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Synthesis and characterization of tetracarbonyl complexes of molybdenum and tungsten with functionalized imines. Crystal structure of *cis*-$Mo(CO)_4[(CH_3)(C_6H_5)C{=}N(CH_2)]_2$

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Abstract

A series of octahedral *cis*-iminetetracarbonyl molybdenum and tungsten complexes of the general formula $[M(CO)_4L_2]$, where $L_2 = R_1R_2C{=}N(CH_2)CH(R_3)N{=}CR'_1R'_2$ have been prepared and characterized by IR, ^1H and ^{13}C NMR spectroscopies. These imine chelates complexes of molybdenum and tungsten have exocyclic double bonds. A consistent structural feature of these complexes appears to be the chelate bonding of the imine ligand with consequent rotation around the carbon–nitrogen bond. This phenomenon leads to isomeric compounds: **4** and **5**; **8** and **9**; **11** and **12**. NMR data analysis established unambiguously the configuration of the following nine complexes: $M(CO)_4L_2$ [$R_1 = R'_2 = CH_3$, $R'_1 = R_2 = C_6H_5$, $R_3 = H$, M = Mo (**4**), M = W (**8**)]; [$R_1 = R'_1 = C_6H_5$, $R_2 = R'_2 = CH_3$, $R_3 = H$, M = Mo (**5**), M = W (**9**)]; [$R_1 = R'_1 = R_2 = R'_2 = C_6H_5$, $R_3 = H$, M = Mo (**6**), M = W (**10**)]; [$R_1 = R'_1 = R_2 = R'_2 = CH_3$, $R_3 = H$, M = Mo (**7**)]; [$R_1 = R'_2 = C_6H_5$, $R'_1 = R_2 = CH_3$, $R_3 = CH_3$, M = Mo (**11**)]; [$R_1 = R'_1 = C_6H_5$, $R_2 = R'_2 = CH_3$, $R_3 = CH_3$, M = Mo (**12**)]. Long-range coupling constants ^5J(H–H) have confirmed the configuration and chemical shifts assignments for complexes **11** and **12**. The ^{13}C chemical shifts of the carbonyl groups are particularly useful in the characterization of the molybdenum compounds. Single-crystal X-ray diffraction studies of **4** confirm the formation of the nonsymmetric complex *cis*-[*trans*-2,7-diphenyl-3,6-diaza-2,6-octadiene]tetracarbonylmolybdenum. The complex crystallizes in the space group $P2_1/n$ with the unit cell parameters a = 11.112(1) Å; b = 19.345(1) Å; c = 11.680(1) Å; β = 102.89(6)°; V = 2447.5(3) Å^3; $Z = 4$, D_x = 1.39 g cm^{-3}. The structure was solved by direct methods and refined by full-matrix least-squares techniques to R and R_w values of 0.052 and 0.064, respectively, for 4706 observed reflections. The data obtained show that the structure has been solvated with half a molecule of benzene. Evidence of monocoordination of imine **1** to $Mo(CO)_4$(NBD) has been obtained by ^{13}C NMR spectroscopy and some insight into the mechanism of complex formation is provided.

Keywords: Molybdenum; Tungsten; Carbonyls; Imines; Stereochemistry

1. Introduction

In extending our studies related to the properties and stereochemistry of the imines [$R_1R_2C{=}N(CH_2)_2N{=}CR_2R_1$; $R_1 = CH_3$, $R_2 = C_6H_5$ (**1**); $R_1 = R_2 = C_6H_5$ (**2**)] [1], the racemic $(CH_3)(C_6H_5)C{=}N(CH_2)CH(CH_3)N{=}C(C_6H_5)(CH_3)$ (**3**) and their corresponding borane adducts, we became interested in the interaction of these molecules with various hexacarbonyl metals $M(CO)_6$ (M = Mo, W). There has been a considerable amount of information regarding the octahedral complexes of type $M(CO)_4L_2$ in which L_2 is a nitrogen bidentate donor ligand [2a]. In particular, extensive chemistry has been carried out with 1,4-disubstituted-1,4-diaza-1,3-butadienes, RN=CR′CR″=NR, since they appear to have unusual electron donor and acceptor properties [3]. Other α-imines including Schiff bases and 2,2′-bipyridine or 1,10-phenanthroline form tetracarbonyl metal complexes [2a]. However, as far as we know, the imines with the structure $R_2C{=}N{-}CR_2{-}CR_2N{=}CR_2$ have not been reported previously. The reactivity of nonconjugated imines towards metal carbonyl compounds has hitherto received limited at-

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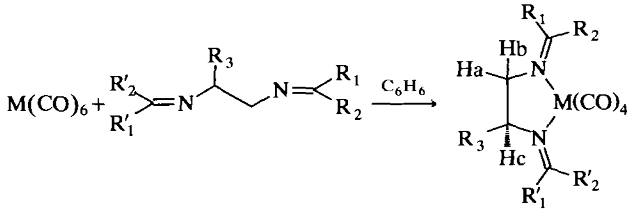


$R_3 = H$
M = Mo $R_1 = R'_2 = CH_3, R'_1 = R_2 = C_6H_5$ (4)
M = Mo $R_1 = R'_1 = C_6H_5, R_2 = R'_2 = CH_3$ (5)
M = Mo $R_1 = R'_1 = R_2 = R'_2 = C_6H_5$ (6)
M = Mo $R_1 = R'_1 = R_2 = R'_2 = CH_3$ (7)
M = W $R_1 = R'_2 = CH_3, R'_1 = R_2 = C_6H_5$ (8)
M = W $R_1 = R'_1 = C_6H_5, R_2 = R'_2 = CH_3$ (9)
M = W $R_1 = R'_1 = R_2 = R'_2 = C_6H_5$ (10)

$R_3 = CH_3$
M = Mo $R_1 = R'_2 = C_6H_5, R'_1 = R_2 = CH_3$ (11)
M = Mo $R_1 = R'_1 = C_6H_5, R_2 = R'_2 = CH_3$ (12)

Scheme 1. Preparation and structure of compounds **4**–**12**.

tention compared to the related conjugated systems. Herein, we describe the preparation and the unambiguous establishment of the configuration of the imine molybdenum and tungsten complexes $[M(CO)_4(R_1R_2C{=}N(CH_2)CH(R_3)N{=}CR'_1R'_2)]$ (**4**–**12**), in which the double bonds of the imine fragment are exocyclic.

2. Results and discussion

Imine tetracarbonyl complexes (**4**–**6**, **8**–**12**) of Group 6 may be prepared from imines **1**, **2** or **3** and hexacarbonyl metals $M(CO)_6$ (M = Mo, W) via thermal or photochemical activation (Scheme 1).

Unsuccessful attempts to isolate the imine $(CH_3)_2C{=}N(CH_2)_2N{=}C(CH_3)_2$ prompted us to synthesize compound **7** directly from ethylenediamine, acetone and hexacarbonyl molybdenum as reported previously for the analogous derivatives [4]. In each case, the reaction was monitored by IR spectroscopy. No identifiable $M(CO)_5L$ species were detected during the formation of the *cis*-$M(CO)_4L_2$ complexes, which suggest that if a σ-N bond occurs first, the conversion to a σ,σ-N,N-bonded product is a fast reaction. However, evidence of monocoordination has been observed by ^{13}C NMR spectroscopy when the reaction between $Mo(CO)_4(NBD)$ and the free imine **1** was carried out under mild conditions (vide infra).

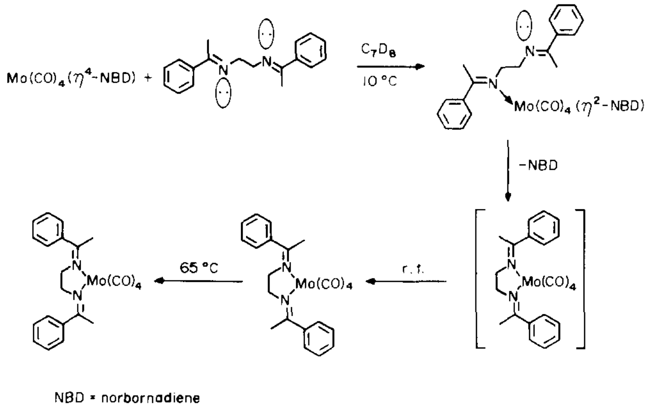
Even with excess imine ligands, there was no evidence of the $M(CO)_2L_4$ species, which is in agreement with the σ-donor capability expected for these species. The same behavior has been reported for $[Mo(CO)_4$ bipyridine] even though the bipyridine is considered to act as a π-acceptor ligand [5].

All the complexes are stable in the solid state when stored under nitrogen, and are soluble in chlorinated solvents such as CH_2Cl_2 and $CHCl_3$. In the infrared spectra, the tetracarbonyl metal complexes display four carbonyl stretching bands (see Experimental details) with medium, very strong, shoulder and strong intensities from high to low frequencies. However, some of the spectra showed overlap of the two central features. These bands have been assigned (through the use of group theory) to a local C_{2v} symmetry of the *cis* geometry of the imine ligand. A comparison of CO stretching frequencies between these imine complexes **4**–**12** and related complexes, such as those with π-accepting α-imine ligands [5,6], or those in which the chelate N=N is a bidentate saturated nitrogen ligand [7], supports the σ-ligand character of the nonconjugated imines for complexes **4**–**12**. However, similar CO frequencies were found for complexes **4**–**12** and 1,4-diazabutadiene species [8] regardless of their σ- and π-ligand character, respectively. Apparently, some solvent effects are probably important [7,9] and a careful comparison in the solid state or in more hydrocarbon-like solvents of these species is necessary in order to establish the σ,π contribution via IR spectroscopy. The strong free imine C=N stretching band ($\nu \simeq 1630$ cm^{-1}) was not observed after formation of the complexes. The presence of other strong bands below 1600 cm^{-1} prevented us from assigning them.

A consistent structural feature of complexes **4**–**12** appeared to be the chelate bonding of the imine ligand. The existence of free imines **1** and **3** in the E conformation [1], in which the lone pair is *cis* to C_6H_5, implies that upon coordination to the metal center, rotation around the carbon–nitrogen bond must have taken place to give the observed *Z* conformation present in complexes **4**, **5**, **8**, **9**, **11** and **12**. As a result of imine **1** coordination to $Mo(CO)_6$, three isomers would be expected, a nonsymmetric species such as in compounds **4** or **8**, and two symmetric species in which both methyl or phenyl substituents are *cis* to the metal atom. In addition to the nonsymmetric **4** and **8**, we obtained only isomers **5** or **9** in which the methyl groups are *cis* to the metal. This fact reflects a complete stereoselectivity in the formation of the symmetric compounds and the relevance of unambiguously determining the structure and configuration of all compounds. The determination of the configuration by means of NMR techniques is also supported in the solid state by the X-ray diffraction study of complex **4**.

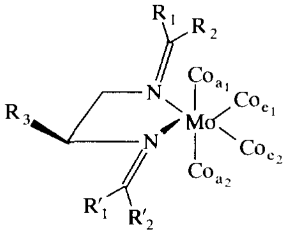
In order to determine whether the exclusive formation of complexes **5** and **9** may be merely due to the relatively vigorous reaction conditions employed, i.e. refluxing benzene, we carried out an experiment using $Mo(CO)_4(NBD)$ as the starting material, since this reagent reacts under much milder conditions due to the labile η^4-norbornadiene ligand [2b]. Thus, the reaction of 1 equiv. of imine **1** with $Mo(CO)_4(NBD)$ was carried out at 0°C in C_7D_8 and followed by ^{13}C NMR spectroscopy. After 20 min and when the temperature was allowed to reach 10°C, the initial monocoordination of imine **1** was observed. New methyl signals appeared at δ 15.70 and 22.91 ppm, as well as CH_2 signals at δ 56.10 and 66.61 ppm corresponding to the noncoordinated and coordinated imine chelate fragments, respectively. At room temperature, and even more clearly after 5 min at 40°C, the spectrum also showed the presence of two signals at δ 179.14 and 179.84 ppm assigned to the C=N groups, along with all the corresponding signals for complex **4**. A new methyl signal would be expected at δ ca. 30–33 ppm if a complex were formed with both methyl groups *cis* to each other and *trans* to the $Mo(CO)_4$ moiety. However, we never observed new signals in this region, which suggests that this intermediate is not favored.

In view of these results, we propose that monocoordination occurs first and the monocoordinated compound is then transformed into an intermediate species, in which both phenyl groups are *cis* to the $Mo(CO)_4$ moiety, as described in Scheme 2. However, the rota-



Scheme 2. Molecular structure of complex 4.

Table 1
^{13}C NMR data for compounds **4**–**12** [a] (δ, ppm; J, Hz)



	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	J(C–H)
R_1 [b]	23.5	138.9	137.9	22.2	24.2	143.9	138.1	138.9	138.9 [d]	
R_2 [b]	143.6	32.2	142.4	32.5	144.2	31.6	142.5	32.4	32.3	128.9
R'_1 [b]	138.6	138.9	137.9	22.2	138.5	143.9	138.1	23.5	139.9 [d]	
R'_2 [b]	34.6	32.2	142.4	32.5	33.3	31.6	142.5	144.7	32.8	128.9
R_3								17.1	18.3	125.6
CHR_3	57.7	58.5	60.2	55.3	57.8 [d]	60.2	62.2	58.8	60.1	137.7
CH_2	55.6	58.5	60.2	55.3	57.4 [d]	60.2	62.2	63.4	63.4	138.8
C=N	178.7	179.6	180.1	178.1	179.8	180.4	180.6	180.3	179.2	
C′=N	179.2	179.6	180.1	178.1	180.4	180.4	180.6	178.2	180.5	
CO_{a1}	206.0	206.0	208.1	206.3	205.5	204.5	206.2	207.4 [d]	206.8 [d]	
CO_{a2}	206.0	206.0	208.1	206.3	205.5	204.5	206.2	206.7 [d]	206.0 [d]	
CO_{e1}	217.0	222.0	219.7	222.5	[c]	211.2	211.6	223.2	222.3 [d]	
CO_{e2}	222.0	222.0	219.7	222.5	210.3	211.2	211.6	217.5	222.0 [d]	
R_1 or R'_1										
C – *o*	125.8	125.6	128.1 or 128.2		125.9	125.8	128.2 or 128.4	125.7	124.7 [e] 125.7	
C – *m*	129.1	129.0	128.6 or 128.7		128.8	128.6	128.5 or 128.8	128.0	129.0 [e] 128.9	
C – *p*	129.3	129.2	130.0		129.4	129.4	130.1	129.1	128.7 [e] 129.1	
R_2 or R'_2										
C – *o*	126.2		128.1 or 128.2		126.3		128.2 or 128.4	125.8		
C – *m*	128.3		128.6 or 128.7		129.1		128.5 or 128.8	129.0		
C – *p*	129.4		130.0		129.5		130.1	129.2		

[a] Spectra recorded in $CDCl_3$, 270 MHz. Shifts in ppm relative to Me_4Si.

[b] *ipso* carbon or methyl group.

[c] Not observed. [d] Assignment may be reversed. [e] R'_1.

tion for the labilized C=N bond seems to be much more rapid allowing the asymmetric compound **4** to be obtained immediately afterwards. It is also possible to propose monocoordination, followed by rotation of the C=N bond. However, as far as the steric requirements are concerned and considering the absence of new methyl signals in the ^{13}C spectrum, we think the former mechanism more likely in the formation of complex **4**.

The isolation of isomers **4** and **5** may be achieved selectively, as is described in the Experimental details. The reaction of $Mo(CO)_6$ in benzene with 2 equiv. of **1** affords complex **5** (56% yield) as a major isomer, while using a 1:1 molar ratio gives isomer **4** preferentially in 71% yield.

In an attempt to understand the influence of excess imine in the reaction between $Mo(CO)_6$ and imine **1**, we undertook experiments in an NMR tube using pure complex **4** in deuterated benzene and heating both in the presence of 1 equiv. of imine **1** and in its absence. There was a 15% conversion from **4** to **5** after 3 h at 70°C, when 1 equiv. had been added. Meanwhile, under the same reaction conditions no isomerization was observed after 11 h in the absence of imine **1**. In contrast, when the nonsymmetric complex **4** was allowed to reflux during 4 h in toluene, the formation of complex **5** was observed by ^{1}H NMR spectroscopy providing evidence of the kinetic and thermodynamic products, respectively. This suggests that the energy required for isomerization is higher that the temperature of refluxing benzene (72.5°C/587 mmHg). When the ligand was present, a mixture of benzene-imine showed that the reflux temperature increased by 1.5°C. Apparently, the temperature is an important factor in the isomerization processes. We can not discriminate that the concentration of the imine could be important too. However, the lack of the formation of the $Mo(CO)_2L_4$ species and the fact that the chelated derivative should be more stable than several monocoordinated imine ligands prevented us determining how the imine increases the rate of isomerization. Probably, the presence of an excess of this ligand modifies the reaction equilibrium.

We were not able to separate the corresponding tungsten isomers **8** and **9** by crystallization or by column chromatography on Florisil. The presence of a methyl group in the imine ligand **3** should give, after metal coordination, four possible isomers. However, only one diastereomer (the *dl* pair) has been obtained in each system, i.e. **11** and **12**, respectively. These isomers can be easily separated by chromatography on Florisil with a mixture of diethyl ether/petroleum ether as eluant, leading initially to the collection of complex **12**. Since **12** is formed with the phenyl groups *cis* to the methylene bearing the methyl group, an analog to **11** with the methyl and phenyl groups on the imine nitrogens inverted (i.e. $R_1 = R'_2 = CH_3$ and $R'_1 = R_2 = C_6H_5$) could also be expected to be formed. However, this compound was not observed. This might be due to the fact that the stronger electron density on the imine nitrogen atom closer to $R_3 = CH_3$ makes rotation of the C=N bond more difficult than that of the other imine nitrogen atom. Complex **11** would then be formed exclusively and with some extra energy would favor the rotation of the CH_3–CH–C=N bond affording the thermodynamic complex **12** which exhibits less steric hinderance.

2.1. NMR spectral studies

^{13}C NMR studies

Unequivocal assignment of the structure of these isomers has been carried out by ^{13}C NMR spectroscopy (Table 1) of complexes **4–7** in which the CO region was extremely useful. The axial carbonyl carbon atoms are observed between δ 206–208 ppm, and the equatorial carbonyl carbon atoms are found at higher frequencies (δ 217–222 ppm). Complex **6**, with four phenyl groups substituted in the imine, exhibits the equatorial CO at δ 219.7 ppm, while in complex **7**, with four methyl groups, this occurs at δ 222.5 ppm. The chemical shift of the equatorial carbonyl groups thus indicates if a methyl or a phenyl group is near. This appears to be a systematic behavior in the molybdenum compounds, since the equatorial CO groups near the methyl substituents always appear at δ 222 ppm, while those near the phenyl groups appear at δ 217 ppm. The corresponding equatorial COs for the nonsymmetric isomer **4** are found at δ 217 and 222 ppm, while the symmetric isomer **5** shows a signal at δ 222 ppm. From the carbonyl data of **6** and **7**, it is possible to assign the CO groups and the imine configuration for **4** and **5**. Thus, it was interesting to find that the chemical shift of the equatorial carbonyl group is a very useful tool for the determination of the configuration of the imine ligands, owing to the fact that the electronic effects have been transmitted through the metal atom and through space.

On the other hand, the previous assignment can also be supported from the corresponding chemical shifts of the methyl and the *ipso*-carbon atoms. The data for **6** and **7** allowed us to assign **4** and **5**, respectively. The carbon atoms *trans* to the metal center appear at higher field than the corresponding groups in the *cis* positions. A comparison between these chemical shifts and those reported for imine-boranes [1] shows that analogous groups *trans* to BH_3 have similar values to their molybdenum counterparts, reflecting the Lewis acid character of boron and the metal atom; in contrast, the *cis* groups in the metallic complexes show an important deshielding effect due to the diamagnetic current of the equatorial CO groups.

Another systematic correlation of NMR data supporting the configuration assignment of the complexes comes from the methylene carbon atoms in compounds **4**–**7** which are sensitive to the spatial neighboring group. The methylene carbon atoms closer to a methyl group are observed at δ 55 ppm, while those close to a phenyl group appear at δ 58–60 ppm.

In complexes **11** and **12**, the complete nonequivalence of all carbon atoms is evident. Their axial carbonyl groups can be easily assigned by comparison with compounds **4** and **5**, respectively. Also, the chemical shifts of the axial CO groups permit us to determine their *cis* or *trans* relationship with the methyl group. The configuration of the imines in the nonsymmetric compound **11** is also clearly understood. Dreiding models and molecular mechanics calculations [10] show that the equatorial position for the methyl substituent is not favored because of a strong interaction with the imine substituent group. An envelope conformation is proposed, with the methyl group in the axial position, which defines two different imine groups and two faces of the ring; this is also supported by the different ^{13}C chemical shifts of the axial carbonyl groups. Such an envelope conformation was observed in the X-ray diffraction study of **4**.

^1H NMR studies

The ^1H NMR spectra (Table 2) of complexes **4**,**5** and **8**,**9** show clearly their isomeric relationship. The presence of a symmetry plane for **5** and **9** is reflected by the simple pattern of singlets for the methylene and methyl groups, while for **4** and **8** the absence of this plane is evident from the characteristic complex coupling pattern for methylene groups, along with two signals for the nonequivalent methyl groups. Further evidence to support the proposed structure of **4** and **5** was obtained from a NOESY experiment in complex **4**, which showed spatial correlation between the methylene signal at high field (δ 3.5 ppm) and the corresponding signal of the phenyl groups.

The similarity of the NMR spectra of **8**–**10** to those of **4**–**6** led us to believe that all these complexes have the same imine ligand conformation. The evidence for only two isolated species **11** and **12**, analogous to **4** and **5**, is clear from the chemical shifts of the four corresponding methyl signals at δ 2.32, 2.79 and 2.74, 2.84

Table 2
^1H NMR data for compounds **4**–**12** [a]

	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
R_1	2.30 (m)	7.3–7.6 (m)	7.1–7.6 (m)	2.10 (s)	2.33 (s)	7.1–7.3 (m)	7.1–7.7 (m)	7.4 (m) 7.16 (d, 8.1) (d, 1.7)	7.37 (m)
R'_1	7.2–7.5 (m)	7.3–7.6 (m)	7.1–7.6 (m)	2.10 (s)	7.1–7.5 (m)	7.1–7.3 (m)	7.1–7.7 (m)	2.32 (s)	7.06 (d, 6.2) (d, 1.6) 7.09 (d, 6.1) (d, 1.8)
R_2	7.2–7.5 (m)	2.80 (s)	7.1–7.6 (m)	2.50 (s, br)	7.1–7.5 (m)	2.78 (s)	7.1–7.7 (m)	2.79 (d, 1.7)	2.84 (d, 1.6)
R'_2	2.78 (s)	2.80 (s)	7.1–7.6 (m)	2.50 (s, br)	2.61 (s)	2.78 (s)	7.1–7.7 (m)	7.4 (m) 7.28 (d, 8.1) (d, 1.8)	2.74 (s)
R_3	3.80 (t, 6.0)	3.40 (s)	3.78 (s)	3.60 (s)	3.93 (t, 5.7)	3.99 (s)	3.82 (s)	1.06 (d, 6.7)	0.86 (d, 6.6)
H_c	3.80 (t, 6.0)	3.40 (s)	3.78 (s)	3.60 (s)	3.93 (t, 5.7)	3.99 (s)	3.82 (s)	4.00 (d, 4.1) (d, 1.5) (q, 6.7)	3.74 (d, 3.4) (d, 1.8) (q, 6.6)
H_a, H_b	3.50 (t, 6.0)	3.40 (s)	3.78 (s)	3.60 (s)	3.57 (t, 5.7)	3.99 (s)	3.82 (s)	3.77 (d, 12.5) (d, 4.1) (q, 1.7) 3.65 (d, 12.5) (d, 1.5)	3.43 (d, 12.5) (d, 3.4) (q, 1.6) 3.37 (d, 12.5) (d, 1.8)

[a] Spectra recorded in $CDCl_3$, 270 MHz; shifts in ppm relative to Me_4Si.
Multiplicities and coupling constants (Hz) in parentheses. For numbering, see Scheme 1.

ppm, respectively; and from the multiplicity pattern, a singlet for the methyl groups at high field and a doublet with a $^{5}J_{HH}(CH_3\text{-}C{=}NCH_b) \simeq 1.6$ Hz for both signals at low field. This ^{5}J-coupling constant indicates the planar imine system [11] as well as the preferred conformation of the five-membered ring. In addition, it corroborates the configuration and the NMR assignment of the complexes. A dihedral angle between H_b and the imine carbon of 6° was determined [10]. This coupling has been considered as a probe for the C=N double bond configuration, and its value depends on the zigzag planar arrangement of the bonds involved in the coupling [12]. In alkyl amines, it has been found that the *E* isomer has a ^{5}J value smaller than 0.8 Hz, whereas the *Z* isomer shows values between 1.2–1.5 Hz [11]. The value of 1.6 Hz for **11** and **12** is in agreement with a *Z* configuration. A similar pattern is observed for complex **7**. However, the doublet is not well-resolved, being a broad singlet with half height, which also supports the assignment of the CH_3 groups *cis* or *trans* to the metal.

In complexes **11** and **12**, the position of the methyl substituent on a methylene carbon was found to be axial, as established from the coupling constants: $^{2}J(H_a\text{-}H_b) \simeq 12.5$ Hz; $^{3}J(H_b\text{-}H_c) \simeq 1.8$ Hz; $^{3}J(H_b\text{-}H_c) \simeq 3.4$ Hz. The methylene proton signals H_a and H_b appear as an AB system while H_b and H_c (Scheme 1) have a complex pattern from which all the coupling constants may be obtained (Table 2).

2.2. *Solid-state structure of 4*

The molecular structure of **4** was determined by an X-ray diffraction study. An ORTEP drawing is shown in Fig. 1. Bond lengths and angles are listed in Table 3 and the atomic coordinates and their temperature factors in Table 4. The complex has a distorted octahedral arrangement of the CO ligands around the metal atom. An envelope conformation for the five-membered ring is found with C-2 out of the ring plane. The *cis*-imine chelate ligand has the shortest bond angle N1–Mo–N2 [75.7(1)°]. Steric compression of the ligand is reflected by the wide angles observed for Mo–N1–C3 [131.2(3)°] and Mo–N2–C21 [132.4(3)°] as well as for the corresponding to N2–Mo–C12 angle [98.8(2)°] and, even more obvious, for N1–Mo–C11 [102.3(2)°]. The last angle is probably due to the presence of a phenyl group on the same side of the carbonyl group C11–O11. According to the torsion angles N2–C21–C23–C28 (61°) and N1–C3–C4–C5 (69°), the phenyl groups are out of the plane because of their steric hindrance.

Table 3
Bond distances (Å) and angles (°) for compound **4** [a]

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
MO	N1	2.294(3)	C3	C4	1.493(7)
MO	N2	2.278(4)	C3	C10	1.514(7)
MO	C11	1.927(6)	C4	C5	1.391(8)
MO	C12	1.928(4)	C4	C9	1.406(7)
MO	C13	2.026(5)	C5	C6	1.42(1)
MO	C14	2.015(6)	C6	C7	1.40(1)
O11	C11	1.171(7)	C7	C8	1.37(1)
O12	C12	1.175(6)	C8	C9	1.40(1)
O13	C13	1.149(7)	C21	C22	1.508(7)
O14	C14	1.144(8)	C21	C23	1.492(7)
N1	C1	1.491(7)	C23	C24	1.398(8)
N1	C3	1.279(6)	C23	C28	1.398(8)
N2	C2	1.486(6)	C24	C25	1.410(9)
N2	C21	1.278(6)	C25	C26	1.41(1)
C1A	C1B	1.39(2)	C26	C27	1.38(1)
C1A	C1C	1.40(2)	C27	C28	1.41(1)
C1	C2	1.540(7)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
N1	MO	N2	75.7(1)	N1	C1	C2	108.8(4)
N1	MO	C11	102.3(2)	N2	C2	C1	106.8(4)
N1	MO	C12	174.5(2)	N1	C3	C4	119.8(4)
N1	MO	C13	91.4(2)	N1	C3	C10	125.3(5)
N1	MO	C14	92.0(2)	C4	C3	C10	114.8(4)
N2	MO	C11	175.4(2)	C3	C4	C5	119.5(5)
N2	MO	C12	98.8(2)	C3	C4	C9	120.2(5)
N2	MO	C13	97.2(2)	C5	C4	C9	120.2(5)
N2	MO	C14	90.5(2)	C4	C5	C6	119.3(6)
C11	MO	C12	83.2(2)	C5	C6	C7	120.0(6)
C11	MO	C13	87.0(2)	C6	C7	C8	120.3(7)
C11	MO	C14	85.4(2)	C7	C8	C9	120.6(6)
C12	MO	C13	89.0(2)	C4	C9	C8	119.7(5)
C12	MO	C14	88.3(2)	MO	C11	O11	175.0(4)
C13	MO	C14	172.1(2)	MO	C12	O12	178.2(5)
MO	N1	C1	111.6(3)	MO	C13	O13	173.4(5)
MO	N1	C3	131.2(3)	MO	C14	O14	173.6(6)
C1	N1	C3	116.7(4)	N2	C21	C22	120.6(5)
MO	N2	C2	108.2(3)	N2	C21	C23	124.1(4)
MO	N2	C21	132.4(3)	C22	C21	C23	115.2(4)
C2	N2	C21	118.8(4)	C21	C23	C24	120.5(5)
C1B	C1A	C1C	125.0(1)	C21	C23	C28	118.5(5)
C24	C23	C28	120.8(5)	C25	C26	C27	120.3(7)
C23	C24	C25	118.6(6)	C26	C27	C28	119.6(6)
C24	C25	C26	120.6(6)	C23	C28	C27	120.0(6)

[a] Numbers in parentheses are estimated standard deviations in least significant digits.

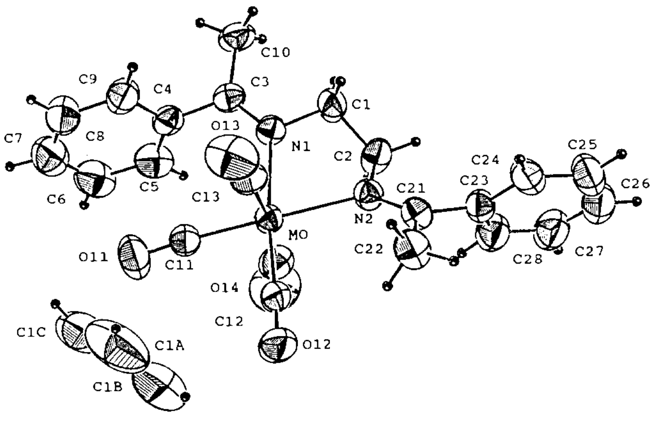


Fig. 1. Molecular structure of complex **4**.

Table 4
Atomic coordinates and temperature factors for compound **4** [a]

Atom	x	y	z	B_{eq}
MO	0.66180(3)	0.16986(2)	0.53700(3)	3.285(6)
O11	0.5444(4)	0.2230(3)	0.7371(4)	6.7(1)
O12	0.9003(4)	0.2038(2)	0.7236(4)	6.2(1)
O13	0.6545(5)	0.3272(2)	0.4598(5)	7.9(1)
O14	0.6549(6)	0.0264(3)	0.6638(5)	9.5(2)
N1	0.4959(3)	0.1418(2)	0.3888(3)	3.54(8)
N2	0.7478(3)	0.1230(2)	0.3951(3)	3.71(8)
C1A	0.505(1)	0.0607(7)	0.944(1)	15.8(5)
C1	0.5358(5)	0.1149(3)	0.2835(4)	4.5(1)
C1B	0.617(1)	0.0255(8)	0.972(1)	16.1(5)
C1C	0.395(1)	0.0376(6)	0.9698(9)	14.9(4)
C2	0.6571(4)	0.0744(3)	0.3245(5)	4.5(1)
C3	0.3803(4)	0.1524(2)	0.3776(4)	3.63(9)
C4	0.3327(4)	0.1767(3)	0.4805(4)	3.86(9)
C5	0.3264(5)	0.1305(3)	0.5704(5)	5.3(1)
C6	0.2734(6)	0.1525(4)	0.6640(6)	6.5(2)
C7	0.2274(6)	0.2198(4)	0.6650(6)	6.8(2)
C8	0.2343(6)	0.2649(4)	0.5760(6)	6.1(2)
C9	0.2857(5)	0.2440(3)	0.4823(5)	4.9(1)
C10	0.2822(5)	0.1409(3)	0.2665(5)	5.0(1)
C11	0.5834(4)	0.2023(3)	0.6583(5)	4.3(1)
C12	0.8112(4)	0.1905(3)	0.6517(4)	4.1(1)
C13	0.6576(5)	0.2691(3)	0.4809(5)	4.5(1)
C14	0.6603(5)	0.0764(3)	0.6129(5)	5.1(1)
C21	0.8570(4)	0.1253(3)	0.3769(4)	3.9(1)
C22	0.9474(5)	0.1795(3)	0.4359(5)	5.0(1)
C23	0.9065(4)	0.0749(3)	0.3025(4)	4.0(1)
C24	0.9528(5)	0.0976(3)	0.2071(5)	5.1(1)
C25	1.0066(6)	0.0488(4)	0.1442(5)	6.3(2)
C26	1.0160(6)	−0.0210(4)	0.1783(6)	6.5(2)
C27	0.9683(6)	−0.0431(4)	0.2718(6)	6.5(2)
C28	0.9140(5)	0.0053(3)	0.3354(6)	5.4(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $B_{eq} = 4/3[a^2B_{1,1} + b^2B_{2,2} + c_2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$.

The structure of compound **4** closely resembles that for 2,6[1-(2,2-dimethylpropanimino)ethyl]pyridinetetracarbonyl molybenum [13] in which some delocalization of charge in the chelate ring was proposed. However, the C=N double-bond lengths [1.279(6) Å and 1.278(6) Å] in complex **4** are shorter than the corresponding one in the 2,6-diiminopyridine complex [1.295(12) Å] which suggests that no delocalization of charge is present in the chelate ring of **4**. This comparison must take into account the high observed standard deviations reported for the pyridine derivative [13].

Other reported examples, such as the corresponding saturated nitrogen chelate complex [Mo{(PhCH$_2$)HNCH$_2$CH$_2$NMe$_2$}(CO)$_4$] [7] showed longer Mo–N distances [2.317(3) Å and 2.342(3) Å] than **4** [2.278(4) Å and 2.294(3) Å] which indicates a stronger Mo–N interaction in the latter complex. The C=N double-bond length [1.279(6) Å] in the coordinate ligand is very similar to that of a typical noncoordinated C=N bond length [1.279 Å] [14].

As expected, the two carbonyls which are *trans* to the two nitrogen donor atoms have shorter M–C distances (≃ 0.9–1 Å) than the other two carbonyls. The Mo–C bond length for the carbonyls *trans* to the bidentate imine ligand are very similar [(1.927(6) Å and 1.928(4) Å] and slightly shorter than those in the corresponding saturated nitrogen bidentate ligand [1.932(5) Å and 1.953(4) Å]. Complex **4** crystallized in the presence of benzene and a half a molecule of benzene is present in the unit cell. However, several microanalyses of complex **4** showed that only a quarter of the benzene molecule is present.

3. Experimental details

3.1. General

All reactions described in this paper were carried out under an atmosphere of dinitrogen using Schlenk-line techniques. Solvents were dried, distilled and deairated before use. Melting points were taken in sealed capillaries and are uncorrected.

The imine compounds **1–3** [1] and the complex Mo(CO)$_4$(NBD) [15] were prepared by published methods. Mo(CO)$_6$ and W(CO)$_6$ were purchased from Strem Chemicals. Elemental microanalyses (C,H and N) were performed by Oneida Research Services, Whitesboro, NY, USA. IR spectra were recorded on a Unicam SP$_3$-200 and Nicolet MX-1-FT spectrophotometers. ^{13}C and ^{1}H NMR spectra in CDCl$_3$ were recorded on JEOL FX-90 and GSX-270 MHz spectrometers. The spectra were calibrated against TMS.

3.2. X-ray analysis of compound 4

Compound **4** was obtained from the reaction of Mo(CO)$_6$ with the corresponding imine in benzene. Single crystals of **4** were grown by crystallization from diethyl ether : hexane (1.5 : 1).

Crystal data: $C_{22}H_{20}N_2O_4Mo \cdot \frac{1}{2}C_6H_6$, M = 511.41; monoclinic, a = 11.112(1), b = 19.345(1), c = 11.680(1) Å, β = 102.89(6)°; V = 2447.5 Å^3 (by least-squares refinement on diffractometer angles for 24 automatically-centered reflections, Mo Kα), space group $P2_1/n$, $Z = 4$, D_x = 1.39 g cm^{-3}, μ(Mo Kα) = 5.5 cm^{-1}, T = 293 K, $F(000)$ = 1138.

X-Ray data collection, structure resolution and refinement were undertaken using an Enraf-Nonius CAD4 diffractometer equipped with graphite monochromated Mo Kα radiation and an ω–2θ scan technique. A total of 7632 unique reflections were measured ($2 \le 2\theta \le 60°$) and 4706 were considered as observed [$F_o > 3.0\sigma(F_o)$]. Monitoring of check reflections showed no signs of decay. Absorption correction was achieved using DIFABS.

The structure was solved by direct methods and subsequent difference Fourier synthesis. A Killian–Lawrence weighting scheme was used [16]. Final R and R_w values were 0.052 and 0.064, respectively. Highest and lowest peaks in final difference map were at 0.70 and −0.18 e Å^{-3}. All calculations were carried out using MOLEN [17] in a VAX 4000 computer.

3.3. Preparation of complexes

cis[$(CO)_4Mo\{CH_3(C_6H_5)C{=}N(CH_2)_2{-}N{=}C(CH_3)$-$C_6H_5\}$] (**4**) and (**5**): Addition of 0.5 g of **1** (1.89 mmol) to a suspension containing an equimolar quantity of $Mo(CO)_6$ (0.5 g 1.89 mmol) in benzene (40 cm^3) followed by heating for 8 h under reflux afforded a yellow colored solution. The reaction mixture was cooled to 10°C giving a yellow greenish precipitate which was filtered and recrystallized from CH_2Cl_2/hexane (3:1) affording isomer **5**. Reduction of the volume of the mother liquor to 10 cm^3 and addition of 10 cm^3 of hexane afforded after cooling to −10°C a yellow precipitate of isomer **4**. Several independent recrystallizations of **4** and **5** in CH_2Cl_2/hexane (2:1) gave 258 mg (29%) and 87 mg (9.7%), respectively. A similar procedure to the above, starting from $Mo(CO)_6$ (0.5 g, 1.89 mmol) and **1** (1 g, 3.78 mmol) under reflux for 6 h afforded 78 mg (8.7%) of **4** and 505 mg (56.4%) of **5**. The same method with equimolar quantities (0.5 g, 1.89 mmol) of $Mo(CO)_6$ and **1** under reflux for only 6 h afforded isomer **4** in 71% yield (640 mg). Complex **4**: IR ν(CO) ($CHCl_3$) (cm^{-1}): 2010; 1890; 1870; 1820. M.p. 95°C (dec.). Anal. Calc. for $MoC_{23.5}H_{21.5}N_2O_4$: C, 57.38; H, 4.41; N, 5.69% Found: C, 57.1; H, 4.44; N, 5.48%. Complex **5**: ν(CO) ($CHCl_3$) (cm^{-1}): 2010; 1890; 1870; 1820. M.p. 92°C (dec.). Anal. Calc. for $MoC_{22}H_{20}N_2O_4$: C, 55.94; H, 4.27; N, 5.93%. Found: C, 55.78; H, 4.18; N, 5.97%.

cis-[$(CO)_4Mo\{(C_6H_5)_2C{=}N(CH_2)_2N{=}C(C_6H_5)_2\}$(**6**): Addition of 0.5 g of **2** (1.29 mmol) to a suspension of an equimolar quantity of $Mo(CO)_6$ (0.34 g, 1.29 mmol) in benzene (40 cm^3) was followed by heating for 5 h under reflux. The solution was cooled to room temperature, filtered, the volume reduced and hexane added. The red precipitate obtained was filtered, washed with hexane and dried in vacuo. Several recrystallizations from CH_2Cl_2/hexane (2:1) afforded fine red needles in 89% yield (634 mg), m.p. 100°C (dec.). IR ν(CO) ($CHCl_3$) (cm^{-1}): 2008; 1895; 1879; 1836. Anal. Calc. for $MoC_{32}H_{24}N_2O_4$: C, 64.43; H, 4.05; N, 4.69%. Found: C, 63.64; H, 3.80; N, 4.57%.

cis-[$(CO)_4Mo$-$\{(CH_3)_2C{-}N(CH_2)_2N{=}C(CH_3)_2\}$] (**7**): $Mo(CO)_6$ (0.5 g, 1.89 mmol) was allowed to react with $NH_2CH_2CH_2NH_2$ (0.114 g, 0.127 ml, 1.89 mmol) and CH_3COCH_3 (0.219 g, 0.28 ml, 3.78 mmol) under reflux of benzene (40 cm^3) for 5 h. The reaction mixture was filtered to remove a precipitate. Evaporation of the benzene and extractions with hexane afforded, after cooling at 0°C, 75 mg of a pale yellow solid in a yield of 11.4%, m.p. 80°C (dec.). IR ν(CO) ($CHCl_3$) (cm^{-1}): 2013; 1899; 1870; 1819.

cis[$(CO)_4W\{CH_3(C_6H_5)C{=}N(CH_2)_2N{=}C(CH_3)$-$C_6H_5\}$] (**8**) and (**9**): A mixture of $W(CO)_6$ (0.5 g, 1.42 mmol) and **1** (0.38 g, 1.42 mmol) in benzene (100 cm^3) was irradiated at room temperature with a Hanovia mercury arc lamp for 30 h. The resulting brown–orange solution was evaporated and $W(CO)_6$ was recovered by sublimation under reduced pressure. The remaining solid was crystallized from CH_2Cl_2/hexane (1:3) giving a bright yellow solid (65%) corresponding to the mixture of isomers **8** and **9** in a 3:2 ratio. IR ν(CO) ($CHCl_3$) (cm^{-1}): 2010; 1887; 1870; 1826.

[$(CO)_4W\{(C_6H_5)_2C{=}N(CH_2)_2N{=}C(C_6H_5)_2\}$] (**10**): A similar procedure as above using $W(CO)_6$ (1 g, 2.84 mmol) and **2** (1.10 g, 2.84 mmol) and irradiating for 24 h afforded a red–brown solution. Removal of the solvent under vacuum gave an oil which was taken up in a minimum amount of CH_2Cl_2. The residue was passed through a Florisil column (21.5 × 2.5 cm) and eluted with a mixture of petroleum ether and diethyl ether. The volume of the eluant was reduced and crystals were filtered to give a 9.2% yield. IR ν(CO) ($CHCl_3$) (cm^{-1}) 2000; 1885; 1862; 1845.

[$(CO)_4Mo\{(CH_3)(C_6H_5)C{=}NCH_2CH(CH_3)N{=}C(CH_3)(C_6H_5)\}$] (**11**) and (**12**): Addition of 0.5 g of **3** (1.8 mmol) to a suspension of an equimolar amount of $Mo(CO)_6$ in benzene (40 cm^3) followed by heating for 4 h under reflux led to a yellow colored solution which was filtered and evaporated to dryness under reduced pressure. The residue was chromatographed through a Florisil column and eluted with a mixture of petroleum ether/diethyl ether. The first eluant fraction in a ratio of 12:2 afforded complex **12**, while the second (12:6) gave complex **11**. The eluant was evaporated to dryness and, in each case, the complex was obtained by extracting the residue with CH_2Cl_2 and precipitating with hexane. Yields: 100 mg, 10.1% (**11**) and 125 mg, 12.6% (**12**). Complex **11**: IR ν(CO) ($CHCl_3$) (cm^{-1}): 2010; 1875; 1855; 1810; m.p. 99–103°C. Complex **12**: IR ν(CO) ($CHCl_3$) (cm^{-1}): 2010; 1880; 1855; 1820; m.p. 175–177°C (dec.). Anal. Calc. for $MoC_{23}H_{22}N_2O_4$: C, 56.10; H, 4.74; N, 5.66%. Found: C, 56.79; H, 4.56; N, 5.76%.

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Note added in proof

Recently, the crystal structure of compound **12** has been determined and shown to have the proposed structure. Data will be published elsewhere.