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Journal of Organometallic Chemistry 664 (2002) 214–222
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Hemilability of the primary amine–metal bond in polyamine-(Group 6) metal carbonyl complexes

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Received 17 July 2002; accepted 20 September 2002

Abstract

A series of *cis*-$LM(CO)_4$ complexes was prepared by reaction of non symmetrical diamines ($L = R^1R^2N–(CH_2)_n–NH_2$, with R^1 and R^2 = alkyl groups) with metal carbonyls $M(CO)_6$, (M = Cr, Mo, W). Only the primary amine of these complexes reacted with mono or dialdehydes, thus leading to mono or dinuclear imine complexes, stabilized by the metal moiety and strongly suggesting that the NH_2–metal bond has a hemilabile character.

Keywords: Polyamines; Metal carbonyl complexes; Imines; Hemilability

1. Introduction

During the last decade, polyamines, especially spermidine and spermine derivatives, have been the subject of considerable works owing to their potential biological activities as antimicrobial, antitumoral, DNA transfection agents for instance [1]. The achievement of new properties generally requires structural modification of the polyamine [2] or its stepwise synthesis using the classical protection/deprotection techniques [3].

In this context, we recently described the selective ω,ω′-N difunctionnalization of linear tetraamines L via the use of their *fac*-$LM(CO)_3$ complexes **1** (M = Cr, Mo, W) involving the reductive amination of aldehydes and ketones [4] (Scheme 1). This was the first example of the use of transition metal intermediates in which the metal is in the zero oxidation state. It must be recalled here that it has long been known that reductive amination of ketones is readily catalyzed by cationic transition metals. It goes through an imine intermediate, which could be characterized in the absence of the reducing agent [5].

We also suspected transient formation of imines in our systems. Indeed, monoimines **3** (resulting from the reaction of one equivalent of an aldehyde on complex **1**) were fully characterized [6]. Reaction of two equivalents of an aldehyde gave diimine complexes **2**, isolated as a mixture of *EE*, *EZ* stereoisomers rendering very difficult the interpretation of ^{1}H- and ^{13}C-NMR spectra (overlapping signals).

Contrary to tetraamines shown in Scheme 1 which, on complexation with the metal carbonyl gave a mononuclear complex, spermine gave a dinuclear *cis*-$L[M(CO)_4]_2$ complex **4** [7] (Scheme 2), in which all the amino groups are coordinated, and thus potentially deactivated towards reaction with aldehydes. Nevertheless, when submitted to the reductive amination, under the same conditions as for the ω,ω′-difunctionnalization of tetraamines via their *fac*-$LM(CO)_3$ complexes, terminal amino groups were also selectively alkylated [8] (Scheme 3). So, coordinated or not, a terminal primary amino group can react with an aldehyde. These results suggest that both *cis*-$LM(CO)_4$ and *fac*-$LM(CO)_3$ complexes can transiently liberate selectively their metal bound primary amino function,

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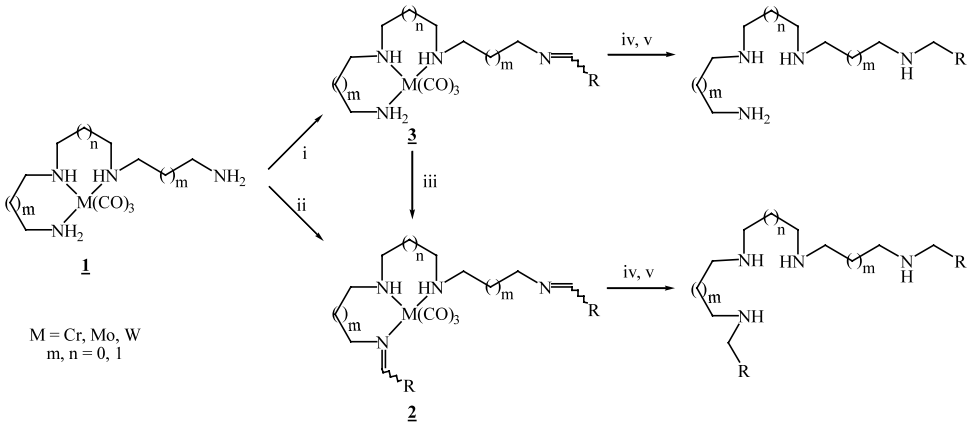
PII: S0022-328X(02)01992-7



i : RCHO (1 eq) / THF, DMF, Δ ; ii : RCHO (2 eq) / THF, DMF, Δ ; iii : RCHO (1 eq) / THF, DMF, Δ ;
iv : $NaBH_4$; v : O_2 / H_3O^+.

Scheme 1.

allowing them to react with an aldehyde to afford an imine able at once to recoordinate to the metal.

In order to shed light on this situation (also met in the reductive amination catalysed by transition metal cations) we undertook the synthesis of simpler complexes and the study of their behaviour towards aldehydes.

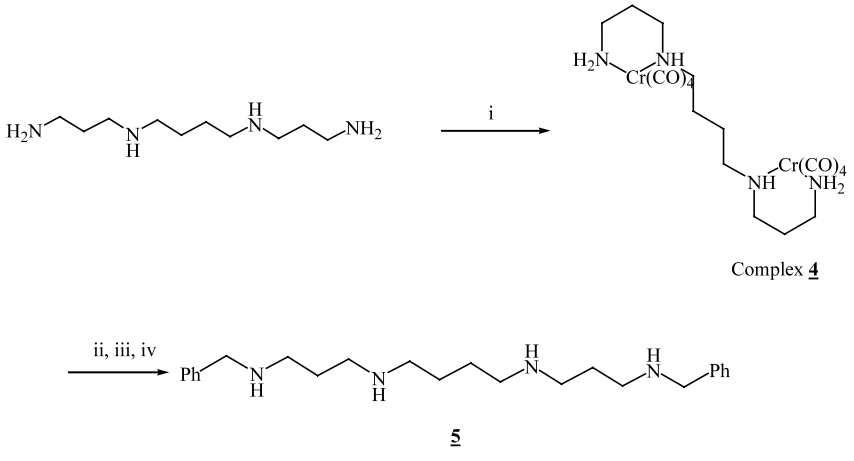
2. Results and discussion

2.1. Amino complexes

A series of *cis*-$LM(CO)_4$ complexes was prepared by reaction of non symmetrical diamines ($L = R^1R^2N–(CH_2)_n–NH_2$) with metal carbonyls (Scheme 3, Table 1). IR data (see experimental section) are consistent with a $M(CO)_4$ group having a local C_2v symmetry since the four expected ν(CO) IR stretching band are observed ($2A_1+B_1+B_2$) [9]. ^{13}C-NMR spectra are also in agreement with this $LM(CO)_4$ structure: four (ratio 1:1:1:1; $R^1 \neq R^2$) or three (ratio 2:1:1; $R^1 = R^2$) non equivalent signals appear for the carbon monoxide ligands (Table 1). As better yields were obtained with $Mo(CO)_6$, mainly the reactivity of *cis*-$LMo(CO)_4$ complexes towards aldehydes was studied.

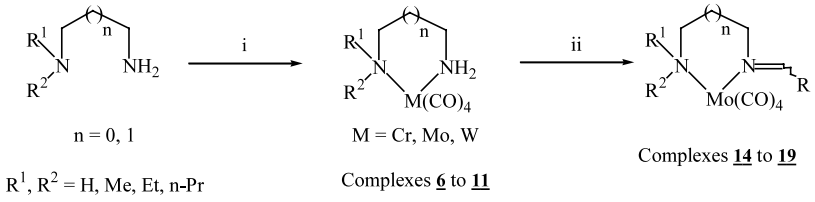
2.2. Imino derivatives with aldehydes RCHO

The reaction was run at 100 °C in DMF in presence of THF, $MgSO_4$ and a stoechiometric amount of an aldehyde (RCHO). Red–brown microcrystalline solids were obtained and characterized first by ^{13}C-NMR and IR spectroscopy. IR spectroscopy proved to be most helpful for the identification of the resulting complexes (Table 2) and indicated that the $Mo(CO)_4$ pattern was maintained since the four characteristic ν(CO) bands were still present. In addition, the disappearance of the νNH_2 stretching bands (doublet; 3250, 3300 cm^{-1}), was



i : $Cr(CO)_6$, Bu_2O, Δ. ii : PhCHO (2 eq) / THF, DMF, Δ ; iii : $NaBH_4$; iv : O_2, H_3O^+

Scheme 2.



Scheme 3.

accompanied by a new absorption ($\sim$1665 cm^{-1}) ascribable to a –C=N– double bond. Actually this was confirmed by ^{13}C-NMR which in addition to the carbonyl resonances, exhibited the characteristic sp^2 carbon atom signal of an imine at 150–160 ppm.

When R is aryl or heteroaryl, complexes are obtained as *E*,*Z* mixtures of stereoisomers (complexes **14** to **16** and **18**). Suitable monocrystals could be grown for complex **15** (only the *Z* isomer crystallized) and analyzed by X ray diffraction (Fig. 1, Tables 3 and 4) clearly showing the tight bonding of the imino–nitrogen atom N^1, since the Mo–N^1 bond appears significantly shortened.

The Mo–N^2 distance is essentially the same as the corresponding bond lengths in other complexes with saturated amines [10–12]. The strong electron donor

Table 1
^{13}C-NMR selected data and yields of complexes **6** to **11**

No.	R1	R2	*n*	M	Yield	^{13}C-NMR [a] (δ_{CO})
6a	H	Me	0	Cr	35	215.1; 215.9; 226.5; 227.6
6b	H	Me	0	Mo	87	207.5; 208.2; 221.2; 222.4
6c	H	Me	0	W	30	204.4; 205.4; 213.5; 214.1
7a	H	Et	0	Cr	31	215.8; 216.9; 226.9; 228.4
7b	H	Et	0	Mo	75	207.1; 208.0; 220.7; 221.9
7c	H	Et	0	W	35	204.4; 205.6; 213.4; 213.8
8a	H	*n*-Pr	0	Cr	30	215.1; 216.4; 226.4; 228.0
8b	H	*n*-Pr	0	Mo	93	207.1; 208.0; 220.6; 222.0
8c	H	*n*-Pr	0	W	37	204.3; 205.5; 213.2; 213.8
9a	H	Me	1	Cr	40	214.9; 215.5; 224.7; 226.1
9b	H	Me	1	Mo	90	206.9; 207.7; 219.6; 221.0
9c	H	Me	1	W	40	204.4; 205.6; 211.8; 212.4
10a	Me	Me	0	Cr	54	214.9 [b]; 226.2; 228.6
10b	Me	Me	0	Mo	85	206.9 [b]; 220.2; 223.0
10c	Me	Me	0	W	25	205.3 [b]; 213.2; 214.4
11a	Me	Me	1	Cr	35	214.2 [b]; 223.9; 226.5
11b	Me	Me	1	Mo	77	206.5 [b]; 219.0; 221.6
11c	Me	Me	1	W	40	205.5 [b]; 212.2; 213.0

[a] In DMSO-d_6 (75.47 MHz).
[b] Double intensity.

Table 2
Selected data for imine complexes **14** to **19**

Starting *cis*-Mo(CO)$_4$L complexes				Imine complexes				
							IR (cm^{-1}) [a]	
No.	R1	R2	*n*	No.	R	Yield	ν(C=N)	ν(CO)
6b	H	Me	0	**14**	2-Furyl	77	1675 (w)	1825 (m) 1870 (s,sh) 1885 (vs) 2000 (w)
10b	Me	Me	0	**15**	2-Furyl	70	1670 (w)	1820 (m) 1865 (s,sh) 1880 (s) 2000 (w)
10b	Me	Me	0	**16**	Phenyl	70	1670 (w)	1820 (m) 1865 (s,sh) 1880 (vs) 2000 (w)
10b	Me	Me	0	**17**	H	88	1670 (w)	1820 (m) 1865 (s,sh) 1880 (vs) 2000 (w)
11b	Me	Me	1	**18**	Phenyl	70	1675 (w)	1820 (m) 1865 (s,sh) 1880 (vs) 2000 (w)
11b	Me	Me	1	**19**	H	73	1675 (w)	1820 (m) 1865 (s,sh) 1880 (vs) 2000 (w)

[a] In CH_2Cl_2.

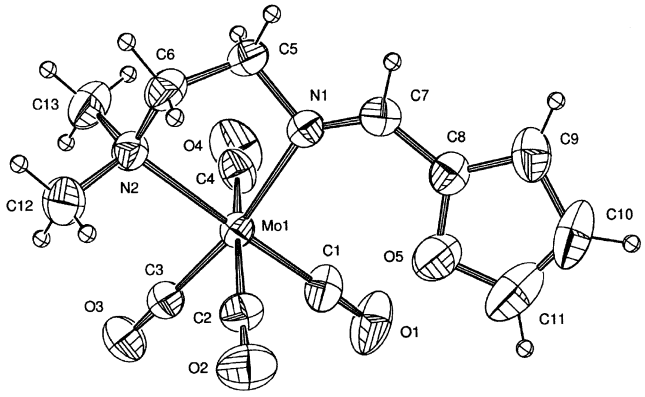


Fig. 1. ORTEP drawing of the molecular structure of complex **15** (*Z* isomer).

Table 3
Selected bond lengths (Å) and bond angles (°) for complex **15**

Bond lengths			
Mo–N(1)	2.283(2)	O(4)–C(4)	1.135(4)
Mo–N(2)	2.342(2)	O(5)–C(8)	1.356(4)
Mo–C(1)	1.942(3)	O(5)–C(11)	1.361(5)
Mo–C(2)	2.029(3)	N(1)–C(5)	1.469(3)
Mo–C(3)	1.940(3)	N(1)–C(7)	1.268(3)
Mo–C(4)	2.024(3)	N(2)–C(6)	1.474(4)
O(1)–C(1)	1.154(4)	N(2)–C(12)	1.474(4)
O(2)–C(2)	1.140(3)	N(2)–C(13)	1.482(4)
O(3)–C(3)	1.155(3)	C(5)–C(6)	1.503(4)
Bond angles			
N(1)–Mo–N(2)	76.94(8)	C(1)–Mo–C(3)	88.7(1)
N(1)–Mo–C(1)	101.3(1)	C(1)–Mo–C(4)	85.2(1)
N(1)–Mo–C(2)	92.8(1)	C(2)–Mo–C(3)	89.3(1)
N(1)–Mo–C(3)	169.8(1)	C(2)–Mo–C(4)	170.3(1)
N(1)–Mo–C(4)	94.5(1)	C(3)–Mo–C(4)	84.7(1)
N(2)–Mo–C(1)	177.9(1)	Mo–C(1)–O(1)	177.7(3)
N(2)–Mo–C(2)	94.2(1)	Mo–C(2)–O(2)	173.8(3)
N(2)–Mo–C(3)	92.9(1)	Mo–C(3)–O(3)	178.7(3)
N(2)–Mo–C(4)	93.7(1)	Mo–C(4)–O(4)	171.6(3)
C(1)–Mo–C(2)	87.1(1)		

effect of the bidentate ligand is clearly indicated by the short molybdenum–carbon (CO) bonds trans to the nitrogen atoms (π-back bonding). The N^1–Mo–N^2 angle is acute, as observed in other tetracarbonyl molybdenum complexes with chelating diamines or diphosphines [10,13,14]. This kind of imine complexes is usually prepared starting from a preformed imine which is then reacted with the metal [15]. We also checked this route and observed that an *E* imine on reaction with hexacarbonyl metals led to a mixture of *E* and *Z* imines, probably as a result of an unfavourable interaction of the R group of the starting imine with the $M(CO)_4$ moiety.

2.3. Imino derivatives with formaldehyde HCHO

When R is hydrogen, stable monomeric methanimines are obtained (complexes **17** and **19**). Generally formaldehyde imines polymerize [16] but in some rare cases they have been isolated in the condensed state when the nitrogen atom bears a bulky substituent [17]. Thus, coordination to the metal moiety stabilizes the imine (CH_2=N–R). The ^{1}H-NMR spectra of metal–methanimines, which can also be represented as formal resonating metalate–iminium limit species (Scheme 4) exhibit a characteristic AB quartet centred at 7.5 ppm (see Section 4 for NMR detailed data). The high field doublet (J_{AB} = 14.1 Hz) is strongly enhanced by NOE interaction with the N–CH_2 group (triplet at 2.7 ppm).

To our knowledge, this constitutes the first example of a methanimine stabilization by a bulky zero oxidation state metallic center which sterically prevents from cyclotrimerisation, as do *t*-butyl and bis trimethylsilylmethane substituents [17].

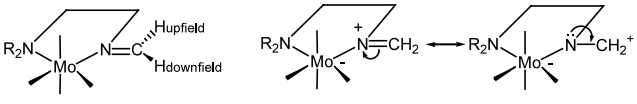
Interestingly the reaction of the ethylene diamine complex **12** with two equivalents of formaldehyde led to the stable bis methanimine complex **20** (Scheme 5).

Table 4
Positional parameters and estimated standard deviations for complex **15**

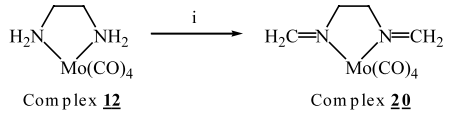
Atom	*x*	*y*	*z*	*B* (A^2)
Mo	0.36922(2)	0.17987(2)	0.70608(4)	3.526(5)
O(1)	0.1259(2)	0.1453(2)	0.7348(4)	8.47(9)
O(2)	0.3976(3)	−0.0011(2)	0.8636(4)	7.17(8)
O(3)	0.3619(2)	0.2513(2)	1.0733(3)	6.00(7)
O(4)	0.2937(3)	0.3627(2)	0.6171(4)	8.59(9)
O(5)	0.2281(2)	0.0199(2)	0.4928(4)	6.69(7)
N(1)	0.4053(2)	0.1377(2)	0.4332(3)	3.84(6)
N(2)	0.5520(2)	0.2083(2)	0.6772(4)	4.29(6)
C(1)	0.2168(3)	0.1572(2)	0.7210(5)	5.27(9)
C(2)	0.3926(3)	0.0632(2)	0.8121(5)	4.64(8)
C(3)	0.3645(3)	0.2235(2)	0.9376(5)	4.18(7)
C(4)	0.3248(3)	0.2970(2)	0.6376(5)	5.15(9)
C(5)	0.5046(3)	0.1793(3)	0.3806(4)	4.79(8)
C(6)	0.5869(3)	0.1687(3)	0.5167(5)	5.01(9)
C(7)	0.3609(3)	0.0920(2)	0.3232(4)	4.18(8)
C(8)	0.2673(3)	0.0413(2)	0.3378(5)	4.41(8)
C(9)	0.2091(3)	0.0062(3)	0.2155(5)	6.1(1)
C(10)	0.1260(4)	−0.0391(3)	0.2982(8)	8.0(1)
C(11)	0.1418(4)	−0.0293(3)	0.4596(8)	8.6(1)
C(12)	0.6161(3)	0.1738(3)	0.8187(6)	6.6(1)
C(13)	0.5756(3)	0.2988(3)	0.6681(6)	6.3(1)

Starred atoms were refined isotopically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:

$$(4/3) \times [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)].$$

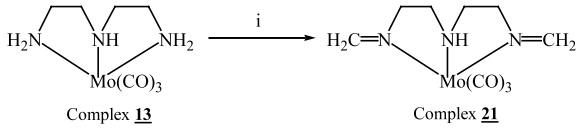


Scheme 4.



i : HCHO (2 eq) / THF, DMF, Δ.

Scheme 5.



i : HCHO (2eq) / THF, 50°C.

Scheme 6.

We may infer that the two imines are not formed simultaneously by complete liberation of the diamine (if so, polymeric formol polyaminal would have been produced) but successively.

Under slightly modified conditions (see Section 4) the ethylenetriamine complex **13** leads to the corresponding ω,ω′-bis methanimine complex **21** (Scheme 6).

Even more convincing, the reaction of the tris cyclohexylamine– $Mo(CO)_3$ complex **22** with formaldehyde in the presence of THF gave the *fac*-cyclic hexahydrotriazine $Mo(CO)_3$ complex **23**, obviously resulting from the progressive release of the amine from the metal, followed by the transient imine formation, cyclotrimerisation and subsequent recoordination to the $Mo(CO)_3$ moiety (Scheme 7). This complex is identical to that obtained by reacting the preformed cyclic triazine with $Mo(CO)_6$ [18].

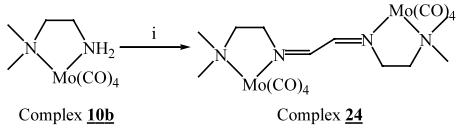
2.4. Imino derivatives with glyoxal $(CHO)_2$

An extension of the study of reactivity of primary/tertiary diamine complexes has been obtained with a particular aldehyde: glyoxal. Under the conditions previously described for non heteroaromatic aldehydes, glyoxal reacts with two equivalents of the *cis*-$Mo(CO)_4L$ complex **10b** of *N*,*N*-dimethylethylenediamine to give the new bis-imine dinuclear complex **24** (Scheme 8).

The IR spectrum of this complex exhibits the four $\nu(CO)$ stretching bands for the $Mo(CO)_4$ groups and the new $\nu(C{=}N)$ absorption band for the two imine functions. ^{13}C-NMR spectrum is in agreement with a symmetrical *cis*-$Mo(CO)_4L$ complex and presents only one set of signals: three signals (ratio 2:1:1) for the carbonyl ligands, one peak for the two equivalent carbon atoms of the imine functions, and three signals for the carbon atoms α to nitrogen (methyl groups are equivalent). The presence of only one set of peaks on the spectrum led us to conclude to the formation of only one isomer, among three possible, probably the *E*,*E* isomer, sterically favoured.

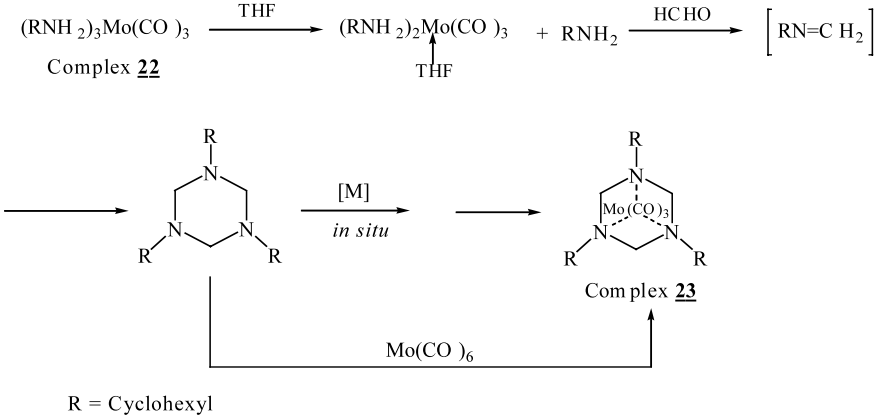
By now we call back to mind that we first reported the direct regiofunctionnalization of cyclic and linear tetraamine chromium complexes with alkyl halides (instead of carbonyl compounds) as electrophiles; at that time, we observed that in the case of linear tetraamines, only special activated alkyl halides such as α,α′-orthodibromoxylene gave a selective alkylation at the pendant arm amino function, leading to a new ω-tertiary amine. When applied to other mono alkyl halides, benzyl or allyl bromides for instance, this methodology led to the non selective polyalkylation of the tetramine [19].

The reason for this failure with simple alkyl halides lies in the fact that in this case, the new secondary amine produced by ω-N alkylation competes immediately at the metal center to liberate the hemilabile ω-NH_2 function which is then polyalkylated.



i : CHOCHO (0.5 eq) / THF, DMF, Δ.

Scheme 8.



Scheme 7.

So the replacement of alkyl halides by aldehydes or ketones as electrophiles opened a wider field of applications, since the coordinating ability of an imine is actually weaker than that of a primary amine, itself weaker than that of a secondary amine; from these observations we thus propose the following order of binding strength for nitrogen ligands toward Group 6 metal carbonyls:

$$R{-}CH{=}N{-} < RNH_2 < R_2NH$$

3. Conclusion

The isolation of stable formaldehyde imine of both *fac*-$LM(CO)_3$ and *cis*-$LM(CO)_4$ complexes starting from the parent amino complexes strongly suggests the hemilability of the primary amino function bound to the metal. The facile opening of such chelating unsymmetrical diamines appears thus to begin with the previously observed regioselective ω,ω′-dialkylation of linear tetraamines, while secondary metal bound amines cannot be displaced.

Noteworthy is the stabilizing effect of the $M(CO)_3$ and $M(CO)_4$ moieties on methanimines which has the same effect as the bulky bis trimethylsilyl methane group for instance [17b]. Moreover, the metal bound imine although stabilized by the metal fragment is still reactive and is easily reduced by $NaBH_4$ for instance. So methanimines lead to the corresponding *N*-monomethylamine quantitatively.

The reactivity of these new metal stabilized imines is now under investigation.

4. Experimental

All reactions were carried out under nitrogen atmosphere using the Schlenk technique, and all solvents were freshly distilled under an inert atmosphere on appropriate dryers. All reagents were purchased from commercial suppliers and used without further purifications. Infrared spectra were obtained using a Perkin–Elmer 1430 spectrophotometer. NMR spectra were recorded on either Bruker AC 300 (FT 300 MHz, ^{1}H; 75.47 MHz, ^{13}C) or Bruker Advance PRX 400 (FT 400 MHz, ^{1}H 100 MHz, ^{13}C) spectrometers. Chemical shifts for ^{1}H and ^{13}C spectra were referenced using internal solvent resonance and are reported relative to TMS. Elemental analyses were performed by the Service National de Microanalyses du CNRS, at Vernaison, France.

4.1. General procedure for the synthesis of complexes **6** to **11**

$M(CO)_6$ (M = Cr, Mo, W) (1.1 mmol) and diamine or triamine (1.0 mmol) were heated at reflux (142 °C) in di-*n*-butylether (20 ml)/THF (3 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. After cooling to room temperature (r.t.), the solvent was removed under reduced pressure and the residue was washed several times with hexane at −10 °C. The resulting yellow powder was then dried in vacuum at 50 °C.

4.1.1. *cis*-[{$MeNH(CH_2)_2NH_2$}$Cr(CO)_4$] (**6a**)

Yield: 35%. ^{13}C-NMR (DMSO-d_6): δ 42.7 (Cα-N); 44.1 (Me); 54.3 (Cα-N); 215.1, 215.9, 226.5, 227.6 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

4.1.2. *cis*-[{$MeNH(CH_2)_2NH_2$}$Mo(CO)_4$] (**6b**)

Yield: 87%. ^{13}C-NMR (DMSO-d_6): δ 43.4 (Cα-N); 44.5 (Me); 54.6 (Cα-N); 207.5, 208.2, 221.2, 222.4 (CO). IR (CH_2Cl_2): cm^{-1} 1825 (m), 1865 (s, sh), 1885 (vs), 2005 (w) ν(CO).

4.1.3. *cis*-[{$MeNH(CH_2)_2NH_2$}$W(CO)_4$] (**6c**)

Yield: 30%. ^{13}C-NMR (DMSO-d_6): δ 44.2 (Cα-N); 45.4 (Me); 55.1 (Cα-N); 204.4, 205.4, 213.5, 214.1 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

4.1.4. *cis*-[{$EtNH(CH_2)_2NH_2$}$Cr(CO)_4$] (**7a**)

Yield: 31%. ^{13}C-NMR (DMSO-d_6): δ 14.4 (Me); 42.7, 51.0, 51.5 (Cα-N); 215.8, 216.9, 226.9, 228.4 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

4.1.5. *cis*-[{$EtNH(CH_2)_2NH_2$}$Mo(CO)_4$] (**7b**)

Yield: 75%. ^{13}C-NMR (DMSO-d_6): δ 14.2 (Me); 42.7, 51.2, 51.7 (Cα-N); 207.1, 208.0, 220.7, 221.9 (CO). IR (CH_2Cl_2): cm^{-1} 1820 (m), 1860 (s, sh), 1870 (vs), 2005 (w) ν(CO).

4.1.6. *cis*-[{$EtNH(CH_2)_2NH_2$}$W(CO)_4$] (**7c**)

Yield: 35%. ^{13}C-NMR (DMSO-d_6): δ 14.5 (Me); 43.8, 52.5 (2C) (Cα-N); 204.4, 205.6, 213.4, 213.8 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO). Anal. Calc.: C, 25.04; H, 3.13; N, 7.30. Found: C, 25.12; H, 3.31; N, 7.33%.

4.1.7. *cis*-[{*n*-$PrNH(CH_2)_2NH_2$}$Cr(CO)_4$] (**8a**)

Yield: 30%. ^{13}C-NMR (DMSO-d_6): δ 11.5 (Me); 21.5 (Cβ-N); 42.3, 51.0, 59.0 (Cα-N); 215.1, 216.4, 226.4, 228.0 (CO). IR (CH_2Cl_2): cm^{-1} 1820 (m), 1860 (s, sh), 1870 (vs), 2005 (w) ν(CO).

*4.1.8. cis-[{n-PrNH(CH$_2$)$_2$NH$_2$}Mo(CO)$_4$] (**8b**)*
Yield: 93%. ^{13}C-NMR (DMSO-d_6): δ 11.5 (Me); 21.8 (Cβ-N); 42.6, 52.1, 58.9 (Cα-N); 207.1, 208.0, 220.6, 222.0 (CO). IR (CH_2Cl_2): cm^{-1} 1825 (m), 1865 (s, sh), 1885 (vs), 2010 (w) ν(CO).

*4.1.9. cis-[{n-PrNH(CH$_2$)$_2$NH$_2$}W(CO)$_4$] (**8c**)*
Yield: 37%. ^{13}C-NMR (DMSO-d_6): δ 11.4 (Me); 22.0 (Cβ-N); 43.6, 52.8, 60.1 (Cα-N); 204.3, 205.5, 213.2, 213.8 (CO). IR (CH_2Cl_2): cm^{-1} 1825 (m), 1860 (s, sh), 1870 (vs), 2005 (w) ν(CO).

*4.1.10. cis-[{MeNH(CH$_2$)$_3$NH$_2$}Cr(CO)$_4$] (**9a**)*
Yield: 40%. ^{13}C-NMR (DMSO-d_6): δ 27.2 (Cβ-N); 46.1 (Cα-N); 46.8 (Me); 57.6 (Cα-N); 214.9, 215.6, 224.7, 226.1 (CO). IR (CH_2Cl_2): cm^{-1} 1810 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

*4.1.11. cis-[{MeNH(CH$_2$)$_3$NH$_2$}Mo(CO)$_4$] (**9b**)*
Yield: 90%. ^{13}C-NMR (DMSO-d_6): δ 27.3 (Cβ-N); 46.0 (Cα-N); 46.2 (Me); 57.4 (Cα-N); 206.9, 207.7, 219.6, 221.0 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1860 (s, sh), 1875 (vs), 2005 (w) ν(CO).

*4.1.12. cis-[{MeNH(CH$_2$)$_3$NH$_2$}W(CO)$_4$] (**9c**)*
Yield: 40%. ^{13}C-NMR (DMSO-d_6): δ 27.1 (Cβ-N); 46.5 (Cα-N); 47.4 (Me); 57.7 (Cα-N); 204.4, 205.6, 211.8, 212.4 (CO). IR (CH_2Cl_2): cm^{-1} 1810 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

*4.1.13. cis-[{Me$_2$N(CH$_2$)$_2$NH$_2$}Cr(CO)$_4$] (**10a**)*
Yield: 54%. ^{13}C-NMR (DMSO-d_6): δ 41.1 (Cα-N); 55.4 (2Me); 62.7 (Cα-N); 214.9 (2C), 226.2, 228.6 (CO). IR (CH_2Cl_2): cm^{-1} 1815 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO). Anal. Calc.: C, 38.09; H, 4.77; N, 11.11. Found: C, 37.91; H, 4.83; N, 11.26%.

*4.1.14. cis-[{Me$_2$N(CH$_2$)$_2$NH$_2$}Mo(CO)$_4$] (**10b**)*
Yield: 85%. ^{13}C-NMR (DMSO-d_6): δ 41.5 (Cα-N); 55.1 (2Me); 63.0 (Cα-N); 206.9 (2C), 220.2, 223.0 (CO). IR (CH_2Cl_2): cm^{-1} 1820 (m), 1860 (s, sh), 1875 (vs), 2005 (w) ν(CO). Anal. Calc.: C, 32.43; H, 4.10; N, 9.46. Found: C, 32.70; H, 4.12; N, 9.76%.

*4.1.15. cis-[{Me$_2$N(CH$_2$)$_2$NH$_2$}W(CO)$_4$] (**10c**)*
Yield: 25%. ^{13}C-NMR (d_6–DMSO): δ 42.6 (Cα-N); 56.5 (2Me); 63.9 (Cα-N); 205.3 (2C), 213.2, 214.4 (CO). IR (CH_2Cl_2): cm^{-1} 1810 (m), 1845 (s, sh), 1855 (vs), 2000 (w) ν(CO).

*4.1.16. cis-[{Me$_2$N(CH$_2$)$_3$NH$_2$}Cr(CO)$_4$] (**11a**)*
Yield: 35%. ^{13}C-NMR (DMSO-d_6): δ 24.9 (Cβ-N); 45.7 (Cα-N); 56.2 (2Me); 66.2 (Cα-N); 214.2 (2C), 223.9, 226.5 (CO). IR (CH_2Cl_2): cm^{-1} 1810 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

*4.1.17. cis-[{Me$_2$N(CH$_2$)$_3$NH$_2$}Mo(CO)$_4$] (**11b**)*
Yield: 77%. ^{13}C-NMR (DMSO-d_6): δ 25.4 (Cβ-N); 46.1 (Cα-N); 59.3 (2Me); 66.5 (Cα-N); 206.5 (2C), 219.0, 221.6 (CO). IR (CH_2Cl_2): cm^{-1} 1820 (m), 1865 (s, sh), 1880 (vs), 2005 (w) ν(CO). Anal. Calc.: C, 34.84; H, 4.52; N, 9.03. Found: C, 35.11; H, 4.56; N, 9.32%.

*4.1.18. cis-[{Me$_2$N(CH$_2$)$_3$NH$_2$}W(CO)$_4$] (**11c**)*
Yield: 40%. ^{13}C-NMR (DMSO-d_6): δ 25.4 (Cβ-N); 46.8 (Cβ-N); 57.3 (2Me); 67.0 (Cα-N); 205.5 (2C), 212.2, 213.0 (CO). IR (CH_2Cl_2): cm^{-1} 1810 (m), 1855 (s, sh), 1865 (vs), 2000 (w) ν(CO).

*4.1.19. cis-[{H$_2$N(CH$_2$)$_2$NH$_2$}Mo(CO)$_4$] (**12**)*
^{13}C-NMR (DMSO-d_6): 40.7(Cα-N); 227.4, 229.2 (CO). IR (nujol): cm^{-1} 2005 (s), 1885 (vs), 1865 (vs), 1825 (m) ν(CO).

*4.1.20. fac-[{H$_2$N(CH$_2$)$_2$NH(CH$_2$)$_2$NH$_2$}Mo(CO)$_3$] (**13**)*
^{13}C-NMR (DMSO-d_6): 40.4 (Cα-NH$_2$); 49.0 (Cα-NH); 227.7 (2CO); 229.9 (CO). IR (CH_2Cl_2): cm^{-1} 1885 (s), 1770 (vs) ν(CO).

*4.2. General procedure for the synthesis of imines **14** to **21***

To a solution of *cis*-Mo(CO)$_4$L complex (1.0 mmol) in DMF (10 ml) in presence of THF (3 ml) and an excess of dry $MgSO_4$, was added a stoechiometric amount of an aldehyde (1.0 mmol) (if the aldehyde is heteroaromatic, the addition of the co-solvent (THF) is not necessary). After 3–4 h of stirring at 100 °C, the mixture was cooled to r.t. and the solvent was removed under reduced pressure. The residue adsorbed on $MgSO_4$ was extensively extracted with dichloromethane; after evaporation of the solvent, a red–brown microcrystalline solid was obtained. IR data are given in Table 2.

*4.2.1. Complex **14** (mixture of E and Z isomers)*
Yield: 77%. ^{13}C-NMR (DMSO-d_6) isomer *E* (maj.): δ 43.6 (CH_3); 54.0, 55.4 (Cα-N); 110.7, 120.5, 144.7, 149.4 (C_4H_3O); 158.5 (C=N); 206.8, 207.9, 221.1, 222.3 (CO); isomer *Z* (min.): δ 44.6 (CH_3), 54.1, 65.8 (Cα-N); 108.9, 122.6, 144.6, 149.7 (C_4H_3O); 163.2 (C=N); 206.4, 208.0, 221.2, 222.4 (CO).

*4.2.2. Complex **15** (mixture of E and Z isomers)*
Yield: 70%. ^{13}C-NMR (CD_2Cl_2) of isomer *E* (maj.): δ 54.2 (Cα-N); 55.0 (Me); 64.3 (Cα-N); 113.1, 120.7, 147.0, 148.7 (C_4H_3O); 152.9 (C=N); 206.7 (2CO), 222.1, 222.4 (CO); isomer *Z* (min.): δ 56.2 (Cα-N); 63.0 (Me); 64.6 (Cα-N); 112.9, 120.5, 147.0, 148.9 (C_4H_3O); 157.3 (C=N); 207.2 (2C), 222.9, 223.3 (CO).

4.2.3. Crystallographic study of complex **15**

Suitable crystals for single-crystal X-ray diffraction studies were obtained from a 1:1 hexane–diethylether mixture at r.t. The crystal data and the structure refinement are collected in Tables 3 and 4. The sample ($0.30 \times 0.20 \times 0.20$ mm^3) is studied on an automatic diffractometer CAD4 NONIUS with graphite monochromatized Mo–K_α radiation [22]. The cell parameters are obtained by fitting a set of 25 high-theta reflections. The data collection ($2\theta_{max} = 54°$, scan $\omega/2\theta = 1$, $t_{max} = 60$ s, range *hkl*: *h* −14,14 *k* 0,18 *l* 0,9) gives 2954 unique reflections from which 2208 with $I > 2.0\sigma(I)$. After Lorenz and polarization corrections [26] and also absorption corrections (psi scans) the structure was solved with SIR-97 [20] which reveals the non-hydrogen atoms of the compound. After anisotropic refinement a Fourier difference reveals many hydrogen atoms. The whole structure was refined with SHELXL-97 [24] by the full-matrix least-square techniques (use of F^2 magnitude; x, y, z, β_{ij} for Mo, C, O and N atoms, x, y, z in riding mode for H atoms; 191 variables and 2742 observations; calc $w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.61P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.023$, $R_w = 0.058$ and $S_w = 1.011$ (residual $\Delta\rho \leq 0.46$ e Å^{-3}).

Atomic scattering factors from International Tables for X-ray Crystallography [21]. ORTEP views realized with PLATON-98 [25] and ORTEP-3 [23].

4.2.4. Complex **16** (mixture of *E* and *Z* isomers)

Yield: 70%. ^{13}C-NMR (CD_2Cl_2) of isomer *E* (maj.): δ 55.8 (Cα-N); 56.0 (2Me); 64.2 (Cα-N); 128.7, 129.4, 131.4, 135.2 (C_6H_5); 171.7 (C=N), 207.0 (2CO); 221.2, 222.7 (CO); isomer *Z* (min.): δ 55.4 (2Me); 63.4 (2 Cα-N); 129.2, 129.8, 131.5, 132.5 (C_6H_5); 168.2 (C=N), 206.5 (2C); 220.5, 222.1 (CO).

4.2.5. Complex **17**

Yield: 88%. ^{13}C-NMR (CD_2Cl_2): δ 55.5 (2Me); 60.9, 63.6 (Cα-N); 161.8 (C=N); 206.8 (2C), 221.8, 222.4 (CO). ^{1}H-NMR (CD_2Cl_2): δ 2.70 (t, 2H, $J = 5.6$ Hz, CH_2α-N); 2.80 (s, 6H, 2Me); 3.76 (t, 2H, $J = 5.6$ Hz, CH_2α-N); 7.52 (d, 1H, $J = 14.1$ Hz, H imine); 7.67 (d, 1H, $J = 14.1$ Hz, H imine).

4.2.6. Complex **18** (mixture of *E* and *Z* isomers)

Yield: 70%. ^{13}C-NMR (CD_2Cl_2) of isomer *E* (maj.): δ 28.9 (Cβ-N); 56.3 (2Me); 56.6, 66.3 (Cα-N); 128.8, 128.9, 129.2, 132.5 (C_6H_5); 171.0 (C=N); 206.4 (2CO), 221.0, 221.6 (CO); isomer *Z* (min.): δ 31.3 (Cβ-N); 55.7 (2Me); 66.6, 69.0 (Cα-N); 128.5, 128.6, 131.0, 136.5 (C_6H_5); 173.1 (C=N); 206.2 (2CO), 221.0, 221.6 (CO).

4.2.7. Complex **19**

Yield: 73%. ^{13}C-NMR (CD_2Cl_2): δ 27.9 (Cβ-N); 56.3 (2Me); 66.6, 68.3 (Cα-N); 163.3 (C=N); 206.2 (2CO), 220.6, 221.6 (CO). ^{1}H-NMR (CD_2Cl_2): δ 1.88 (quintuplet, 2H, $J = 5.6$ Hz, CH_2β-N); 2.67 (s, 6H, 2Me); 2.78 (t, 2H, $J = 5.6$ Hz, CH_2α-N); 3.83 (t, 2H, $J = 5.6$ Hz, CH_2α-N); 7.51 (d, 1H, $J = 14.1$ Hz, H imine); 7.60 (d, 1H, $J = 14.1$ Hz, H imine).

4.3. Complexes **20** and **21**

These were prepared according to the general procedure described for imine complexes **14** to **19** but from two equivalents of formaldehyde, in THF at 50 °C.

4.3.1. Complex **20**

Yield: 60%. ^{13} C-NMR (CD_2Cl_2): δ 64.1 (CH_2α-N); 162.1 (C=N); 207.4 (2CO), 222.3 (2C) (CO). ^{1}H-NMR (CD_2Cl_2): δ 3.72 (s, 4H, CH_2α-N); 7.59 (d, 2H, $J = 14.1$ Hz, N=CH_{trans}); 7.71 (d, 2H, $J = 14.1$ Hz, N=CH_{cis}). IR (CH_2Cl_2): cm^{-1} 1820 (m), 1865 (s, vs), 1885 (vs), 2000 (w) ν(CO); 1670 ν(C=N).

4.3.2. Complex **21**

The reaction was run in THF at a temperature kept below 60 °C.

Yield: 60%. ^{13}C-NMR (CD_2Cl_2): δ 49.8 (2C) (CH_2α-NH); 61.3 (2C) (CH_2α-N=CH_2); 162.5 (2C) (C=N); 229.3 (CO), 229.7 (2CO). ^{1}H-NMR (DMSO-d_6): 2.61(m); 2.96(m); 3.40–3.65(m) (CH_2α-N); 7.51 (dt, H_{trans} imine, $J = 14.6$ Hz); 7.57 (dt, H_{cis} imine, $J = 14.6$ Hz). IR (CH_2Cl_2): 1770 (vs), 1882 (s) ν(CO); 1670 ν(C=N).

4.4. Complex **22**

This was prepared according to the procedure described for complexes **6** to **11** but from three equivalents of cyclohexylamine.

Yield: 47%. ^{13} C-NMR (DMSO-d_6): δ 24.7 (Cγ); 25.4 (Cδ) ; 35.22 (Cβ); 50.0 (Cα).

4.5. Complex **23**

This was prepared according to the procedure described for complexes **20** and **21**.

Yield: 34%. ^{13} C-NMR ($CDCl_3$): δ 25.0, 24.2, 28.6, 62.0 (C_6H_{11}); 75.2 (NCH_2N); 231.6 (3CO). IR (CH_2Cl_2): cm^{-1} 1770 (vs), 1905 (s).

4.6. Complex **24**

This was prepared according to the procedure described for complexes **14** to **19** but from 0.5 equivalent of glyoxal.

Yield: 68%. ^{13} C-NMR (CD_2Cl_2): δ 42.5 (CH_2α-N); 55.8 (CH_3); 63.5 (CH_2α-N); 162.6 (C=N); 206.5 (2CO), 220.4, 222.4 (CO). ^{1}H-NMR (CD_2Cl_2): δ 2.48 (t, 4H, $J = 5.6$ Hz, CH_2α-N); 2.76 (s, 12H, CH_3); 3.00 (t, 4H, $J = 5.6$ Hz, CH_2α-N); 7.94 (s, 2H, CH=N). IR (CH_2Cl_2):

cm^{-1} 1820 (m), 1860 (s, vs), 1875 (vs), 2000 (w) ν(CO); 1670 ν(C=N).

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