CO)$_3$] (12a)*

Yield: 80%. ^{13}C NMR (DMSO-d$_6$): δ 232.8, 232.6, 230.7 (*C*O); 56.8, 56.0, 55.4, 53.3, 49.9, 47.9, 44.4, 42.3 (*C*α-N); 23.9, 23.2 (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1890 (s), 1755 (vs, br). Anal. Found: C, 46.08; H, 7.19;

Table 6
Positional and thermal parameters for [(permethylcyclam)Mo(CO)$_4$] (**17b**)

Atom	x	y	z	B(Å^2)
MO	0.45110(3)	0.25171(2)	0.20439(3)	3.581(5)
N1	0.6886(3)	0.2888(2)	0.2481(3)	3.62(7)
N2	0.7764(4)	0.4780(2)	0.2565(4)	5.54(9)
N3	0.4467(5)	0.5178(2)	0.2289(4)	6.8(1)
N4	0.4196(4)	0.3348(2)	0.3374(3)	4.17(7)
O1	0.1280(4)	0.2110(2)	0.1584(3)	7.8(1)
O2	0.4645(5)	0.1348(2)	0.3766(4)	8.9(1)
O3	0.3723(5)	0.3397(2)	−0.0058(3)	8.9(1)
O4	0.5205(4)	0.1464(2)	0.0308(3)	6.87(9)
C1	0.2497(5)	0.2263(2)	0.1787(4)	4.9(1)
C2	0.4664(5)	0.1798(2)	0.3197(4)	5.4(1)
C3	0.4084(5)	0.3110(2)	0.0731(4)	5.2(1)
C4	0.4957(5)	0.1861(2)	0.0964(4)	4.6(1)
C10	0.7981(5)	0.2350(2)	0.2473(4)	5.6(1)
C11	0.7302(4)	0.3410(2)	0.1706(3)	4.24(9)
C12	0.8800(5)	0.3745(2)	0.1945(4)	5.1(1)
C13	0.8641(5)	0.4479(2)	0.1756(4)	6.1(1)
C20	0.8626(7)	0.4874(3)	0.3623(5)	8.3(2)
C21	0.7087(6)	0.5394(3)	0.2195(6)	8.1(2)
C22	0.5700(6)	0.5541(3)	0.2755(5)	7.7(2)
C30	0.3876(8)	0.5498(4)	0.1291(6)	12.2(3)
C31	0.3345(8)	0.5097(3)	0.3047(6)	13.2(2)
C32	0.3133(7)	0.4510(3)	0.3552(5)	8.9(2)
C33	0.3315(5)	0.3891(2)	0.2853(4)	5.7(1)
C40	0.3474(6)	0.3094(3)	0.4337(4)	6.6(1)
C41	0.5673(5)	0.3609(2)	0.3753(4)	5.3(1)
C42	0.6844(5)	0.3123(2)	0.3641(3)	4.8(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

Cr, 15.60. $C_{13}H_{24}CrN_4O_3$ Calc.: C, 46.42; H, 7.14; Cr, 15.47%.

3.4.5. *fac-[cyclamMo(CO)$_3$] (12b)*

Yield: 87%. ^{13}C NMR (DMSO-d$_6$): δ 228.9, 228.4, 227.6 (*C*O); 55.7, 55.4, 55.2, 53.4, 50.3, 48.1, 44.7, 43.1 (*C*α-N); 24.2, 23.9 (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1895 (s), 1765 (vs, br).

3.4.6. *fac-[cyclamW(CO)$_3$] (12c)*

Yield: 60%. ^{13}C NMR (DMSO-d$_6$): δ 224.6, 223.7, 223.3 (*C*O); 57.6, 56.7, 55.8, 54.6, 50.4, 47.9, 45.2, 43.2 (*C*α-N); 23.8 (2C) (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1875 (s), 1740 (vs, br).

3.4.7. *fac-[(2333)Cr(CO)$_3$] (13a$_1$ + 13a$_2$)*

Yield: 80%. ^{13}C NMR (DMSO-d$_6$): **13a$_1$** δ 231.7, 231.3, 230.8 (*C*O); 59.0, 56.4, 52.7, 51.7, 50.9, 48.5, 46.5, 45.9 (*C*α-N); 28.3, 26.0, 19.8 (*C*β-N); **13a$_2$**: δ 232.8, 232.3, 231.0 (*C*O); 61.9, 58.0, 56.6, 51.7, 50.7, 49.9, 49.8, 45.3 (*C*α-N); 27.2, 26.3, 23.9 (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1890 (s), 1750 (vs, br). Anal. Found: C, 47.77; H, 7.73; Cr, 14.70. $C_{14}H_{26}CrN_4O_3$ calc.: C, 48.0; H, 7.73; Cr, 14.85%.

3.4.8. *fac-[(2333)Mo(CO)$_3$] (13b$_1$ + 13b$_2$)*

Yield: 75%. ^{13}C NMR (DMSO-d$_6$): **13b$_1$** δ 227.6, 227.3, 226.6 (*C*O); 59.1, 56.5, 52.7, 51.7, 51.2, 48.3, 46.8, 45.5 (*C*α-N); 29.3, 25.8, 20.4 (*C*β-N); **13b$_2$**: δ 228.8, 228.2, 228.0 (*C*O); 62.2, 58.3, 57.3, 53.4, 51.8, 50.8, 50.3, 45.4 (*C*α-N) 27.7, 26.9, 24.2 (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1885 (s), 1755 (vs, br).

3.4.9. *fac-[(2333)W(CO)$_3$] (13c$_1$ + 13c$_2$)*

Yield: 60%. ^{13}C NMR (DMSO-d$_6$): **13c$_1$** δ 223.2 (J_{CW} = 184 Hz), 223.0 (J_{CW} = 187 Hz), 221.4 (J_{CW} = 189 Hz) (*C*O); 60.2, 56.8, 53.4, 51.5, 51.2, 48.7, 47.5, 45.6 (*C*α-N); 29.0, 25.9, 20.5 (*C*β-N); **13c$_2$**: δ 224.8 (J_{CW} = 186 Hz), 224.3 (J_{CW} = 188 Hz), 223.1 (J_{CW} = 188 Hz) (*C*O); 63.5, 59.2, 57.7, 54.4, 51.3, 50.3, 50.2, 46.2 (*C*α-N); 27.5, 26.6, 23.9 (*C*β-N). IR (CH_2Cl_2): ν_{CO} 1880 (s), 1865 (s), 1750 (vs, br), 1710 (vs).

3.4.10. *cis-[(3333)Cr(CO)$_4$] (14a)*

Yield: 67%. ^{13}C NMR (DMSO-d$_6$): insoluble complex. IR (CH_2Cl_2): ν_{CO} 1995 (w), 1870 (vs), 1855 (s), 1810 (m).

3.4.11. *cis-[(3333)Mo(CO)$_4$] (14b$_1$)* + fac-[(3333)Mo(CO)$_3$] *(14b$_2$)*

Yield: 70–75%. ^{13}C NMR (DMSO-d$_6$): insoluble complex. IR (CH_2Cl_2): ν_{CO} 1995 (w), 1870 (vs), 1855 (s), 1810 (m) 1890 (s), 1755 (vs, br).

3.4.12. *fac-[(3333)W(CO)$_3$] (14c)*

Yield: 55%. ^{13}C NMR (DMF-d$_7$): δ 223.7 (2C) (J_{CW} not distinguishable because of the weak solubility of the complex), 223.4 (*C*O); 61.2, 52.9, 50.8, 48.1 (*C*α-N); 27.0, 26.0 (*C*β-N). IR (Nujol): ν_{CO} 1870 (s), 1740 (vs, br).

3.4.13. *cis-[(3434)Cr(CO)$_2$] (15a)*

Yield: 62%. ^{13}C NMR (C_6D_6): δ 215.3 (*C*O); 50.9, 50.0 (*C*α-N); 29.5, 28.2 (*C*β-N). IR (hexane): ν_{CO} 1923 (s), 1903 (m). ^{15}NMR (ref. CH_3NO_2 in CD_2Cl_2): δ − 338.0.

3.4.14. *cis-[(3434)Mo(CO)$_4$] (15b)*

Yield: 82%. ^{13}C NMR (CD_2Cl_2): δ 221.2 (2C), 208.4, 207.2 (*C*O); 60.5, 56.5, 50.0, 47.9 (*C*α-N); 31.3, 30.4, 29.9 (2C), 26.0 (2C) (*C*β-N). IR (CH_2Cl_2): ν_{CO} 2004 (w), 1860 (vs), 1844 (s), 1804 (s).

3.4.15. *cis-[(3434)W(CO)$_4$] (15c)*

Yield: 64%. ^{13}C NMR (DMSO-d$_6$): δ 213.4 (2C), 206.3, 206.2 (*C*O); 62.2, 58.1, 51.2, 48.3 (*C*α-N); 31.8; 30.8, 30.4 (2C), 26.8 (2C) (*C*β-N). IR (CH_2Cl_2): ν_{CO}

1998 (w), 1864 (vs), 1846 (s), 1810 (s). ^{15}NMR (ref. CH$_3$NO$_2$ in CD$_2$Cl$_2$): δ − 336.4, −354.3.

3.4.16. *fac-[(Me$_4$cyclen)Cr(CO)$_3$] (16a)*

Yield: 77%. ^{13}C NMR (DMSO-d$_6$): δ 233.9 (*C*O); 56.3, 50.8 (*C*α-N). IR (CH$_2$Cl$_2$): ν_{CO} 1892 (s), 1765 (vs), 1735 (vs).

3.4.17. *fac-[(Me$_4$cyclen)Mo(CO)$_3$] (16b)*

Yield: 81%. ^{13}C NMR (DMSO-d$_6$): δ 230.1 (*C*O); 54.9, 50.8 (*C*α-N). IR (CH$_2$Cl$_2$): ν_{CO} 1897 (s), 1765 (vs), 1742 (vs).

3.4.18. *fac-[(Me$_4$cyclen)W(CO)$_3$] (16c)*

Yield: 55%. ^{13}C NMR (DMSO-d$_6$): δ 225.0 (J_{CW} = 187 Hz) (*C*O); 53.1, 51.6 (*C*α-N). IR (CH$_2$Cl$_2$): ν_{CO} 1884 (s), 1758 (vs), 1727 (vs).

3.4.19. *cis-[(Me$_4$cyclam)Cr(CO)$_4$] (17a)*

Yield less than 5%. ^{13}C NMR (CD$_2$Cl$_2$): δ 228.3 (2C), 215.3, 214.2 (*C*O); 61.3, 57.6, 56.5, 55.9, 50.5, 41.1 (*C*α-N); 20.5 (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 1999 (w), 1871 (vs), 1860 (s), 1835 (s).

3.4.20. *cis-[(Me$_4$cyclam)Mo(CO)$_4$] (17b)*

Yield: 82%. ^{13}C NMR (C$_6$D$_6$): δ 222.7 (2C), 207.9, 206.9 (*C*O); 60.9, 57.4, 56.3, 54.5, 50.5, 41.3 (*C*α-N); 20.6 (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 1998 (w), 1872 (vs), 1865 (s), 1833 (s).

3.4.21. *cis-[(Me$_4$cyclam)W(CO)$_4$] (17c)*

Yield: 47%. ^{13}C NMR (CD$_2$Cl$_2$): δ 214.1 (2C) (J_{CW} not distinguishable), 207.3, 207.0 (*C*O); 62.1, 58.2, 56.5, 55.3, 51.7, masked peak (*C*α-N); 21.0 (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 1998 (w), 1861 (vs), 1846 (s), 1813 (s).

3.4.22. *cis-[{Me$_4$(2333)}Cr(CO)$_4$] (18a)*

Yield: 75%. ^{13}C NMR (CD$_2$Cl$_2$): δ 227.9 (2C), 214.6, 213.8 (*C*O); 63.2, 56.5, 55.1, 54.5, 51.0, 42.5 (*C*α-N); 27.1, 20.2 (2C) (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 2000 (w), 1875 (vs), 1870 (s), 1820 (s).

3.4.23. *cis-[{Me$_4$(2333)}Mo(CO)$_4$] (18b)*

Yield: 75%. ^{13}C NMR (C$_6$D$_6$): δ 222.3 (2C), 207.9, 206.9 (*C*O); 62.0, 56.2, 54.7, 53.8, 50.6, 42.2 (*C*α-N); 26.6, 20.4 (2C) (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 2005 (w), 1885 (vs), 1870 (s), 1830 (s).

3.4.24. *cis-[{Me$_4$(2333)}W(CO)$_4$] (18c)*

Yield: 60%. ^{13}C NMR (CD$_2$Cl$_2$): δ 214.1 (2C) (J_{CW} = 168 Hz), 207.5 (J_{CW} = 139 Hz), 207.1 (J_{CW} = 139 Hz) (*C*O); 64.1, 56.3, 56.2, 54.3, 52.3, 42.4 (*C*α-N); 26.9, 21.3 (2C) (*C*β-N). IR (CH$_2$Cl$_2$): ν_{CO} 2001 (w), 1875 (vs), 1855 (s), 1825 (s). Anal. Found: C, 39.96; H, 5.78; W, 33.98. C$_{19}$H$_{34}$N$_4$O$_4$W calc.: C, 40.15; H, 6.32; W, 34.18%.

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References

[1] E. Kimura, *Tetrahedron, 48* (1992) 6217.

[2] 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.

[3] V. Panetta, J.J. Yaouanc and H. Handel, *Tetrahedron Lett., 33* (1992) 5505.

[4] (a) S.W. Kirtley, in G. Wilkinson, F. Gordon, A. Stone and E.W. Abel (Eds.), *Comprehensive Organometallic Chemistry*, Vol. 3, Pergamon Press, 1982; (b) R.W. Hay, I. Fraser and G. Ferguson, *J. Chem. Soc., Chem. Commun.*, (1987) 1715; R.W. Hay, I. Fraser and G. Ferguson, *J. Chem. Soc., Dalton Trans.*, (1989) 2183.

[5] B.M. Trost and C.A. Merlic, *J. Am. Chem. Soc., 112* (1990) 9590.

[6] (a) C.S. Kraihanzel and F.A. Cotton, *Inorg. Chem., 2* (1963) 533; (b) F.A. Cotton, *Inorg. Chem., 3* (1964) 702.

[7] (a) J.E. Ellis and G.L. Rochefort, *Organometallics, 5* (1982) 683; (b) V. Zanotti, V. Rutar and R.J. Angelici, *J. Organomet. Chem., 414* (1991) 177.

[8] F. Carré, C. Chuit, R.J.P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem., Int. Edn. Engl., 33* (1994) 1097.

[9] K.-B. Shiu, S.-L. Wang and F.-L. Liao, *J. Organomet. Chem., 420* (1991) 207.

[10] P.N.W. Baxter, J.A. Connor, J.D. Wallis and D.C. Povey, *J. Organomet. Chem., 426* (1992) 187.

[11] C.-H. Ueng and L.-C. Leu, *Acta Crystallogr., C47* (1991) 725.

[12] J.L. Atwood and D.J. Darensbourg, *Inorg. Chem., 16* (1977) 2314.

[13] F.A. Cotton, D.J. Darensbourg, S. Klein and B.W.S. Kolthammer, *Inorg. Chem., 21* (1982) 1651.

[14] E.K. Barefield and F. Wagner, *Inorg. Chem., 12* (1973) 2435.

[15] B.A. Frenz, The Enraf-Nonius CAD4-SDP, *Computing in Crystallography*, University Press, Delft, Holland, 1978.

[16] D.T. Cromer and J.T. Waber, *International Tables for X-ray Crystallography*, Vol. 4, Kynoch, Birmingham, 1975.

[17] N. Walker and D. Stuart, *Acta Crystallogr., A39* (1983) 158.