Modes of complexation of bis-aminals of linear tetraamines with Group 6 metal carbonyls

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Abstract

On reaction with Group 6 metal carbonyls $M(CO)_6$, *vic* type bis-aminals L, issued from the condensation of an α-dicarbonyl compound on a linear tetraamine, give rise to mononuclear *cis*-$M(CO)_4L$ complexes. © 1999 Elsevier Science S.A. All rights reserved.

1. Introduction

Polyamines form with Group 6 hexacarbonyl metals (Cr, Mo, W) stable complexes by successive substitutions of the carbonyl groups [1]. Behrens et al. have first realized the complexation of ethylenediamine (L) with hexacarbonylchromium [2], and later, complexes of molybdenum and tungsten have been described [3]. Infrared spectroscopic studies show in every case the structure *cis*-$M(CO)_4L$ of C_{2v} local symmetry. Using a linear or cyclic triamine, the trisubstitution to the metal is observed and the reaction gives rise to a facial tricarbonyl complex *fac*-$M(CO)_3L$, with C_{3v} local symmetry. Some of these complexes have been known for several years, particularly those issued from diethylenetriamine [4].

The first example of complexation of a cyclic tetraamine was reported by Frazer et al. [5]. This tetraazamacrocycle, C-*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, potentially tetradentate, behaves like a tridentate ligand and IR spectroscopy of the complex is in agreement with a *fac*-$M(CO)_3$ configuration of C_{3v} local symmetry.

In previous works, we have described studies of the coordination modes of cyclic and linear tetraamines, with Group 6 metal carbonyls [6,7]. The linear tetraamine-ligands lead to mononuclear *fac*-$M(CO)_3L$, *cis*-$M(CO)_4L$ or dinuclear *cis*-$[M(CO)_4]_2L$ complexes according to the size of the metal and the chain lengths; the two secondary amino function are always implicated in the coordination to the metal, and we have observed that the formation of the maximum of five membered metallocycles is the driving force of the reaction [6]. With cyclic tetraamines (cyclam, cyclen, homocyclen), whatever the metal used, the reactions of complexation lead to *fac*-$M(CO)_3L$ compounds, through the formation of internal five or six-membered metallocycles [7]. An original dicarbonyl complex $Cr(CO)_2L$ has been obtained from a larger macrocycle: 1,6,11,16-tetraazacycloeicosane.

In this paper, we report the complexation with Group 6 metal carbonyls of various bis-aminals, issued from the condensation of an α-dicarbonyl compound on a linear tetraamine. These compounds can be considered as rigidified linear polyamines that possess secondary and tertiary amino functions. From this point of view, it seemed interesting to study their complexation modes and the opportunity to obtain *cis*-$M(CO)_4L$ complexes with a coordination to the metal of the secondary and/or tertiary amino functions

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[8,9] and the eventual formation of dinuclear complexes.
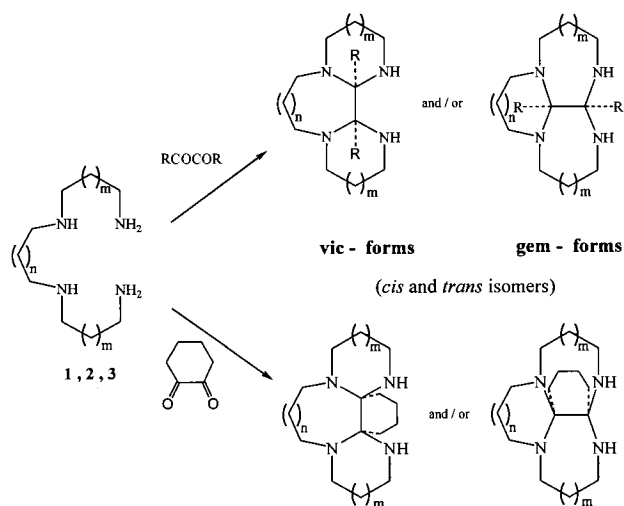
2. Results and discussion

2.1. Bis-aminals

In principle, the condensation of a linear tetraamine on a α-dicarbonyl reagent can lead to a mixture of tricyclic compounds containing a bis-aminal bridge [10]. According to Scheme 1, condensation of a series of three tetraamines (1–3) on two linear dicarbonyl reagents, glyoxal and butanedione, and a cyclic one, cyclohexanedione, is able to lead to a mixture of four stereoisomers.

The reactions are undertaken under identical conditions i.e. dicarbonyl compound and amine (one equivalent) in acetonitrile or ethanol. The results are summarized in Table 1. All compounds issued from glyoxal condensation on a tetraamine have been cited in the literature [10–12]; in the cases of 7 and 10 yields have been optimized and a study of 4, which exists in a mixture of four stereoisomers has been published [13]. In previous papers, we have described the synthesis of bis-aminals 5, 8, 11 and their use as precursors of macrocycles [14]. To our knowledge, bis-aminals 6, 9, 12 are original. All these products (4–12) have been characterized by ^{1}H-, ^{13}C-NMR and by X-ray analysis for two of them [14].
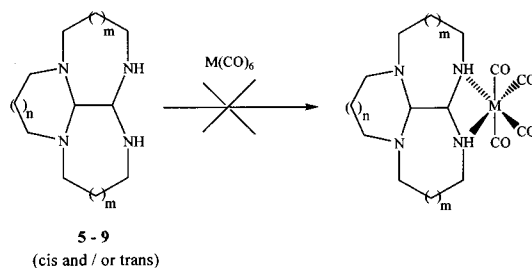
Table 1

Scheme 1.

1 : m = 0 , n = 0 : triethylenetetraamine or (222)
2 : m = 0 , n = 1 : N,N' - bis(2-aminoethyl)-1,3-propanediamine or (232)
3 : m = 1 , n = 0 : N,N'- bis(3-aminopropyl)-ethylenediamine or (323)
R = H (glyoxal); R = Me (butanedione)

Scheme 2.

In fact, these condensations lead to the most stable products characterized by a maximum of six-membered fused rings. The *trans* stereochemistry can be easily distinguished from the *cis* one using dynamic ^{13}C-NMR. In fact, *cis*-fused rings are well known for their temperature ^{13}C-NMR dependence [15]. We have observed exchange phenomena for the three cyclohexanedione bis-aminals **6**, **9**, **12**, showing their *cis* configuration.

2.2. Reactions of complexation of bis-aminals

The complexation of these ligands was run according to previously described conditions [6,7], using a slight excess of $M(CO)_6$ in refluxing dibutylether under nitro-

gen at atmospheric pressure. The reaction yielded yellow to brown crystalline powders which precipitated from the reaction medium.

Bis-aminals **5**–**9**, appearing exclusively in a *gem* configuration do not lead to the formation of complexes (Scheme 2), therefore, they are entirely recovered. These results are the expression of the impossibility to form four-membered metallocycles when the bis-aminal is *gem* type, whatever the metal used, probably because the two secondary amino functions are not correctly positioned for a coordination to the metal.

When bis-aminals only exist in a *vic* configuration, in the case of compounds **10**–**12**, complexation occurs. Results of these complexations are summarized in Table 2. In all cases, IR spectroscopy indicates that the secondary amine stretching band is shifted to low frequencies (ca. 100 cm^{-1}), in agreement with the coordination of the N–H nitrogen atoms to the metal, via a five-membered metallocycle. Furthermore, the IR spectra of all adducts **13**–**20** are consistent with the presence of a *cis*-$M(CO)_4$ moiety since the four ($2A_1/B_1/B_2$) expected $v(CO)$ bands for a structure possessing a local C_{2v} symmetry are observed. ^{13}C-NMR spectra are consistent with this last interpretation and prove moreover that initial configurations of bis-aminals are maintained.
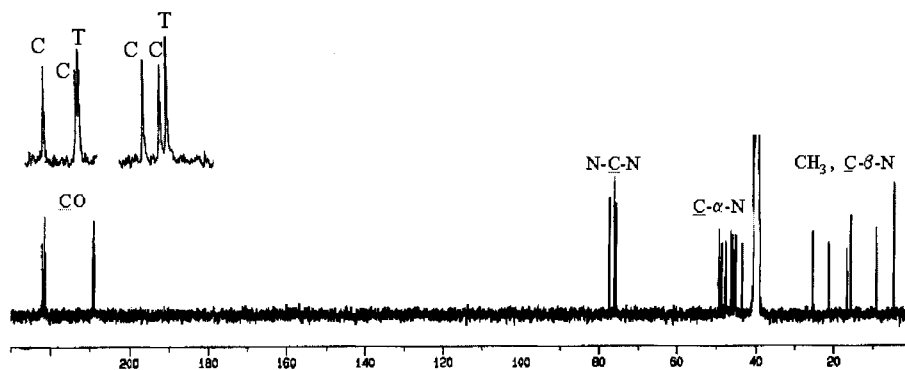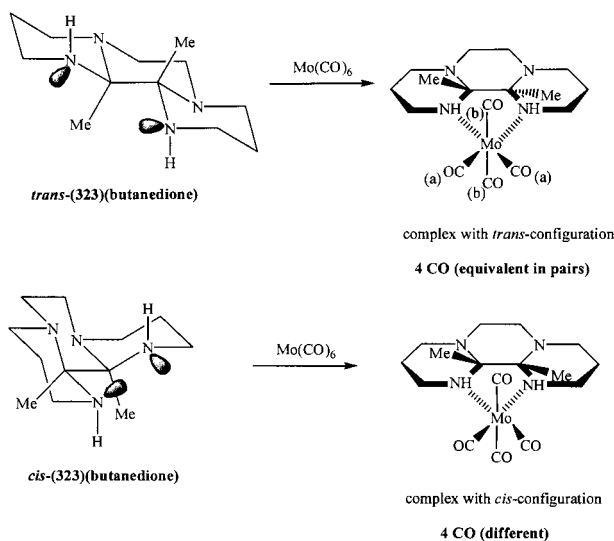
Fig. 1. ^{C}: [cis-(323)(butanedione)]Mo(CO)$_4$. ^{T}: [trans-(323)(butanedione)]Mo(CO)$_4$.

Table 2

| Aminal	M(CO)$_6$	Complexes	Configuration	Yields (%)	N°
	Cr		*Mixture of two complexes* ratio 1:4	85	**13'; 13**
10	Mo		*trans*	80	**14**
	W		*trans*	30	**15**
	Cr		*cis + trans* ratio 2:1	60	**16**
11	Mo		*cis + trans* ratio 2:1	95	**17**
	W		*trans*	20	**18**
	Cr		*cis*	72	**19**
12	Mo		*cis*	84	**20**
	W	---------		------	------

Scheme 3.

Thus, in the case of ligand **11**, which is constituted by a mixture of *cis* and *trans* isomers in ratio 2:1, complexation with Cr(CO)$_6$ or Mo(CO)$_6$ leads to the formation of two complexes in the initial proportions (Fig. 1).

The *trans*-configuration ligand, symmetrical, is well known to be rigid and possess a C$_2$ axis which make equivalent in pairs the atoms of the molecule (Scheme 3). One can note that, in the minor form of the complex **17**, the C$_2$ axis is retained. This form shows only two peaks for the carbonyl groups which indicates a symmetrical structure, i.e. the *trans* configuration. Thus, either carbonyl groups (a), *trans* to nitrogen, and the other ones (b), *trans* to each other, are equivalent. In return, ligands with a *cis* configuration are conformationally labile and ^{13}C-NMR spectra show, at low temperature, one signal for each atom of the molecule which indicates an unsymmetrical conformation. Molecular models examination is consistent with three six-membered fused rings in chair conformation with, consequently, one alkyl group in axial position and the other one in equatorial position (Scheme 3). The lack of symmetry is also visible in the major form of the complex **17**: all the carbon atoms are distinguished and the four distinct signals with equivalent intensity, near 220–230 ppm (Fig. 1) are attributed to the four carbonyl groups of the *cis* form of the complex. One should note that with W(CO)$_6$, only the *trans* one is complexed while the *cis* configuration is unreactive.

In the case of bis-aminal **12**, present exclusively in *cis* configuration, complexations with chromium and molybdenum provide the attempted disubstituted complexes *cis*-M(CO)$_4$L. With W(CO)$_6$, the complexation has failed as with ligand **11**: it seems that *cis* configurations are not favorable to the complexation perhaps because of the size of this metal.

Another phenomenon can be put forward: a partial dehydrogenation is observed; the reaction of bis-aminals **10**, with Cr(CO)$_6$ in dibutylether, leads to a mixture of two species in ratio 1:4. The two complexes **13** and **13′**, which exhibit a C$_{2v}$ local symmetry in IR spectroscopy, are identified by ^{13}C-NMR spectroscopy: while the major one **13** exhibits the seven signals awaited for the symmetrical complex issued from the *trans* bis-aminal, the minor compound **13′** presents 14 peaks indicating an unsymmetrical molecule. Moreover a quaternary sp^2 carbon atom is present at 154 ppm, and only one aminal-type carbon is detected. These observations are consistent with the loss of a dihydrogen molecule from the ligand, under the influence of the metal in the reaction conditions (Bu$_2$O, reflux). Such a dehydrogenation of polyamines by metals has been reported with palladium [16].

Bis-aminal **4,** which exists in a mixture of four stereoisomers, (*cis*/*trans*)-*vic* forms and (*cis*/*trans*)-*gem* ones, behaves differently towards metal carbonyls. In a recent paper, we have brought to the fore the irreversible isomerization of the different configurations of this ligand [14]. On warming, the mixture evolves to give only *gem* forms. The reaction of complexation of this mixture with Cr(CO)$_6$ leads to a single unsaturated compound **21** (Scheme 4) whose structure is similar to complex **13′** i.e. issued from dehydrogenation (Table 2). The yield of the complexation (35%) seems to indicate that only the *vic* forms are complexed. With Mo(CO)$_6$, the reaction of complexation leads to a mixture of the two *vic* complexes **22** (*cis*/*trans*), while the two *gem* forms of initial bis-aminals are recovered in the filtrate of the reaction. We suppose that this metal is reactive enough to coordinate to the *vic* forms before their complete isomerization.
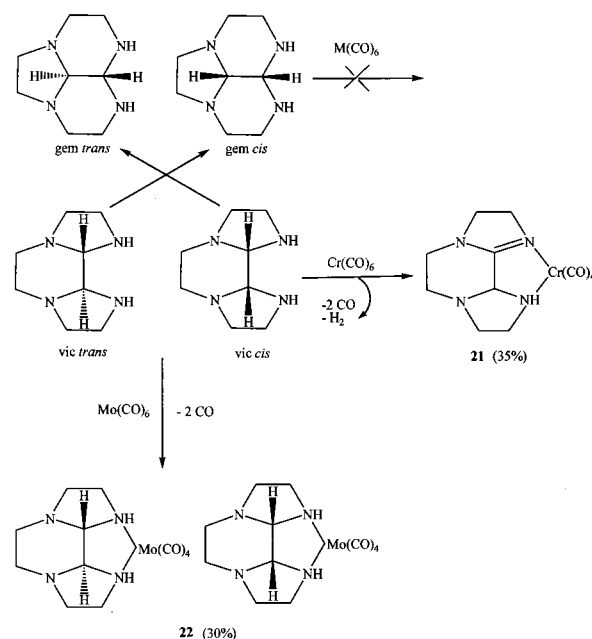
Scheme 4.

In the case of complexation with $W(CO)_6$, we do not observe any coordination with bis-aminals. This metal, as previously seen, is weakly reactive, thus in the reaction conditions (high temperature for many hours), isomerization of the *vic* forms into the *gem* configurations, which are inert towards complexation, proceeds faster than coordination.

3. Conclusions

As summarized in Table 2, it appears that each bis-aminal possessing a *vic* configuration, is able to coordinate to Group 6 metal carbonyls to form mononuclear *cis*-$M(CO)_4L$ complex via exclusive coordination of the two secondary amino functions while *gem* forms are unreactive. Moreover, the reactions of complexation seem to be a complementary method, to dynamic ^{13}C-NMR, for the determination of the stereochemistry of bis-aminals. Indeed, the coordination to the metal proceeds with maintain of the configurations and proportions of the initial ligands. For this purpose, the use of $Mo(CO)_6$ is preferable as this metal reacts readily without by-products and leads to stable complexes.

4. Experimental

4.1. General comments

All reactions of complexation were carried out under a nitrogen atmosphere 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 or hexane).Tetraamines are available from Acros and metal carbonyls from Aldrich.

IR spectra were obtained using a Perkin–Elmer 1430 spectrometer. The NMR spectra were recorded on a Bruker AC 300 (^{13}C: 75.47 MHz; ^1H: 300 MHz) or on a Bruker Advance DRX 400 (^{13}C: 100.62 MHz; ^1H: 400 MHz) spectrometers. Microanalyses were carried out by the Centre de Microanalyses du CNRS de Lyon, France.

4.2. Typical procedure for the synthesis of bis-aminals 4–12

The α-dicarbonyl compound (5 mmol) in solution in CH_3CN (10 ml) or EtOH (10 ml) was added drop-wise to a cooled (between 0 and 5°C) and stirred solution of the tetraamine (5 mmol) in CH_3CN (10 ml) or EtOH (10 ml, with two drops of glacial CH_3COOH). After completion of the reaction (2 h), the solvent was evaporated under reduced pressure to yield the corresponding bis-aminal. It is obtained as a powder (or an oil) which

is taken in toluene (20 ml). The mixture is allowed to stand 15 min and then polymers were eliminated by filtration. The filtrate was evaporated and the procedure repeated twice to yield pure bis-aminal.

4.3. Selected spectroscopic data of bis-aminals

4.3.1. (222)(Glyoxal) (4)
For the mixture of the four stereoisomers of this compound see Ref. [13].

4.3.2. (232)(Glyoxal) (7)
Yield, 95%. ^{13}C-NMR (Toluene-d_8, 75.47 MHz, 250 K): *trans*-**7** (ratio 1:2 vs. *cis*-**7**) δ: 24.7 ($\underline{C}$-β-N); 44.1, 54.3, 55.3 ($\underline{C}$-α-N); 71.6, 88.4 (N-$\underline{C}$-N) ppm; *cis*-**7** δ: 19.8 ($\underline{C}$-β-N); 39.5, 45.4 (2C), 52.8, 55.3, 58.0 ($\underline{C}$-α-N); 67.4, 77.2 (N-$\underline{C}$-N) ppm.

4.3.3. (323)(Glyoxal) (10)
Yield: 95%. m.p.: 104°C. ^{13}C-NMR δ: ($CDCl_3$, 75.47 MHz, 298 K): 25.3 ($\underline{C}$-β-N); 43.6, 51.3, 53.4 ($\underline{C}$-α-N); 77.7 (N-$\underline{C}$-N) ppm. ^1H-NMR δ: ($CDCl_3$, 300 MHz, 298 K): 2.54, (s, 2H, N-C$\underline{H}$-C$\underline{H}$-N) ppm.

4.3.4. (222)(Butanedione) (5), (232)(butanedione) (8), (323)(butanedione) (11)
For these bis-aminals see Ref. [14].

4.3.5. (222)(Cyclohexanedione) (6)
Yield: 90%. ^{13}C-NMR δ: ($CDCl_3$, 100.62 MHz, 298 K): 19.0, 31.6, 32.1, 40.6 ($\underline{C}H_2$ cycle); 40.5, 44.1, 48.4, 50.8, 54.3, 54.8 ($\underline{C}$-α-N); 69.3, 79.3 (N-$\underline{C}$–N) ppm.

4.3.6. (232)(Cyclohexanedione) (9)
Yield: 90%. ^{13}C-NMR δ: ($CDCl_3$, 100.62 MHz, 298 K): 17.4, 18.3, 21.2, 22.4 ($\underline{C}H_2$ cycle); 33.0 ($\underline{C}$-β-N); 39.0, 41.2, 45.7 (2), 47.9, 50.3 ($\underline{C}$-α-N); 66.8, 72.8 (N-$\underline{C}$-N) ppm.

4.3.7. (323)(Cyclohexanedione) (12)
Yield: 95%. ^{13}C-NMR δ: ($CDCl_3$, 75.47 MHz, 298 K): 14.6, 16.0, 20.3, 21.1 ($\underline{C}H_2$ cycle); 25.6, 27.3 ($\underline{C}$-β-N); 37.9 (2C), 44.4, 45.2, 47.7, 48.6 ($\underline{C}$-α-N), 70.5, 71.7 (N-$\underline{C}$-N) ppm.

4.4. Typical procedure for the reactions of complexation

Sublimed $[M(CO)_6]$ (M/Cr, Mo, W) (1.1 mmol) and bis-aminal (1 mmol) were heated under reflux (142°C) in *n*-dibutylether (20 ml) for 2 h (M/Cr, 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 or brown precipitate formed during the reaction. After cooling to room temperature, the solid was separated off, washed with hexane (3 × 20 ml) and then dried in vacuo at 50°C.

4.5. Spectroscopic data of complexes *13*–*22*

All the chemical shifts δ are given relative to the solvent DMSO-d_6.

4.5.1. [(323)(Glyoxal)Cr(CO)₄] (13/13′)

Yield: 85%. IR (CH₂Cl₂) (cm⁻¹): 2000 (w), 1882 (s, sh), 1870 (vs), 1825 (m) ν(CO). ¹³C-NMR (*13*) (ratio 4:1 vs. *13′*) δ: 25.7 (C-β-N); 51.7, 52.8 (2C) (C-α-N); 80.2 (N-C-N); 215.7, 227.0 (CO) ppm; (*13′*) δ: 20.6, 25.6 (C-β-N); 45.3, 47.8, 48.9, 49.1, 52.1, 53.2 (C-α-N); 80.7 (N–C–N); 153.4 (N=C–N); 214.7, 216.4, 227.7, 227.8 (CO) ppm.

4.5.2. [(323)(Glyoxal)Mo(CO)₄] (14)

Yield: 80%. IR (CH₂Cl₂) (cm⁻¹): 2000 (w), 1885 (s, sh), 1865 (vs), 1825 (m) ν(CO). ¹³C-NMR δ: 25.6 (C-β-N); 51.8, 53.0, 53.4 (C-α-N); 80.6 (N-C-N); 207.5, 221.6 (CO) ppm. Anal. Calc. for C₁₄H₂₀N₄O₄Mo: C, 41.58; H, 4.95; N, 13.86; Mo, 23.76. Found: C, 42.01; H, 5.11; N, 14.18; Mo, 23.58.

4.5.3. [(323)(Glyoxal)W(CO)₄] (15)

Yield: 30%. IR (CH₂Cl₂) (cm⁻¹): 1992 (w), 1870 (s, sh), 1855 (vs), 1810 (m), ν(CO). ¹³C-NMR δ: 26.1 (C-β-N); 52.2, 52.9, 54.7 (C-α-N); 81.9 (N–C–N); 205.2, 214.1 (CO) ppm.

4.5.4. [(323)(Butanedione)Cr(CO)₄] (16)

Yield: 60%. IR (CH₂Cl₂) (cm⁻¹): 1995 (w), 1870 (s, sh), 1852 (vs), 1830 (m), ν(CO). ¹³C-NMR *trans*-*16* (ratio 1:2 *vs cis*-*16*): δ: 4.3 (CH₃); 25.3 (C-β-N); 44.6, 46.8, 48.6 (C-α-N); 75.3 (N-C-N); 217.0, 226.9 (CO) ppm; *cis*-*16* δ: 8.6, 15.7 (CH₃); 16.8, 20.5 (C-β-N); 43.1, 44.6, 44.8, 45.7, 47.0, 48.0 (C-α-N); 74.8, 77.0 (N–C–N); 216.8, 217.4, 226.2, 227.0 (CO) ppm.

4.5.5. [(323)(Butanedione)Mo(CO)₄] (17)

Yield: 95%. IR (CH₂Cl₂) (cm⁻¹): 1995 (w), 1890 (s, sh), 1870 (vs), 1825 (m) ν(CO). ¹³C-NMR: *trans*-*17* (ratio 1:2 vs. *cis*-*17*) δ: 4.8 (CH₃); 25.5 (C-β-N); 45.0, 46.2, 49.2 (C-α-N); 76.1 (N-C-N); 220.9, 221.4 (CO) ppm; *cis*-*17* δ:9.2, 15.7 (CH₃); 16.7, 21.3 (C-β-N); 43.4, 45.0, 45.3, 47.3, 47.6, 48.4 (C-α-N); 75.8, 77.4 (N–C–N); 209.0, 209.2, 221.4, 221.9 (CO) ppm. Anal. Calc. for C₁₆H₂₄N₄O₄Mo: C, 44.44; H, 5.56; N, 12.96; Mo, 22.22. Found: C, 44.65; H, 5.43; N, 12.80; Mo, 22.41.

4.5.6. [(323)(Butanedione)W(CO)₄] (18)

Yield, 30%. IR (CH₂Cl₂) (cm⁻¹): 2000 (w), 1870 (s, sh), 1855 (vs), 1825 (m), ν(CO). ¹³C-NMR δ: 4.8, (CH₃); 25.5 (C-β-N); 45.9, 46.7, 49.4 (C-α-N); 77.3 (N–C–N); 207.1, 213.1 (CO) ppm.

4.5.7. [(323)(Cyclohexanedione)Cr(CO)₄] (19)

Yield: 72%. IR (CH₂Cl₂) (cm⁻¹): 1992 (w), 1870 (s, sh), 1855 (vs), 1825 (m), ν(CO). ¹³C-NMR δ: 14.9, 17.0, 19.7 (2C) (CH₂ cycle); 20.6, 22.8 (C-β-N); 43.4, 44.1 (2C), 46.3, 46.8, 47.9 (C-α-N); 74.2, 75.8 (N–C–N); 217.7, 21.9, 226.6, 227.5 (CO) ppm.

4.5.8. [(323)(Cyclohexanedione)Mo(CO)₄] (20)

Yield: 85%. IR (CH₂Cl₂) (cm⁻¹): 1995 (w), 1870 (s, sh), 1855 (vs), 1820 (m) ν(CO). ¹³C-NMR δ: 13.8, 14.7, 19.3, 19.4 (CH₂ cycle); 21.1, 22.6 (C-β-N); 43.0, 43.7, 44.2, 46.4, 46.6, 47.8 (C-α-N); 74.6, 75.6 (N–C–N); 208.6, 209.6, 221.1, 221.9 (CO) ppm. Anal. Calc. for C₁₈H₂₆N₄O₄Mo: C, 47.16; H, 5.68; N, 12.23; Mo, 20.96. Found: C, 47.27; H, 5.51; N, 12.42; Mo, 20.87.

4.5.9. [(222)(Glyoxal)Cr(CO)₄] (21)

Yield: 35%. IR (CH₂Cl₂) (cm⁻¹): 1995 (w), 1870 (s, sh), 1857 (vs), 1820 (m) ν(CO). ¹³C-NMR δ: 42.7, 43.1, 46.2, 53.0, 53.4, 54.3 (C-α-N); 73.9 (N–C–N); 166.8 (N=C); 213.8, 214.8, 227.0, 228.9 (CO) ppm.

4.5.10. [(222)(Glyoxal)Mo(CO)₄] (22)

Yield: 30%. IR (CH₂Cl₂) (cm⁻¹): 2000 (w), 1880 (s, sh), 1865 (vs), 1827 (m) ν(CO). ¹³C-NMR *trans*-*22* δ: 46.9, 47.3, 51.4 (C-α-N); 78.3 (N–C–N); 207.1, 221.6 (CO) ppm. *cis*-*22* δ: 47.5, 48.0, 48.3, 51.7, 54.2, 54.7 (C-α-N); 73.8, 82.0 (N–C–N); 206.5, 207.6, 220.8, 222.0 (CO) ppm.

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