

Stereoselective synthesis and reactivity of *cis*- and *trans*- dimolybdenum nitrosyl derivatives with the bridging bis(dimethylsilanediyl)di(η^5 -cyclopentadienyl) ligand. X-ray molecular structures of *cis*-[$\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$], *trans*-[$\{\text{Mo}(\text{CO})(\text{NO})(\text{CN}^t\text{Bu})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$], *cis*-[$\{\text{Mo}_2(\text{CO})_3(\text{NO})_2(\text{PMe}_3)\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] and *trans*-[$\{\text{Mo}(\text{NO})(\text{CN}^t\text{Bu})_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$]

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Received 21 April 1997; received in revised form 2 June 1997

Abstract

New dimolybdenum nitrosyl [$\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] *cis*-**3** and *trans*-**3** complexes have been isolated from the reaction of the previously reported *cis*-[$\{\text{Mo}(\text{CO})_3\text{H}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] *cis*-**1** and *trans*- $\text{K}_2[\text{Mo}(\text{CO})_3]_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$ *trans*-**2** respectively, with *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{NO})(\text{CH}_3)$ (diazald). The reaction of [$\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] *cis*-**3** and *trans*-**3** with Lewis bases L (L = *tert*-butylisocyanide and trimethylphosphine) under appropriate conditions gave monosubstituted [$\{\text{Mo}_2(\text{CO})_3(\text{NO})_2\text{L}\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] complexes (L = CN^tBu *cis*-**4**; PMe₃ *cis*-**5** and *trans*-**5**), disubstituted [$\{\text{Mo}(\text{CO})(\text{NO})\text{L}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] (L = CN^tBu, *cis*-**6**, *trans*-**6**; PMe₃ *cis*-**7** and *trans*-**7**) and tetrasubstituted [$\{\text{Mo}(\text{NO})\text{L}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] complexes (L = CN^tBu, *cis*-**8** and *trans*-**8**), which were isolated in moderate yields and fully characterized by conventional analytical and spectroscopic methods. Addition of PCl₅ under appropriate conditions to a diethyl ether solution of *cis*-**3** or *trans*-**3** afforded the dichloronitrosyl derivatives *cis*- and *trans*-[$\{\text{MoCl}_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] *cis*-**9** and *trans*-**9**. The ¹³C and variable temperature ¹H NMR spectra of complex *cis*-**9** are consistent with the formation of 18 electron metal centres bridged by two chlorine atoms, providing two *cis*- and *trans*-nitrosyl isomers, which interchange rapidly in solution at room temperature through a postulated 16 electron intermediate. Treatment of *cis*-**8** and *trans*-**8** with stoichiometric amounts of PCl₅ gave the tetrahalo derivatives [$\{\text{Mo}(\text{NO})(\text{CN}^t\text{Bu})\text{Cl}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] *cis*-**10** and *trans*-**10** respectively, whereas the oxidation of *trans*-**6** with PCl₅ under similar conditions gave a mixture of *trans*-**10** and *trans*-[$\{\text{Mo}(\text{CO})(\text{NO})_2(\text{CN}^t\text{Bu})\text{Cl}_4\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$] (*trans*-**11**). In addition, single crystal X-ray crystallographic analyses were performed for *cis*-**3**, *cis*-**5**, *trans*-**6** and *trans*-**8**. All the complexes show two metal fragments bridged by the $\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ ligand, with different dispositions of the metal fragments.

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Keywords: Group 6; Molybdenum; Cyclopentadienyl; Nitrosyl

1. Introduction

Recently, we have reported the synthesis of dinuclear titanium, zirconium and molybdenum complexes bridged by two types of cyclopentadienyl ligand, ($\eta^5\text{-C}_5\text{H}_4$)₂SiMe₂ [1–3] and ($\eta^5\text{-C}_5\text{H}_3$)₂(SiMe₂)₂ [4,5].

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¹ X-ray diffraction studies.

The stereorigidity of the ligand with two SiMe_2 bridges causes the two metal centers to be coordinated *cis* or *trans* with respect to the ligand plane. Stereoselective synthesis of *cis*- and *trans*- carbonyl dimolybdenum complexes has been reported [5]. The mononuclear complexes $\text{CpM}(\text{CO})_2(\text{NO})$ ($\text{M} = \text{Mo}, \text{W}$; $\text{Cp} = \text{C}_5\text{H}_5$) have been extensively studied [6–10].

In this paper, we report the synthesis of new *cis* and *trans* nitrosyl dimolybdenum complexes with the $(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2$ ligand and the chemical behaviour of these complexes in substitution reactions with Lewis bases which replace carbonyl groups, and oxidation reactions with phosphorus pentachloride.

2. Results and discussion

2.1. Dicarbonyl nitrosyl molybdenum complexes

Dicarbonyl nitrosyl molybdenum complexes $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis*-**3** and *trans*-**3** can be prepared by using the method reported for related mononuclear [11–16] and dinuclear [3] complexes, which involves the reaction of $[\{\text{Mo}(\text{CO})_3\text{H}\}_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis*-**1** and $\text{K}_2[\{\text{Mo}(\text{CO})_3\}_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *trans*-**2** respectively with *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{NO})(\text{CH}_3)$ (diazald). In this reaction the diazald NO group is easily transferred to the metal centers of *cis*-**1** and *trans*-**2** with

elimination of CO and transformation of the tricarbonyl hydride or the tricarbonyl metallate into the nitrosyl derivatives. We have shown that reaction times are very important to obtain pure products in these processes (see Section 4).

Both *cis*-**3** and *trans*-**3** complexes are highly soluble in all the common organic solvents and consequently they are obtained as oily crude products which require recrystallization from their concentrated hexane solutions.

Spectroscopic data for *cis*-**3** and *trans*-**3** are given in Section 4. The $\nu(\text{CO})$ frequencies are in the range 2020–1942 cm^{-1} , as expected for terminal carbonyls and the $\nu(\text{NO})$ frequencies between 1680 and 1642 cm^{-1} are consistent with a linear disposition of the nitrosyl group. Their ^1H NMR spectra show one singlet due to the bridging SiMe_2 groups for the *trans* complex, whereas two singlets are observed for the *cis* complex, along with the ABB' spin system for the ring protons of both complexes.

The molecular structure of complex *cis*-**3** was studied by X-ray diffraction methods and is shown in Fig. 1 along with the numbering scheme employed. Relevant bond distances and angles are given in Table 1.

The structure belongs to a *cis* species with the two metal atoms located at the same face of the two cyclopentadienyl rings, with a Mo–Mo distance of 4.962(1) Å. Each molybdenum atom in *cis*-**3** has a ‘three-legged piano-stool’ configuration with one penta-

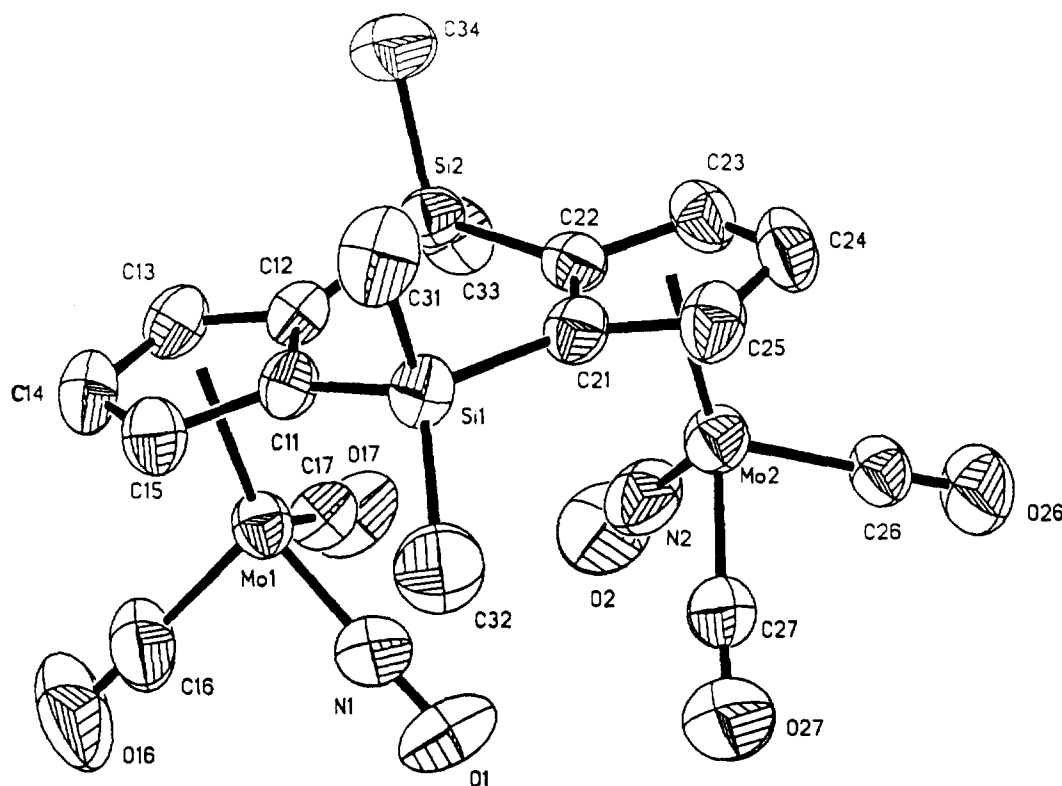


Fig. 1. Molecular structure and atom-labeling scheme for complex *cis*-**3**.

Table 1
Selected bond distances (Å) and bond angles (deg) for *cis-3*

| Distances | | | |
|-------------------|----------|-------------------|----------|
| Mo(1)–N(1) | 1.823(5) | Mo(2)–N(2) | 1.899(5) |
| Mo(1)–C(16) | 1.964(6) | Mo(2)–C(26) | 1.923(5) |
| Mo(1)–C(17) | 1.978(6) | Mo(2)–C(27) | 1.931(7) |
| Mo(1)–C(11) | 2.351(4) | Mo(2)–C(21) | 2.356(5) |
| Mo(1)–C(12) | 2.351(4) | Mo(2)–C(22) | 2.375(5) |
| Mo(1)–C(13) | 2.357(5) | Mo(2)–C(23) | 2.354(6) |
| Mo(1)–C(14) | 2.387(6) | Mo(2)–C(24) | 2.355(5) |
| Mo(1)–C(15) | 2.368(5) | Mo(2)–C(25) | 2.339(5) |
| Mo(1)–Cp(1) | 2.029 | Mo(2)–Cp(2) | 2.022 |
| Si(1)–C(31) | 1.860(5) | Si(2)–C(33) | 1.853(6) |
| Si(1)–C(32) | 1.844(6) | Si(2)–C(34) | 1.860(6) |
| Si(1)–C(11) | 1.866(5) | Si(2)–C(12) | 1.858(5) |
| Si(1)–C(21) | 1.863(5) | Si(2)–C(22) | 1.875(5) |
| C(11)–C(12) | 1.444(7) | C(21)–C(22) | 1.432(7) |
| C(12)–C(13) | 1.429(7) | C(22)–C(23) | 1.435(7) |
| C(13)–C(14) | 1.402(8) | C(23)–C(24) | 1.409(8) |
| C(14)–C(15) | 1.405(7) | C(24)–C(25) | 1.401(8) |
| C(11)–C(15) | 1.434(7) | C(21)–C(25) | 1.426(7) |
| N(1)–O(1) | 1.187(6) | N(2)–O(2) | 1.163(6) |
| O(16)–C(16) | 1.155(7) | O(26)–C(26) | 1.148(6) |
| O(17)–C(17) | 1.127(6) | O(27)–C(27) | 1.164(7) |
| Angles | | | |
| O(1)–N(1)–Mo(1) | 179.0(4) | O(2)–N(2)–Mo(2) | 178.1(6) |
| O(16)–C(16)–Mo(1) | 179.5(7) | O(26)–C(26)–Mo(2) | 177.9(5) |
| O(17)–C(17)–Mo(1) | 178.0(5) | O(27)–C(27)–Mo(2) | 177.3(5) |
| Cp(1)–Mo(1)–N(1) | 131.8 | Cp(2)–Mo(2)–N(2) | 128.3 |
| Cp(1)–Mo(1)–C(16) | 121.1 | Cp(2)–Mo(2)–C(26) | 122.8 |
| Cp(1)–Mo(1)–C(17) | 123.4 | Cp(2)–Mo(2)–C(27) | 124.4 |
| N(1)–Mo(1)–C(16) | 90.7(3) | N(2)–Mo(2)–C(26) | 90.5(2) |
| N(1)–Mo(1)–C(17) | 91.4(2) | N(2)–Mo(2)–C(27) | 91.1(3) |
| C(16)–Mo(1)–C(17) | 85.8(3) | C(26)–Mo(2)–C(27) | 88.4(2) |

Cp(1) is the centroid of C(11)–C(15); Cp(2) is the centroid of C(21)–C(25).

hapto-coordinated cyclopentadienyl ring. If the centroid of each Cp ring is taken as one coordination site, the angles at molybdenum between the centroids and the legs range from 121.1° to 131.8°. The angles between contiguous legs range from 85.8(3)° to 91.4(2)°. The CO and NO ligands have a linear disposition with Mo–C–O angles from 177.3(5)° to 179.5(7)° and Mo–N–O angles between 179.0(4)° for N(1) and 178.1(6)° for N(2). The Mo–X and X–O (X = C, N) distances are normal for terminal carbonyl and nitrosyl groups. The two N–O groups are *trans* with respect to the plane which bisects the cyclopentadienyl rings and contains the two Mo atoms. Although the determination of the position of the carbon and nitrogen atoms by X-ray crystallography is not always clear, the distances and thermal factors are consistent with this assignment, confirmed by other structural and chemical data.

2.2. Substitution reactions

All substitution reactions were monitored by IR spectroscopy to follow the variation of the typical absorption bands of the carbonyl ligands.

Both *cis-3* and *trans-3* were reacted with Lewis bases such as *tert*-butylisocyanide and trimethylphosphine. Different substituted complexes were obtained depending on the molar ratio, the Lewis base and the thermal or photochemical activation of the carbonyl group used in each reaction (see Schemes 1 and 2).

The reaction of *cis-3* with one equivalent of CN^tBu at room temperature yields a mixture containing the starting material, the disubstituted complex $[\{\text{Mo}(\text{CO})(\text{NO})(\text{CN}^t\text{Bu})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-6* and the monosubstituted complex $[\{\text{Mo}_2(\text{CO})_3(\text{NO})_2(\text{CN}^t\text{Bu})\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-4*, whereas the *trans-4* monosubstituted complex could not be detected in the analogous reaction. These compounds were separated by chromatography on florisil, *cis-4* being eluted with dichloromethane and *cis-6* with THF. The reaction between *cis-3* and *trans-3* with CN^tBu in a 1:2 molar ratio led respectively (at room temperature for *cis-3* and heating at 60°C for *trans-3*), to the disubstituted *cis-6* and *trans-6* complexes, in high yields.

When the same reaction was carried out with the addition of four equivalents of CN^tBu and heating at 80°C, the tetrasubstituted complexes $[\{\text{Mo}(\text{NO})(\text{CN}^t\text{Bu})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-8* and *trans-8* were obtained. It was observed by IR spectroscopy that the first step in these reactions is the transformation of all the starting material, *cis-3* and *trans-3*, into the disubstituted complexes *cis-6* and *trans-6*. Therefore, the complexes *cis-8* and *trans-8* can be prepared from the *cis-6* and *trans-6* species with two equivalents of CN^tBu.

Treatment of *cis-3* with one equivalent of PMe₃ under UV irradiation yields a mixture of the monosubstituted complex $[\{\text{Mo}_2(\text{CO})_3(\text{NO})_2(\text{PMe}_3)\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-5*, as the main product, the disubstituted complex $[\{\text{Mo}(\text{CO})(\text{NO})(\text{PMe}_3)\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-7* and the starting material. When the reaction was carried out in a 1:2 molar ratio, the same mixture was also obtained, but the disubstituted *cis-7* complex was the main product. Addition of an excess of PMe₃ led to a mixture of *cis-7* and *cis-5*, without starting material present. In all cases, *cis-7* and *cis-5* can be separated from the mixture by chromatography on florisil, *cis-5* being eluted with toluene and *cis-7* with dichloromethane.

The photochemical treatment of *trans-3* with two equivalent of PMe₃ yielded a mixture of mono- and disubstituted complexes *trans-5* and *trans-7*. Both complexes can be isolated from the mixture by chromatography on florisil. *Trans-7* was eluted with a mixture of toluene and dichloromethane and *trans-5* was obtained as the main product in THF.

The disubstituted complex *trans-7* can be prepared in high yield as a single product by slight warming of *trans-3* with two equiv of PMe₃. Under any of these

cm^{-1} and $1681\text{--}1566\text{ cm}^{-1}$ respectively, consistent with the presence of terminal carbonyl and nitrosyl groups. The molecular structure of *trans*-**8** determined by X-ray diffraction analysis shows a linear disposition of the nitrosyl groups although the observed $\nu(\text{NO})$ is 1566 cm^{-1} , lower than the $\nu(\text{NO})$ frequencies (1610 cm^{-1}) suggested in Ref. [17] as indicative of linear nitrosyl groups. This is an indication of the high electron density at the metal center. The $\nu(\text{CN})$ frequencies of the isocyanide ligands are in the range $2214\text{--}1922\text{ cm}^{-1}$. The IR spectra of *cis*-**8** and *trans*-**8** show two $\nu(\text{CN})$ bands at $2112\text{--}2102\text{ cm}^{-1}$ and $1966\text{--}1922\text{ cm}^{-1}$, which suggests that the isocyanide groups are coordinated in different modes. This behaviour is confirmed by the X-ray molecular structure which shows the presence of one linear and one bent isocyanide ligand on each molybdenum. It is important to note that the IR spectra can distinguish between linear and bent isocyanide groups both in the solid (Nujol mulls) and in solution, whereas by NMR spectroscopy only one signal for all the isocyanide groups is observed, even at low temperature.

The monosubstituted complexes *cis*-**4**, *cis*-**5** and *trans*-**5** are chiral due to the coordination of four different ligands to one of the metal centers (Mo(2) see Scheme 1) as confirmed by the NMR spectra which show the expected signals for asymmetric molecules. Thus, their ^1H NMR spectra (see Section 4) show four singlets for the protons of the bridging SiMe_2 groups and the cyclopentadienyl ring protons appear as two different ABC spin systems, one for each ring. The PMe_3 protons of *cis*-**5** and *trans*-**5** appear as doublets due to coupling with ^{31}P .

The molecular structure of *cis*-**5** was determined by X-ray diffraction and is shown in Fig. 2 along with the

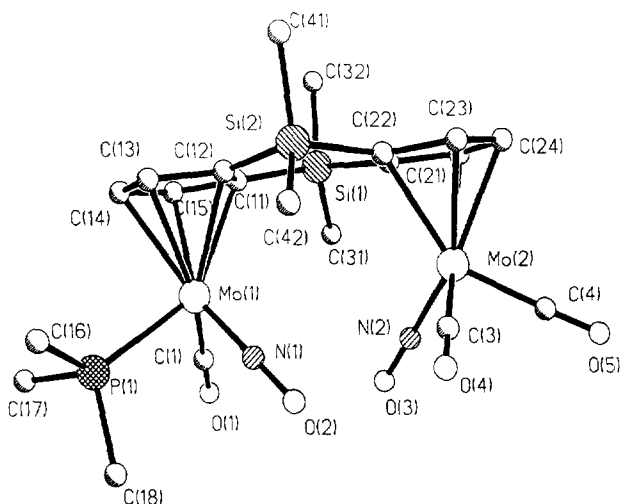


Fig. 2. Molecular structure and atom-labeling scheme for complex *cis*-**5**.

Table 2
Selected bond distances (Å) and bond angles (deg) for *cis*-**5**

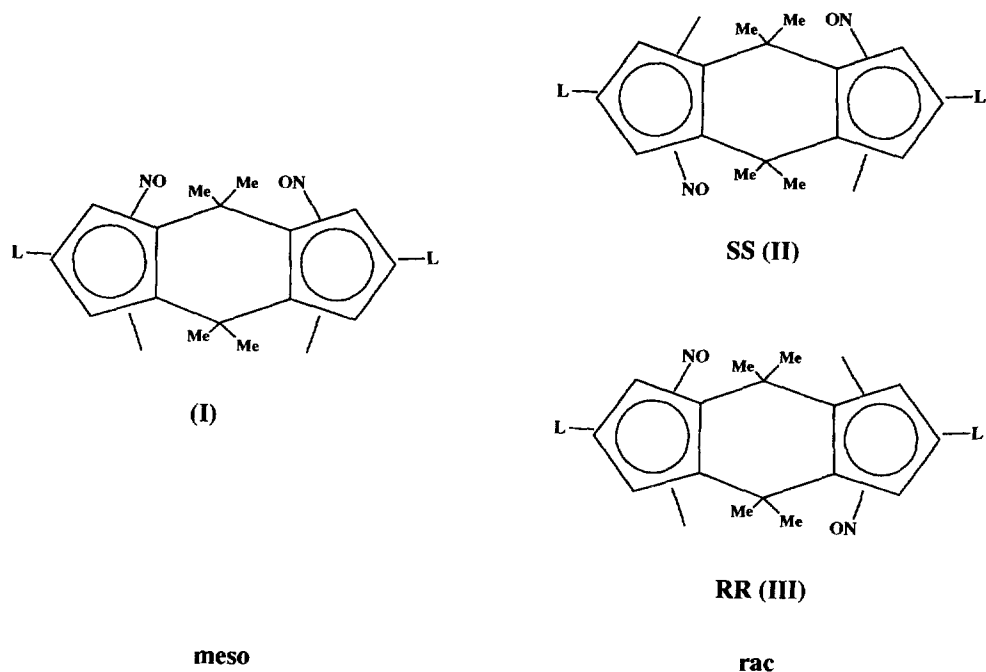
| Distances | | | |
|-------------------|-----------|-------------------|----------|
| Mo(1)–N(1) | 1.806(6) | Mo(1)–C(1) | 1.937(6) |
| Mo(1)–C(12) | 2.339(5) | Mo(1)–C(13) | 2.347(5) |
| Mo(1)–C(11) | 2.369(5) | Mo(1)–C(14) | 2.378(6) |
| Mo(1)–C(15) | 2.386(6) | Mo(1)–P(1) | 2.406(2) |
| Mo(2)–N(2) | 1.863(6) | Mo(2)–C(3) | 1.949(7) |
| Mo(2)–C(4) | 1.950(7) | Mo(2)–C(25) | 2.344(6) |
| Mo(2)–C(21) | 2.354(5) | Mo(2)–C(23) | 2.358(6) |
| Mo(2)–C(22) | 2.364(5) | Mo(2)–C(24) | 2.366(6) |
| Si(1)–C(31) | 1.852(6) | Si(1)–C(32) | 1.858(7) |
| Si(1)–C(11) | 1.862(6) | Si(1)–C(21) | 1.872(6) |
| P(1)–C(18) | 1.806(7) | P(1)–C(17) | 1.816(6) |
| P(1)–C(16) | 1.822(7) | Si(2)–C(42) | 1.845(8) |
| Si(2)–C(12) | 1.852(5) | Si(2)–C(22) | 1.863(6) |
| Si(2)–C(41) | 1.867(6) | N(1)–O(2) | 1.203(7) |
| O(1)–C(1) | 1.156(7) | O(3)–N(2) | 1.173(7) |
| O(4)–C(3) | 1.146(8) | O(5)–C(4) | 1.148(7) |
| C(11)–C(15) | 1.428(8) | C(11)–C(12) | 1.441(7) |
| C(12)–C(13) | 1.428(8) | C(13)–C(14) | 1.406(9) |
| C(14)–C(15) | 1.391(10) | C(21)–C(25) | 1.424(8) |
| C(21)–C(22) | 1.441(7) | C(22)–C(23) | 1.439(7) |
| C(23)–C(24) | 1.386(9) | C(24)–C(25) | 1.412(8) |
| Cp(1)–Mo(1) | 2.033 | Cp(2)–Mo(2) | 2.024 |
| Angles | | | |
| N(1)–Mo(1)–C(1) | 91.7(3) | N(1)–Mo(1)–P(1) | 88.7(2) |
| C(1)–Mo(1)–P(1) | 88.6(2) | N(2)–Mo(2)–C(3) | 91.0(3) |
| N(2)–Mo(2)–C(4) | 90.2(3) | C(3)–Mo(2)–C(4) | 89.5(3) |
| C(31)–Si(1)–C(32) | 109.0(3) | C(31)–Si(1)–C(11) | 113.0(3) |
| C(32)–Si(1)–C(11) | 108.6(3) | C(31)–Si(1)–C(21) | 113.4(3) |
| C(32)–Si(1)–C(21) | 106.2(3) | C(11)–Si(1)–C(21) | 106.4(2) |
| C(18)–P(1)–C(17) | 102.4(3) | C(18)–P(1)–C(16) | 102.2(4) |
| C(17)–P(1)–C(16) | 102.4(3) | C(18)–P(1)–Mo(1) | 114.1(2) |
| C(17)–P(1)–Mo(1) | 117.2(2) | C(16)–P(1)–Mo(1) | 116.4(2) |
| C(42)–Si(2)–C(12) | 113.1(3) | C(42)–Si(2)–C(22) | 113.4(3) |
| C(12)–Si(2)–C(22) | 106.7(2) | C(42)–Si(2)–C(41) | 108.8(4) |
| C(12)–Si(2)–C(41) | 107.7(3) | C(22)–Si(2)–C(41) | 106.8(3) |
| O(2)–N(1)–Mo(1) | 178.7(6) | O(1)–C(1)–Mo(1) | 178.4(7) |
| O(3)–N(2)–Mo(2) | 178.3(6) | O(4)–C(3)–Mo(2) | 177.9(6) |
| O(5)–C(4)–Mo(2) | 178.2(6) | C(1)–Mo(1)–Cp(1) | 122.9 |
| N(1)–Mo(1)–Cp(1) | 134.7 | P(1)–Mo(1)–Cp(1) | 117.6 |
| C(4)–Mo(2)–Cp(2) | 120.8 | C(3)–Mo(2)–Cp(2) | 124.1 |
| N(2)–Mo(2)–Cp(2) | 129.9 | | |

Cp(1) is the centroid of C(11)–C(15); Cp(2) is the centroid of C(21)–C(25).

labelling scheme employed. Selected bond distances and bond angles are given in Table 2.

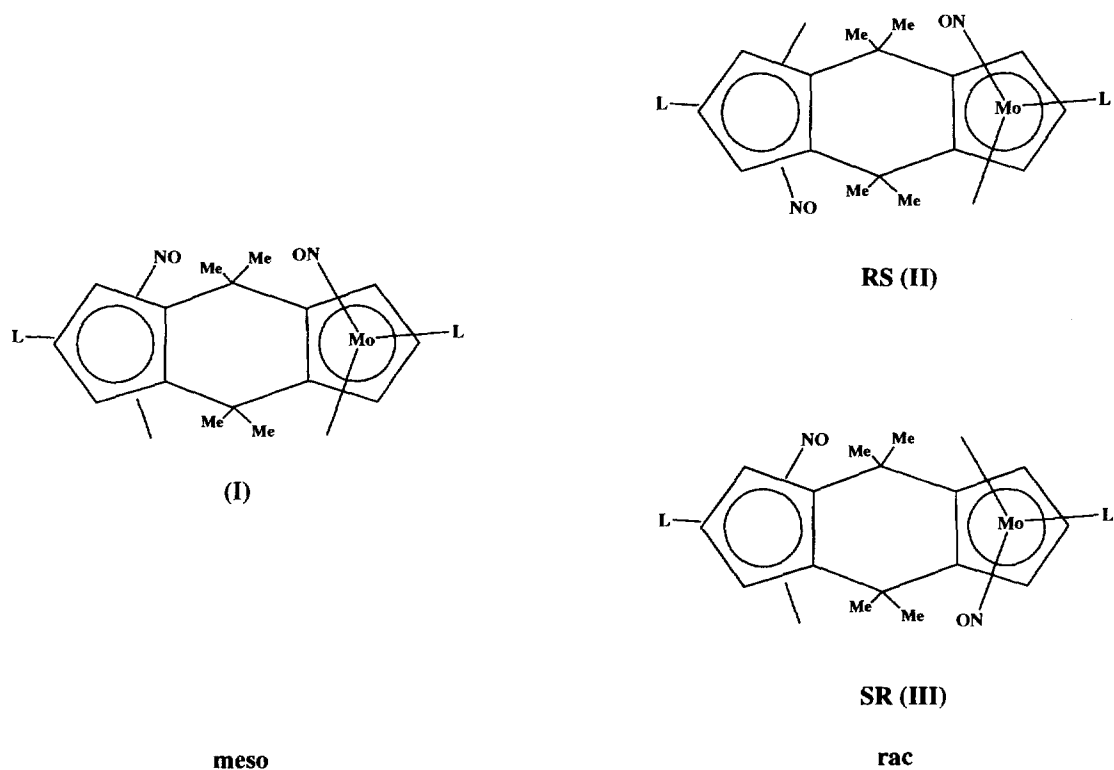
The molecular structure of *cis*-**5** is similar to that of *cis*-**3** previously described, but with one of the CO groups substituted by a PMe_3 group. This substitution does not affect the rest of the molecule which shows the same *trans* disposition of the two NO groups. All CO and NO groups are linear and the C–O, N–O, C–C and P–C distances are in the normal range. The Mo(1)–Mo(2) distance is $4.926(1)\text{ Å}$ slightly shorter than that observed in *cis*-**3**.

Complexes *cis*-**6**, *trans*-**6**, *cis*-**7** and *trans*-**7** have two asymmetric metal centers bonded to four different

Scheme 3. Stereoisomers for complexes *cis*-6 ($L = \text{CN}^t\text{Bu}$) and *cis*-7 ($L = \text{PMe}_3$).

ligands giving rise to a *meso* structure and a racemic mixture of enantiomers. NMR spectroscopy shows that the four methyl groups of the bridging SiMe_2 fragment for the *meso* isomer are not equivalent and give four singlets, whereas the racemic mixture of RR and SS

enantiomers for *cis*-compounds shows two singlets for the two pairs of equivalent methyl groups (Scheme 3). Similar stereoisomers are also present for the *trans* compounds (Scheme 4) for which both show two pairs of equivalent methyl groups giving two singlets. The

Scheme 4. Stereoisomers for complexes *trans*-6 ($L = \text{CN}^t\text{Bu}$) and *trans*-7 ($L = \text{PMe}_3$).

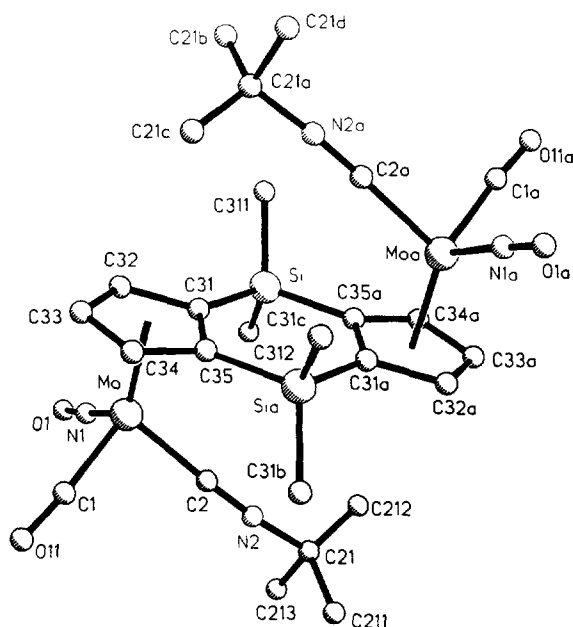


Fig. 3. Molecular structure and atom-labeling scheme for complex *trans-6*.

cyclopentadienyl groups are equivalent in all the complexes and their protons correspond to an ABC spin system.

The two diastereoisomers of the *cis* compounds are in a different molar ratio, probably imposed by the nature of the substituents. The racemic mixture is the main species for complex *cis-6* (1.2:1) whereas it is the minor component for *cis-7* (1:1.35). This fact is only observed for one of the *trans* derivatives, the complex *trans-7*.

The molecular structure of *trans-6* was determined by X-ray diffraction studies and is shown in Fig. 3 with the labelling scheme employed. Selected bond distances and angles are presented in Table 3. The poor quality of this crystal precluded a precise refinement. The molecular structure of *trans-6* comprises in two asymmetric halves bonded together and related by a center of symmetry. The CO, NO and CNR groups are linear with M–C–O, M–N–O and C(1)–N(1)–C(21) angles of 175(3)°, 176(2)° and 175(3)°.

The molecular structure of *trans-8* · 2C₆H₅Me determined by X-ray diffraction structural analysis is shown in Fig. 4 along with the numbering scheme employed. Relevant bond distances and angles are given in Table 4.

The asymmetric unit of the unit cell contains only one half of the molecule. The complete molecule is constructed through a center of symmetry located at the center of the [(C₅H₃)₂(SiMe₂)₂]₂ system. Each molybde-

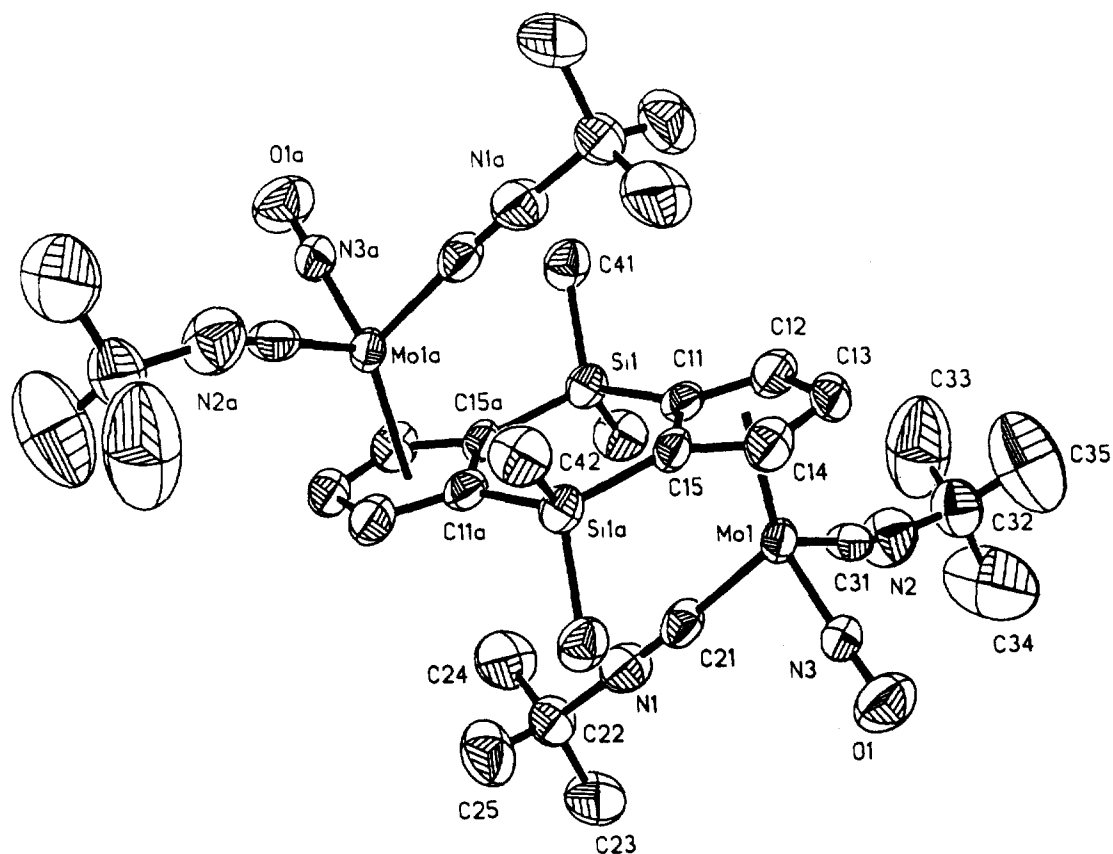


Fig. 4. Molecular structure and atom-labeling scheme for complex *trans-8*.

num atom has a 'three-legged piano stool' configuration with pentahapto-coordinated cyclopentadienyl rings. The angles around molybdenum between the centroid of the cyclopentadienyl ring taken as a coordination site and the legs range from 119.3° to 126.5° and the angles between contiguous legs range from $89.0(4)^\circ$ to $96.3(4)^\circ$. The NO ligand has a linear arrangement with an Mo–N–O angle of $172.1(8)^\circ$. There are two different isocyanide ligands according to the C–N–C angles, $177.7(11)^\circ$ for C(21)–N(1)–C(22) and $154.1(3)^\circ$ for C(31)–N(2)–C(32), typical for related complexes with a similar coordination of isocyanide ligands, such as $\text{Co}_2(\text{CN}^t\text{Bu})_8$ [18] and $\text{Mo}(\text{CNMe})_2(\text{dpe})_2$ [19].

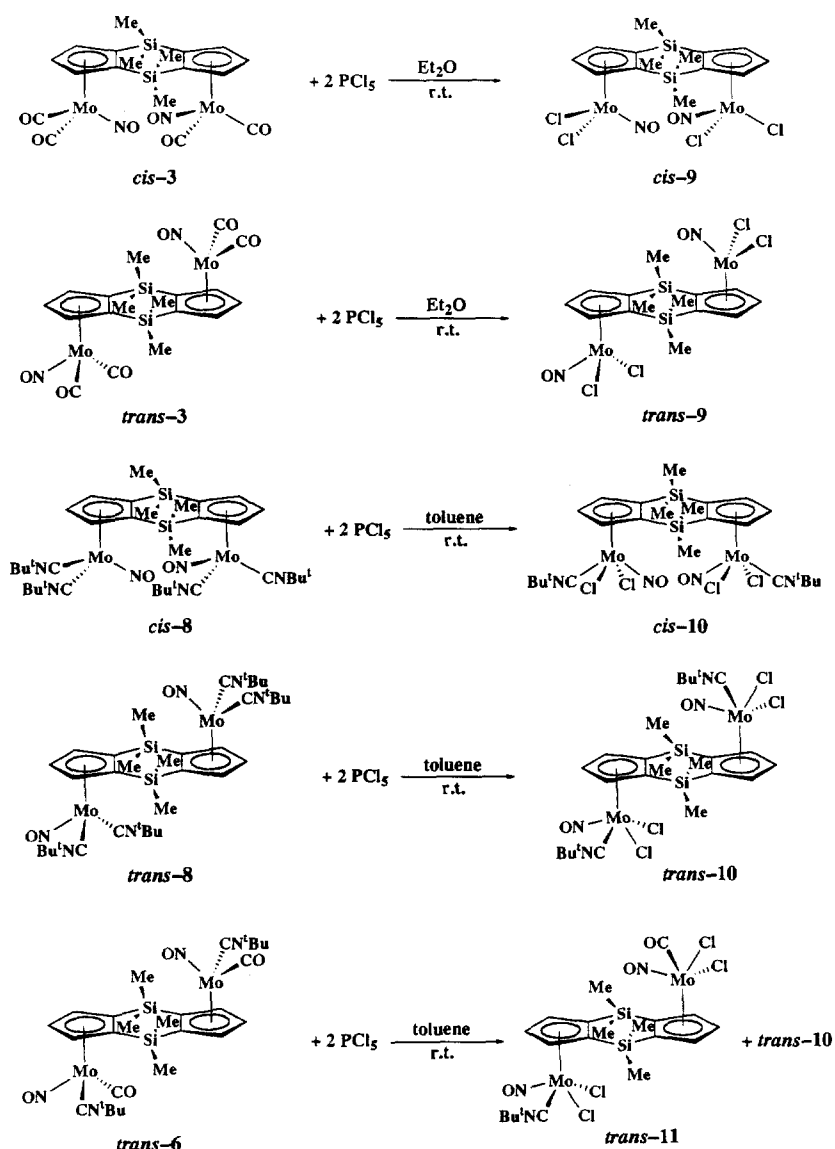
2.3. Oxidation with PCl_5

As shown in Scheme 5, treatment of *cis*-3 and *trans*-3 with PCl_5 as chlorinating agent afforded the

dihalonitrosyl complexes $[\{\text{Mo}(\text{NO})\text{Cl}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis*-9 and *trans*-9 with elimination of CO, in a reaction similar to that used for oxidizing $[\text{MoCp}(\text{CO})_2(\text{NO})]$ (Cp = C_5H_5 , C_5Me_5) [20] and $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_4)_2\text{SiMe}_2\}]$ [3].

These dihalonitrosyl complexes are red solids, slightly soluble in common polar organic solvents such as THF and diethyl ether, *cis*-9 being completely soluble in acetone and dichloromethane.

It has been reported [20] that $[\text{MCp}(\text{NO})\text{X}_2]$ derivatives (Cp = C_5H_5 , C_5Me_5 ; M = Mo, W; X = Cl, I) can exist as green monomeric 16 electron and red dimeric 18 electron systems with two halide bridges. Accordingly, the red colour of solid *cis*-9 and *trans*-9 is probably due to the presence of chloride bridges which must be intermolecular for *trans*-9. The green colour of this complex in ethyl ether solution suggests the formation of an 18 electron species by coordination of the



Scheme 5.

Table 3
Selected bond distances (Å) and bond angles (deg) for *trans*-6

| Distances | | | |
|---------------------------------|-----------|--------------------------------|----------|
| Mo(1)–N(2) | 1.86(3) | Mo(1)–C(2) | 1.89(3) |
| Mo(1)–C(1) | 2.06(2) | Mo(1)–C(11) | 2.36(3) |
| Mo(1)–C(13) | 2.39(3) | Mo(1)–C(15) | 2.33(3) |
| Mo(1)–C(14) | 2.41(3) | Mo(1)–C(12) | 2.40(3) |
| Si(2)–C(12) | 1.85(3) | Si(2)–C(32) | 1.89(3) |
| Si(2)–C(11) ^a | 1.82(3) | Si(2)–C(31) | 1.85(4) |
| C(1)–N(1) | 1.22(3) | N(1)–C(21) | 1.40(3) |
| C(15)–C(14) | 1.38(4) | C(15)–C(11) | 1.47(3) |
| C(12)–C(13) | 1.43(4) | C(12)–C(11) | 1.53(4) |
| C(11)–Si(2) ^a | 1.82(3) | C(2)–O(2) | 113(3) |
| N(2)–O(1) | 1.19(3) | C(13)–C(14) | 1.44(4) |
| C(21)–C(24) | 1.44(6) | C(21)–C(23) | 1.42(5) |
| C(21)–C(22) | 1.42(6) | Mo(1)–Cp(1) | 2.034 |
| Angles | | | |
| N(2)–Mo(1)–C(2) | 91.5(13) | N(2)–Mo(1)–C(1) | 92.5(10) |
| C(2)–Mo(1)–C(1) | 93.4(10) | C(12)–Si(2)–C(32) | 107(2) |
| C(12)–Si(2)–C(11) ^a | 106.2(13) | C(32)–Si(2)–C(11) ^a | 112(2) |
| C(12)–Si(2)–C(31) | 115(2) | C(32)–Si(2)–C(31) | 107(2) |
| C(11) ^a –Si(2)–C(31) | 110(2) | N(1)–C(1)–Mo(1) | 173(2) |
| C(1)–N(1)–C(21) | 175(3) | O(2)–C(2)–Mo(1) | 176(3) |
| O(1)–N(2)–Mo(1) | 177(2) | N(2)–Mo(1)–Cp(1) | 125.1 |
| C(2)–Mo(1)–Cp(1) | 124.4 | C(1)–Mo(1)–Cp(1) | 121.1 |

Cp(1) is the centroid of C(11)–C(15).

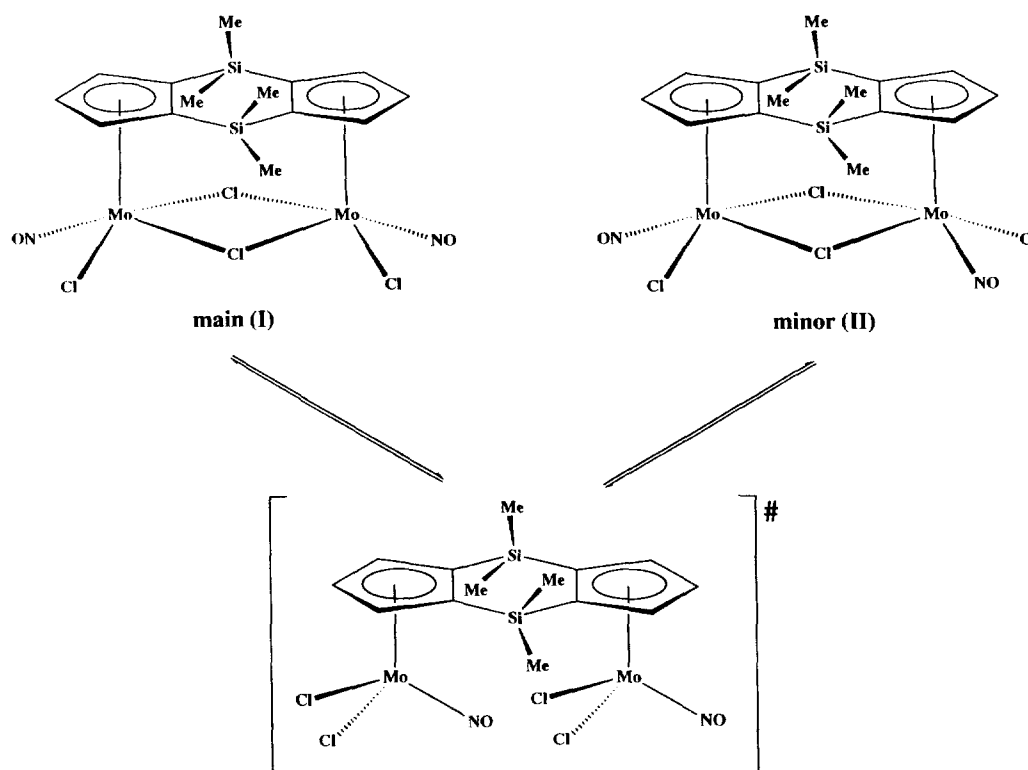
^aSymmetry transformations used to generate equivalent atoms: 1 – x, – y, – z.

Table 4
Selected bond distances (Å) and bond angles (deg) for *trans*-8

| Distances | | | |
|-------------------|-----------|--------------------------|-----------|
| Mo(1)–N(3) | 1.771(9) | Mo(1)–C(21) | 2.046(11) |
| Mo(1)–C(31) | 2.022(12) | Mo(1)–C(11) | 2.386(9) |
| Mo(1)–C(12) | 2.382(11) | Mo(1)–C(13) | 2.366(10) |
| Mo(1)–C(14) | 2.322(10) | Mo(1)–C(15) | 2.342(9) |
| Si(1)–C(11) | 1.873(10) | Si(1)–C(15) ^a | 1.853(10) |
| Si(1)–C(41) | 1.859(11) | Si(1)–C(42) | 1.865(10) |
| C(11)–C(12) | 1.369(14) | C(12)–C(13) | 1.42(2) |
| C(13)–C(14) | 1.38(2) | C(14)–C(15) | 1.444(13) |
| C(11)–C(15) | 1.464(14) | N(3)–O(1) | 1.219(10) |
| N(2)–C(31) | 1.176(14) | N(1)–C(21) | 1.160(13) |
| N(2)–C(32) | 1.45(2) | N(1)–C(22) | 1.471(14) |
| C(32)–C(33) | 1.47(2) | C(22)–C(23) | 1.49(2) |
| C(32)–C(34) | 1.47(2) | C(22)–C(24) | 1.51(2) |
| C(32)–C(35) | 1.46(2) | C(22)–C(25) | 1.49(2) |
| Mo(1)–Cp(1) | 2.030 | | |
| Angles | | | |
| O(1)–N(3)–Mo(1) | 172.1(8) | N(1)–C(21)–Mo(1) | 175.6(9) |
| N(2)–C(31)–Mo(1) | 176.3(10) | Cp(1)–Mo(1)–N(3) | 126.5 |
| Cp(1)–Mo(1)–C(21) | 123.2 | Cp(1)–Mo(1)–C(31) | 119.3 |
| N(3)–Mo(1)–C(31) | 96.3(4) | N(3)–Mo(1)–C(21) | 93.4(4) |
| C(31)–Mo(1)–C(21) | 89.0(4) | C(21)–N(1)–C(22) | 177.7(11) |
| C(31)–N(2)–C(22) | 154.1(13) | | |

Cp(1) is the centroid of C(11)–C(15).

^aSymmetry transformations used to generate equivalent atoms: – x + 1, – y + 1, – z.



Scheme 6. Mechanism of isomerization between stereoisomers I–II. $E_a(\text{Mo–Cl}) = 31.35 \text{ kJ mol}^{-1}$.

solvent, while *cis*-**9** gives red solutions, even upon heating which seem indicate the presence of intramolecular chloride bridges, as evidenced by ^1H NMR spectroscopy. *cis*-**9** shows a dynamic behaviour in solution; the ^1H NMR spectrum at room temperature in CDCl_3 shows two groups of broad signals at δ 6.45 and δ 0.68 ppm. When the solution is heated to 58°C , the spectrum shows two signals due to the cyclopentadienyl ring protons at δ 6.6 (4H, broad signal) and δ 6.2 (2H) and two signals for the methyl groups of the SiMe_2 bridges at δ 0.7 ppm (6H, broad signal) and δ 0.5 ppm (6H). This transformation is reversible because the initial spectrum is restored when the solution is cooled down to room temperature. The ^1H NMR spectrum in CD_2Cl_2 at -80°C shows two groups of signals between δ 6.2 and δ 6.5 for the cyclopentadienyl ring protons, each group being characterized by three resonances, with an intensity ratio 3.3:1 consistent with an ABC spin system for two equivalent cyclopentadienyl rings, indicating that the two metal centers have the same environment. The methyl groups of the SiMe_2 bridges appear as six resonances, four due to the main species (I) and two for the minor component (II) shown in Scheme 6. This spectral behaviour is consistent with

the presence of two isomers and can be explained assuming that a double intramolecular chloride bridge is formed between the two metal centers at low temperature.

In order to determine the thermodynamic and kinetic parameters, we studied the isomerization process recording the ^1H NMR spectra at different temperatures. The spin saturation transfer method (SST) [21] allowed us to assign the three resonances observed in the ^1H NMR spectrum at 223 K, starred (\blacklozenge) in Fig. 5, to the methyl-silyl groups located below the plane of the cyclopentadienyl rings and the other three to the methyl-silyl groups located above the plane. All of these signals broaden as the temperature increases to give two broad resonances at 328 K. The kinetic parameters evaluated calculating the life time values ($\tau = 1/\pi K$, where K is the rate constant) by line form analysis were: $\log A = 13.4 \pm 0.3$; $E_a = 63.9 \pm 2.1$ kJ mol $^{-1}$; $\Delta H^\ddagger = 61.8 \pm 2.1$ kJ mol $^{-1}$; $\Delta S^\ddagger = 0.6 \pm 0.9$ u.e. and $\Delta G_{298\text{ K}}^\ddagger = 62.7$ kJ mol $^{-1}$. The value of $\log A$ indicates that the isomerization is an intramolecular and energetically favourable process and the very small value of ΔS^\ddagger means that the fundamental and the transition states are of the same order. The transition

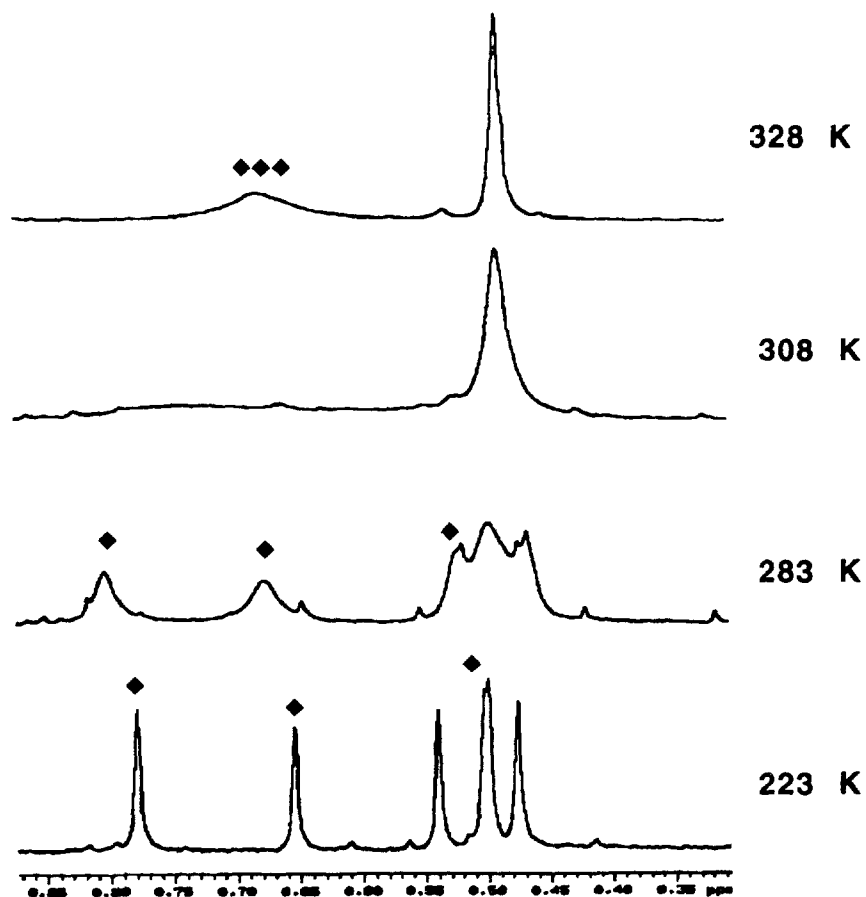


Fig. 5. ^1H NMR variable temperature spectra of *cis*-**9**. SiMe_2 resonances: \blacklozenge = Me groups below the plane.

state corresponds to the cleavage of two Mo–Cl bridging bonds. Therefore, the activation energy for the cleavage of one Mo–Cl bridge is 31.35 kJ mol⁻¹.

Reaction of *cis-8* with two equivalents of PCl₅ gave the dichloroderivative $[\{\text{Mo}(\text{NO})(\text{CN}^t\text{Bu})\text{Cl}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis-10*) in high yield (see Scheme 5). This complex was obtained as a mixture of isomers as discussed below. The related reaction carried out with *trans-8* led to *trans-10*. In contrast, when the same reaction was carried out with *trans-6*, a mixture of *trans-10* and $[\{\text{Mo}_2(\text{CO})(\text{NO})_2(\text{CN}^t\text{Bu})\text{Cl}_4\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*trans-11*) was obtained. Both compounds are highly insoluble in most organic solvents and only slightly soluble in dichloromethane. It was not possible to separate these compounds by chromatography or by recrystallization.

The dichloroderivative *trans-10* shows a ¹H NMR spectrum similar to that observed for the chiral complexes described above. This behaviour is consistent with a *cis* disposition of the chloro substituents. Similar behaviour was observed for *trans-11* but its ¹H NMR spectrum showed twice as many signals due to the asymmetry of the molecule.

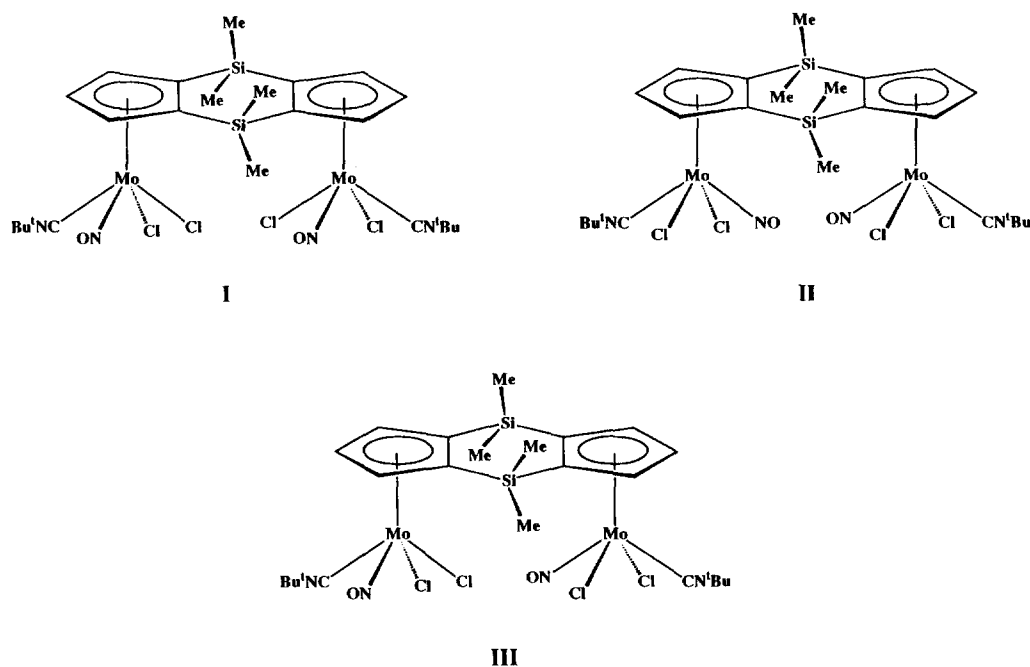
The ¹H NMR spectrum of *cis-10* shows the signals due to three different isomers according to the relative disposition of the two chloro ligands (Scheme 7).

2.4. Comparison of the X-ray molecular structures

Only *trans-8* has one of the four known previously reported structures for complexes of the type

$[\{\text{MLn}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [22]. Fig. 6 shows the diagrammatic representation used by Corey et al. [22] including the four previously reported structural types (I, II, IV, V) and the two new types (III, VI) found for complexes described in this paper. *Trans-8* exhibits the known *trans-II* structure where the central six-membered ring is planar and its angle with the Cp ring planes is 0.7(2)°, the most planar system described to date. Other similar systems previously reported are *trans*- $[\{\text{TiCl}_3\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [4] where this angle is 4(2)°, *trans*- $[\{\text{Mo}(\text{CO})_3\text{Cl}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [5] with a value of 7.8(5)° and *trans*- $[\{\text{TiCp}^*\text{Cl}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [22] where the angle is 9°. However *trans-6* adopts a new structural form corresponding to type III in which the two Cp rings are almost exactly coplanar whereas the central six-membered ring shows a chair conformation with one of the silicon atoms located 0.20 Å over and the other 0.20 Å below the plane.

Both *cis-3* and *cis-5* are also the first examples of the new structural form *cis-VI*. In this structure the two Cp rings are also coplanar, whereas the central six-membered ring shows the two silicon atoms located above the plane at 0.3 Å for *cis-3* and 0.25 Å for *cis-5* in contrast to the arrangement found in other *cis*-dinuclear complexes in which the planes of the two cyclopentadienyl rings make an angle of 23° for *cis*- $[\{\text{Co}(\text{CO})_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [23], 30° for *cis*- $[\{\text{Mo}(\text{CO})_3\text{Cl}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [5] and 50° for *cis*- $[\{\text{TiCp}^*\text{Cl}_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ [22]. The distances between the two metal atoms, 4.962(1) Å for



Scheme 7. Stereoisomers for complex *cis-10*.

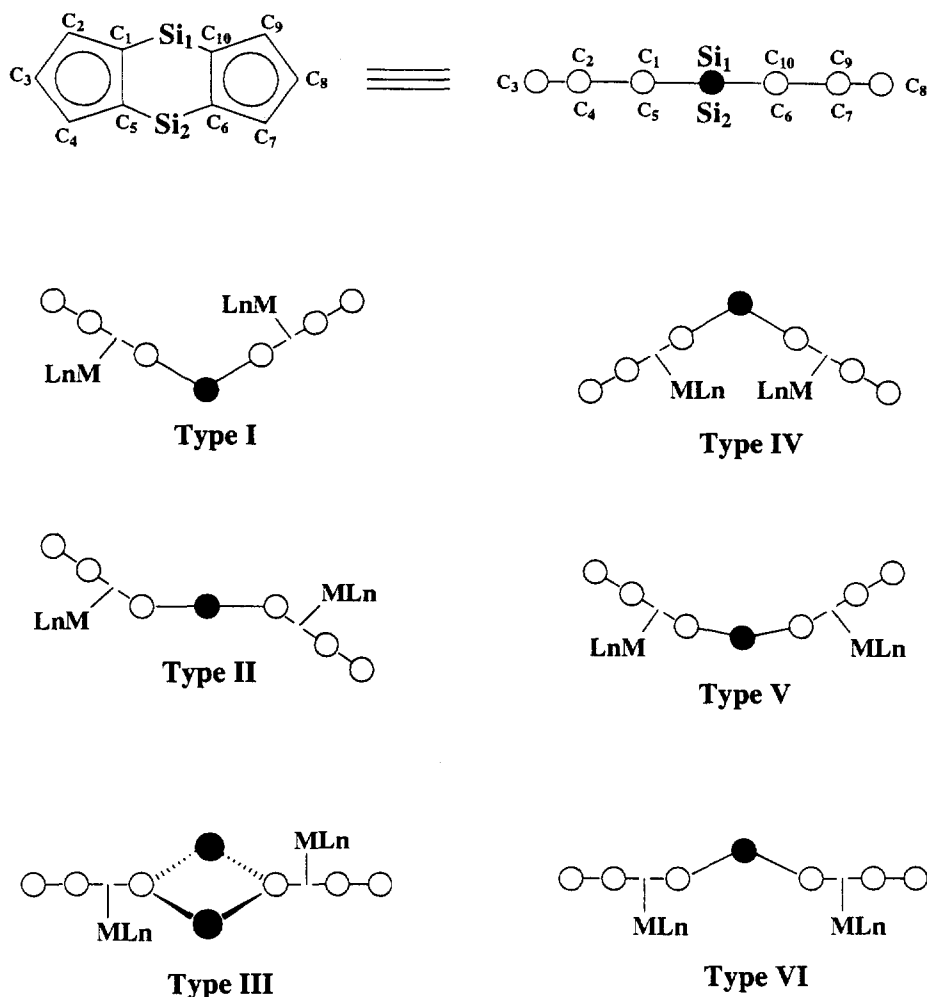


Fig. 6. Diagrammatic representations of the structural types for MLM complexes ($L = \{(\text{SiMe}_2)_2(\eta^5\text{-C}_5\text{H}_3)_2\}$).

cis-3 and 4.926(1) Å for *cis*-5, are in the range reported for *cis*- $\{[\text{Co}(\text{CO})_2]_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$, 4.25 Å in spite of the presence of the bulkier $\text{Mo}(\text{CO})_2(\text{NO})$ fragments without any metal–metal interaction.

3. Conclusions

Reactions of the previously reported dinuclear molybdenum hydridotricarbonyl and carbonylate complexes containing the bridging bis(dimethylsilanediyl)dicyclopentadienyl ligand with diazald lead to the new nitrosyl derivatives *cis*- and *trans*- $\{[\text{Mo}(\text{CO})_2(\text{NO})]_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$. Substitution of CO by appropriate stoichiometric amounts of $\text{CN}(\text{tert-Bu})$ takes place to give mono-, di- and tetra-substituted compounds *cis*- and *trans*- $\{[\text{Mo}_2(\text{CO})_{4-n}\text{L}_n(\text{NO})_2]\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$ ($n = 1, 2, 4$) at room temperature or by heating in toluene to 60–80°C, whereas for similar complexes with PMe_3

only take place under UV irradiation or slight thermal treatment. Oxidation of all these compounds with PCl_5 afforded the 16 electron complexes *cis*- and *trans*- $\{[\text{Mo}(\text{NO})\text{Cl}_2]_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$ whereas 18 electron derivatives *cis*- and *trans*- $\{[\text{MoL}(\text{NO})\text{Cl}_2]_2\{\mu\text{-}(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}$ were obtained when isocyanide was present as ligand. The dynamic behavior of the 16 electron *cis*- complex has been studied by ^1H D NMR spectroscopy, and thermodynamic and kinetic parameters for the 16 to 18 electron system transformation were determined giving an activation energy of 31.3 kJ mol⁻¹ for the intramolecular metal–chlorine bridging bond dissociation. The NO ligand is coordinated as a linear group in all the complexes whereas the isocyanide ligand adopts a linear disposition in the mono- and disubstituted complexes but a bent disposition for one of the isocyanide ligands bonded to each molybdenum in the tetrasubstituted compounds. All of the new nitrosyl complexes reported were characterized by elemental analysis, mass spectrometry and ^1H , ^{13}C and ^{31}P

NMR spectroscopy, which also shows the presence of chiral metal centers in all the asymmetric molecules. The molecular structures of two *cis*- and two *trans*-complexes were determined by X-ray diffraction. Both *cis* complexes $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-3* and $[\{\text{Mo}_2(\text{CO})_3(\text{NO})_2(\text{PMe}_3)\}\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *cis-5* show unprecedented structures with almost exactly coplanar cyclopentadienyl rings and distances between the non-bonded metal fragments of ca. 4.9 Å, shorter than in any other related dinuclear *cis*-complex. $[\{\text{Mo}(\text{CO})(\text{NO})(\text{CN}^i\text{Bu})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *trans-6* is also the first example of a dinuclear *trans* complex exhibiting an exactly planar disposition of the two cyclopentadienyl rings with a chair conformation of the six-membered central ring, whereas $[\{\text{Mo}(\text{NO})(\text{CN}^i\text{Bu})_2\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ *trans-8* shows the structure already reported for other similar compounds.

4. Experimental details

All reactions were carried out in dried Schlenk tubes under argon or nitrogen, and the manipulations were carried out using syringes or cannulas through Sub-seals. Solvents were dried and distilled under nitrogen: diethyl ether and tetrahydrofuran from sodium benzophenone ketyl; hexane from sodium and potassium amalgam; toluene from sodium; dichloromethane from P_2O_5 . Unless otherwise stated, reagents were obtained from commercial sources and used as received. IR spectra were recorded in Nujol mulls for solids over the range 4000–200 cm^{-1} on a Perkin-Elmer 583 spectrophotometer. IR data are given in cm^{-1} . The ^1H and ^{13}C NMR spectra were recorded at 299.95 and 75.43 MHz respectively on a Varian Unity 300 spectrometer and at 499.85 and 125.7 MHz on a Varian Unity 500 Plus spectrometer; chemical shifts, in ppm, are positive down field relative to external SiMe_4 , and coupling constants are in Hz. C, H and N analyses were performed with a Perkin-Elmer 240-B instrument. Mass spectra were recorded with a Hewlett-Packard 5988A spectrometer.

The compounds *cis*- $[\{\text{Mo}(\text{CO})_3\text{H}\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis-1*) and *trans*- $\text{K}_2[\{\text{Mo}(\text{CO})_3\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*trans-2*) were prepared as reported previously, i.e., from reaction of $[\text{Mo}(\text{I},3,5\text{-C}_6\text{H}_3\text{Me}_3)(\text{CO})_3]$ with $[(\text{C}_5\text{H}_4)_2(\text{SiMe}_2)_2]$ or $\text{K}_2[(\text{C}_5\text{H}_3)_2(\text{SiMe}_2)_2]$, respectively.

4.1. Preparation of *cis*- $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis-3*)

The complex *cis-1* (0.96 g, 1.59 mmol) and *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{NO})\text{CH}_3$ (diazald) (0.68 g, 3.18 mmol)

were dissolved in THF (50 ml). The solution was stirred at room temperature for 2 h. The initial orange solution became brown and solvent was removed in vacuo. The brown oil obtained was dissolved in toluene (10 ml) and filtered through a short florisil column. The filtrate was evaporated in vacuo to give an orange oil. Complex *cis-3* was isolated as an orange solid (0.70 g, 72%) by crystallization of the oil from hexane at room temperature. Anal. Found: C, 35.68; H, 2.89; N, 4.88%. $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Si}_2\text{N}_2\text{Mo}_2$. Calc. C, 35.65; H, 2.99; N, 4.62%. IR (Nujol): $\nu(\text{CO}) = 2020\text{vs}, 1942\text{s}$; $\nu(\text{NO}) = 1680\text{vs}, 1642\text{s}$. ^1H NMR (500 MHz; C_6D_6 ; 20°C): $\delta = 5.02$ (1H, C_5H_3 , $^3J(\text{HH}) = 2.5$), 4.94 (2H, C_5H_3), 0.38 (s, 3H, SiMe_2), 0.10 (s, 3H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz; C_6D_6 ; 20°C): $\delta = 227.05$ (CO), 108.03 (C_5H_3 α to the SiMe_2 bridges), 100.81 (C_5H_3 γ to the SiMe_2 bridges), 98.93 (C_5H_3 β to the SiMe_2 bridges), 3.54 (SiMe_2), 1.23 (SiMe_2).

4.2. Preparation of *trans*- $[\{\text{Mo}(\text{CO})_2(\text{NO})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*trans-3*)

A mixture of *trans-2* (3.2 g, 4.7 mmol) and diazald (2.01 g, 9.4 mmol) was stirred for 2 h in THF (25 ml) at room temperature. Carbon monoxide was evolved and a white precipitate appeared. The solid was filtered off and the solution was evaporated in vacuo to give a brown oil. This oil was dissolved in toluene and filtered through a short florisil column. The solvent was removed in vacuo. Complex *trans-3* was obtained as an orange solid (1.91 g, 67%). Anal. Found: C, 35.63; H, 3.23; N, 4.32%. $\text{C}_{18}\text{H}_{18}\text{O}_6\text{Si}_2\text{N}_2\text{Mo}_2$. Calc. C, 35.65; H, 2.99; N, 4.62%. IR (Nujol): $\nu(\text{CO}) = 2016\text{vs}, 1944\text{vs}$; $\nu(\text{NO}) = 1678\text{vs}$. ^1H NMR (300 MHz; C_6D_6 ; 20°C): $\delta = 5.25$ (2H, C_5H_3 , $^3J(\text{HH}) = 2.5$), 4.83 (1H, C_5H_3), 0.22 (s, 6H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz; C_6D_6 ; 20°C): $\delta = 227.19$ (CO), 108.21 (C_5H_3 α to the SiMe_2 bridges), 103.64 (C_5H_3 β to the SiMe_2 bridges), 96.48 (C_5H_3 γ to the SiMe_2 bridges), 2.41 (SiMe_2).

4.3. Preparation of *cis*- $[\{\text{Mo}_2(\text{CO})_3(\text{NO})_2(\text{CN}^i\text{Bu})\}_2\{\mu-(\eta^5\text{-C}_5\text{H}_3)_2(\text{SiMe}_2)_2\}]$ (*cis-4*)

The complex *cis-3* (0.5 g, 0.82 mmol) was dissolved in toluene (25 ml) and CN^iBu (95 μl , 0.82 mmol) was added. The solution was stirred for 7 h at room temperature and then the solvent removed in vacuo to give an orange solid which was a mixture of complexes *cis-4* and *cis-6*. The filtrate was partially evaporated and cooled to -40°C overnight giving more orange solid.

Cis-4 (0.38 g, 73%) was separated by chromatography on florisil using CH_2Cl_2 as eluent and *cis-6* with THF. Anal. Found: C, 41.28; H, 4.39; N, 6.17%. $\text{C}_{22}\text{H}_{27}\text{O}_5\text{Si}_2\text{N}_3\text{Mo}_2$. Calc. C, 39.94; H, 4.11; N, 6.35%. IR (Nujol; (1) and (2) referred to Mo(1) and

Mo(2), see Scheme 1): $\nu(\text{CN}^t\text{Bu}) = 2151\text{s}$; $\nu(\text{CO}(1)) = 2011\text{vs}$, 1938vs ; $\nu(\text{CO}(2)) = 1914\text{vs}$; $\nu(\text{NO}(1)) = 1675\text{s}$; $\nu(\text{NO}(2)) = 1628\text{vs}$, 1611vs . ^1H NMR (500 MHz; C_6D_6 ; 20°C): $\delta = 5.26$, 5.19 , 5.36 (A', B' and C' parts of an A'B'C' spin system, 3H, C_5H_3 , $^3J(\text{A'B}') = 2.5$, $^4J(\text{B'C}') = 1.5$), 5.11 , 5.01 , 5.08 (A, B and C parts of an ABC spin system, 3H, C_5H_3 , $^3J(\text{AB}) = 2.5$, $^4J(\text{BC}) = 1.25$), 0.93 (s, 9H, CNCMe_3), 0.51 (s, 3H, SiMe_2), 0.49 (s, 3H, SiMe_2), 0.24 (s, 3H, SiMe_2), 0.20 (s, 3H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz; C_6D_6 ; 20°C): (1) and (2) referred to Mo(1) and Mo(2), see Scheme 1): $\delta = 238.53$ (CO(2)), 227.78 (CO(1)), 227.21 (CO(1)), 167.55 (CN^tBu), 110.06 , 108.17 , 105.46 , 103.67 (C_5H_3 α to the SiMe_2 bridges), 101.15 , 100.70 , 100.13 , 99.67 , 97.94 , 96.80 (C_5H_3 β and γ to the SiMe_2 bridges), 57.86 (CNCMe_3), 30.18 (CNCMe_3), 3.98 , 3.92 , 1.71 , 1.32 (SiMe_2).

4.4. Preparation of $\text{cis}-\{[\text{Mo}(\text{CO})(\text{NO})(\text{CN}^t\text{Bu})]_2\}[\mu-(\eta^5-\text{C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\}$ (cis-6)

CN^tBu (186 μl , 1.64 mmol) was added to an orange solution of cis-3 (0.50 g, 0.82 mmol) in toluene (25 ml), with a microsyringe. The solution was stirred at room temperature for 7 h and the solvent removed in vacuo. The residue was washed with hexane giving an orange solid (cis-6). The filtrate was partially evaporated and cooled to -40°C overnight to give cis-6 (0.49 g, 85%). Anal. Found: C, 42.46; H, 5.49; N, 7.05%. $\text{C}_{26}\text{H}_{36}\text{O}_4\text{Si}_2\text{N}_4\text{Mo}_2$. Calc. C, 43.58; H, 5.06; N, 7.82%. IR (Nujol): $\nu(\text{CN}^t\text{Bu}) = 2134\text{s}$; $\nu(\text{CO}) = 1902\text{s}$; $\nu(\text{NO}) = 1620\text{s}$. ^1H NMR (500 MHz; C_6D_6 ; 20°C ; I and III see Scheme 3): $\delta = 5.25$, 5.54 , 5.19 (III, A, B and C parts of an ABC spin system, 6H, C_5H_3 , $^3J(\text{A-B}) = 2.73$, $^4J(\text{B-C}) = 1.42$), 5.36 , 5.50 , 5.30 (I, A, B and C parts of an ABC spin system, 6H, C_5H_3 , $^3J(\text{A-B}) = 2.73$, $^4J(\text{B-C}) = 1.44$), 0.99 (s, I and III, 36H, CNCMe_3), 0.65 (s, I, 3H, SiMe_2), 0.60 (s, III, 6H, SiMe_2), 0.54 (s, I, 3H, SiMe_2), 0.35 (s, I and III, 9H, SiMe_2), 0.28 (s, I, 3H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz; C_6D_6 ; 20°C ; I and III see Scheme 3): $\delta = 240.07$ (CO, III), 238.72 (CO, I), 106.35 , 105.41 (I, C_5H_3 α to the SiMe_2 bridges), 107.45 , 103.57 (III, C_5H_3 α to the SiMe_2 bridges), 100.69 , 100.38 (I, C_5H_3 β to the SiMe_2 bridges), 103.08 , 99.63 (III, C_5H_3 β to the SiMe_2 bridges), 98.20 (I, C_5H_3 γ to the SiMe_2 bridges), 95.42 (III, C_5H_3 γ to the SiMe_2 bridges), 57.97 (I, CNCMe_3), 57.79 (III, CNCMe_3), 30.42 (I, CNCMe_3), 30.37 (III, CNCMe_3), CNCMe_3 not observed, 4.38 , 4.33 , 2.88 , 2.11 (I, SiMe_2), 4.63 , 1.76 (III, SiMe_2).

4.5. Preparation of $\text{cis}-\{[\text{Mo}_2(\text{CO})_3(\text{NO})(\text{PMe}_3)]\}[\mu-(\eta^5-\text{C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\}$ (cis-5) and $\{[\text{Mo}(\text{CO})(\text{NO})(\text{PMe}_3)]_2\}[\mu-(\eta^5-\text{C}_5\text{H}_3)_2(\text{SiMe}_2)_2]\}$ (cis-7)

A mixture of cis-3 (0.42 g, 0.69 mmol) and PMe_3 (1.5 ml, 1.5 mmol) in toluene (30 ml) was irradiated

with UV light while stirring for 3 h at room temperature. The colour of the solution changed from orange to dark red. The solution was filtered and evaporated in vacuo to dryness. The residue was chromatographed on florisil. Complex cis-5 was eluted with toluene and cis-7 with dichloromethane.

Complex cis-5: Anal. Found: C, 37.22; H, 3.91; N, 3.67%. $\text{C}_{20}\text{H}_{27}\text{Si}_2\text{N}_2\text{O}_5\text{Mo}_2\text{P}$. Calc. C, 36.70; H, 4.16; N 4.28%. IR (Nujol), (1) and (2) referred to Mo(1) and Mo(2), see Scheme 1): $\nu(\text{CO}(1)) = 2010\text{vs}$, 1938vs ; $\nu(\text{CO}(2)) = 1901\text{vs}$; $\nu(\text{NO}(1)) = 1668\text{vs}$; $\nu(\text{NO}(2)) = 1598\text{vs}$. ^1H NMR (300 MHz; C_6D_6 ; 20°C): $\delta = 5.09$, 5.03 (B', C' and A' parts of an A'B'C' spin system, 3H, C_5H_3 , $^3J(\text{A'B}') = 2.4$), 5.04 , 5.27 , 4.75 (C, B and A parts of an ABC spin system, 3H, C_5H_3 , $^4J(\text{BC}) = 1.2$, $^5J(\text{H}_A-\text{H}_B) = 3.3$, $^3J(\text{AB}) = 2.4$), 0.98 (d, 9H, PMe_3 , $^2J(\text{H}-\text{H}) = 8.7$), 0.58 (s, 3H, SiMe_2), 0.51 (s, 3H, SiMe_2), 0.28 (s, 3H, SiMe_2), 0.26 (s, 3H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz; C_6D_6 ; 20°C): (1) and (2) referred to Mo(1) and Mo(2) see Scheme 1): $\delta = 244.48$ (d, CO(2), $^2J(^{13}\text{C}-\text{H}) = 12.1$), 227.56 , 227.55 (s, CO(1)), 108.16 , 106.21 , 102.86 (s, C_5H_3 α to the SiMe_2 bridges), 100.82 , 98.06 (s, C_5H_3 γ to the SiMe_2 bridges), 99.52 , 99.22 , 98.30 , 97.94 (s, C_5H_3 β to the SiMe_2 bridges), 20.40 (s, PMe_3), 3.72 , 3.65 , 2.51 , 2.12 (s, SiMe_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (125 MHz; C_6D_6 ; 20°C): $\delta = 17.81$ (PMe_3).

Complex cis-7: Anal. Found: C, 38.21; H, 5.21; N, 3.84%. $\text{C}_{18}\text{H}_{24}\text{Si}_2\text{N}_2\text{P}_2\text{O}_4\text{Mo}_2$. Calc. C, 37.61; H, 5.16; N, 3.99%. IR (Nujol): $\nu(\text{CO}) = 1913\text{s}$, 1873s ; $\nu(\text{NO}) = 1620\text{s}$, 1584s . ^1H NMR (500 MHz; C_6D_6 ; 20°C ; I and III see Scheme 3) $\delta = 4.81$, 5.25 , 5.38 (I, A, B and C parts of an ABC spin system, 6H, C_5H_3 , $^3J(\text{H}_A-\text{H}_B) = 2.3$, $^3J(\text{H}_A-\text{H}_B) = 3.0$, $^4J(\text{H}_B-\text{H}_C) = 1.5$), 4.75 , 5.32 , 5.40 (III, A, B and C parts of an ABC spin system, 6H, C_5H_3 , $^3J(\text{H}_A-\text{H}_B) = 2.5$, $^3J(\text{H}_A-\text{H}_B) = 3.0$, $^4J(\text{H}_B-\text{H}_C) = 1.5$), 1.02 (I and III, d, 36H, PMe_3 , $^2J(\text{H}-\text{H}) = 8.5$); 0.75 (I, s, 3H, SiMe_2), 0.70 (I, s, 3H, SiMe_2), 0.43 (I, s, 3H, SiMe_2), 0.37 (I, s, 3H, SiMe_2), 0.74 (III, s, 6H, SiMe_2), 0.40 (III, s, 6H, SiMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz; C_6D_6 ; 20°C ; I and III see Scheme 3) $\delta = 245.03$ (III, d, CO, $^2J(^{13}\text{C}-\text{H}) = 12.12$), 244.78 (I, d, CO, $^2J(^{13}\text{C}-\text{H}) = 12.12$), 107.72 (III, d, C_5H_3 α to the SiMe_2 bridges, $^2J(^{13}\text{C}-\text{H}) = 1.5$), 107.14 (I, d, C_5H_3 α to the SiMe_2 bridges, $^2J(^{13}\text{C}-\text{H}) = 1.5$), 106.05 (I, d, C_5H_3 α to the SiMe_2 bridges, $^2J(^{13}\text{C}-\text{H}) = 2.25$), 105.39 (III, d, C_5H_3 α to the SiMe_2 bridges, $^2J(^{13}\text{C}-\text{H}) = 2.25$), 100.63 , 99.51 (III, s, C_5H_3 β to the SiMe_2 bridges), 100.54 , 99.33 (I, s, C_5H_3 β to the SiMe_2 bridges), 95.60 (I, s, C_5H_3 γ to the SiMe_2 bridges), 95.42 (III, s, C_5H_3 γ to the SiMe_2 bridges), 20.57 (I and III, d, PMe_3 , $^1J(^{13}\text{C}-\text{H}) = 28.1$); 4.75 , 2.57 (III, s, SiMe_2), 4.30 , 4.49 , 2.76 , 2.57 (I, s, SiMe_2). $^{31}\text{P}\{^1\text{H}\}$ NMR (125 MHz; C_6D_6 ; 20°C ; I and III see Scheme 3) $\delta = 18.41$ (I, PMe_3), 18.33 (III, PMe_3).

4.6. Preparation of *trans*-[Mo₂(CO)₃(NO)₂(PMe₃)₂]{μ-(η⁵-C₅H₃)₂(SiMe₂)₂}] (*trans*-5)

PMe₃ (1.94 ml, 1.994 mmol) was added to a solution of *trans*-3 (0.59 g, 0.97 mmol) in toluene (25 ml) at room temperature. The mixture was irradiated with UV light for 45 min. The colour changed from orange to brown. The solvent was removed in vacuo to give a mixture of complexes *trans*-5 and *trans*-7 as brown powders which were chromatographed on florisil. *trans*-5 (0.16 g) was eluted with a mixture of toluene: dichloromethane and *trans*-7 (0.31 g) was obtained in THF.

Complex *trans*-5: Anal. Found: C, 36.48; H, 4.13; N, 4.21%. C₂₀H₂₇Si₂N₂O₅PMo₂. Calc. C, 36.70; H, 4.16; N, 4.28%. IR (Nujol, (1) and (2) referred to Mo(1) and Mo(2), see Scheme 1): ν(CO(1)) = 2012s, 1942s; ν(CO(2)) = 1880s; ν(NO(1)) = 1676s; ν(NO(2)) = 1588s. ¹H NMR (300 MHz; C₆D₆; 20°C): δ = 4.95, 5.37 (A' and B'C' parts of an A'B'C' spin system, 3H, C₅H₃), 4.60, 5.40, 5.32 (A, B and parts of an ABC spin system, 3H, C₅H₃), 0.93 (d, 9H, PMe₃, ²J(¹H-³¹P) = 8.7), 0.47 (s, 3H, SiMe₂), 0.46 (s, 3H, SiMe₂), 0.38 (s, 3H, SiMe₂), 0.33 (s, 3H, SiMe₂). ¹³C{¹H} NMR (125.8 MHz; C₆D₆; 20°C): (1) and (2) referred to Mo(1) and Mo(2), see Scheme 1): δ = 245.53 (d, CO(2), ²J(¹³C-³¹P) = 12), 227.68, 227.65 (CO(1)), 109.37, 109.13, 105.94, 105.39 (C₅H₃ α to the SiMe₂ bridges), 103.54, 103.38, 103.14, 102.82 (C₅H₃ β to the SiMe₂ bridges), 96.62, 93.27 (C₅H₃ γ to the SiMe₂ bridges), 20.66 (d, PMe₃, ¹J(¹³C-³¹P) = 28.12), 3.94, 3.59, 1.69, 1.51 (SiMe₂). ³¹P{¹H} NMR (125 MHz; C₆D₆; 20°C): δ = 17.07 (s, PMe₃).

4.7. Preparation of *trans*-[Mo(CO)(NO)(CN^tBu)]₂{μ-(η⁵-C₅H₃)₂(SiMe₂)₂}] (*trans*-6)

The complex *trans*-3 (0.36 g, 0.59 mmol) was dissolved in toluene (15 ml) and CN^tBu was added with a microsyringe (134 μl, 1.18 mmol). The solution was stirred for 3 h at 60°C. The initial orange solution turned red. After cooling to room temperature hexane (ca. 15 ml) was slowly added to give *trans*-6 as a red solid (0.39 g, 93%) which was washed with toluene and hexane. Anal. Found: C, 45.30; H, 5.17; N, 7.94%. C₂₆H₃₆O₄Si₂N₄Mo₂. Calc. C, 43.58; H, 5.06; N, 7.82%. IR (Nujol): ν(CN^tBu) = 2124s; ν(CO) = 1910s; ν(NO) = 1622s. ¹H NMR (500 MHz; CDCl₃; 20°C): δ = 5.45, 5.70, 5.76 (A, B and C parts of an ABC spin system, 12H, C₅H₃), 1.44 (s, 36H, CNCMe₃), 0.38 (s, 6H, SiMe₂), 0.37 (s, 6H, SiMe₂), 0.36 (s, 6H, SiMe₂), 0.34 (s, 6H, SiMe₂). ¹³C{¹H} NMR (125.8 MHz; CDCl₃; 20°C): δ = 238.55 (CO), 105.83, 105.80 (C₅H₃, α to the SiMe₂ bridges), 105.45, 105.41 (C₅H₃ α to the SiMe₂ bridges), 103.89, 103.85 (C₅H₃ β to the SiMe₂

bridges), 103.05, 102.96 (C₅H₃ β to the SiMe₂ bridges), 95.35, 95.32 (C₅H₃ γ to the SiMe₂ bridges), 167.57 (CNCMe₃), 58.20 (CNCMe₃), 30.81 (CNCMe₃), 3.49, 3.42, 3.20, 3.15 (SiMe₂).

4.8. Preparation of *trans*-[Mo(CO)(NO)(PMe₃)₂]{μ-(η⁵-C₅H₃)₂(SiMe₂)₂}] (*trans*-7)

PMe₃ (1.64 ml, 1.64 mmol) was added to a solution of *trans*-3 (0.5 g, 0.82 mmol) in toluene (25 ml). The solution was stirred for 12 h at 30°C. The initial orange solution turned red and a brown solid appeared. When the solution cooled to the room temperature, hexane was added to facilitate the total precipitation of the product. The supernatant liquid was filtered off and the solid was washed with hexane and toluene. Finally *trans*-7 was obtained as a red powder (0.4 g, 70%). Anal. Found: C, 37.01; H, 5.02; N, 3.91%. C₁₈H₂₄Si₂N₂P₂O₄Mo₂. Cal. C, 37.61; H, 5.16; N, 3.99%. IR (Nujol): ν(CO) = 1884vs; ν(NO) = 1596vs. ¹H NMR (500 MHz; C₆D₆; 20°C; *M* main diastereoisomer and *m* minor diastereoisomer): δ = 4.71, 5.41, 5.48 (*M*, A, B and C parts of an ABC spin system, 3H, C₅H₃, ³J(H_A-³¹P) = 2.6), 4.75, 5.47, 5.51 (*m*, A, B and C parts of an ABC spin system, 3H, C₅H₃, ³J(H_A-³¹P) = 2.6), 0.971 (*M*, d, 9H, PMe₃, ²J(¹H-³¹P) = 9), 0.974 (*m*, d, 9H, PMe₃, ²J(¹H-³¹P) = 9), 0.63 (*M*, s, 3H, SiMe₂), 0.61 (*M*, s, 3H, SiMe₂), 0.57 (*m*, s, 3H, SiMe₂), 0.54 (*m*, s, 3H, SiMe₂). ¹³C{¹H} NMR (125.8 MHz; C₆D₆; 20°C): δ = 246.52 (d, CO, ²J(¹³C-³¹P) = 11.5), 246.29 (d, CO, ²J(¹³C-³¹P) = 11.5), 107.61, 107.33 (C₅H₃ α to the SiMe₂ bridges), 107.05, 106.91 (C₅H₃ α to the SiMe₂ bridges), 103.39 (C₅H₃ β to the SiMe₂ bridges), 102.76 (d, C₅H₃ β to the SiMe₂ bridges, ²J(¹³C-³¹P) = 1.8), 102.68 (d, C₅H₃ β to the SiMe₂ bridges, ²J(¹³C-³¹P) = 1.8), 93.72 (d, C₅H₃ γ to the SiMe₂ bridges, ²J(¹³C-³¹P) = 2.37), 93.63 (d, C₅H₃ γ to the SiMe₂ bridges, ²J(¹³C-³¹P) = 2.37), 21.16 (d, PMe₃, ¹J(¹³C-³¹P) = 28.5), 3.75, 3.52, 3.31 (SiMe₂). ³¹P{¹H} NMR (125 MHz; C₆D₆; 20°C): δ = 16.91 (*m*, PMe₃), 16.85 (*M*, PMe₃).

4.9. Preparation of *cis*-[Mo(NO)(CN^tBu)]₂{μ-(η⁵-C₅H₃)₂(SiMe₂)₂}] (*cis*-8)

CN^tBu (536 μl, 4.76 mmol) was added to a solution of *cis*-3 (0.72 g, 1.19 mmol) in toluene (40 ml). The mixture was stirred for 7 h at 80°C. The orange solution was evaporated in vacuo and the residue was washed with hexane giving a dark yellow powder. The filtrate was partially evaporated and cooled to -40°C overnight to obtain *cis*-8 (0.97 g, 92%). *cis*-8 can also be prepared (0.34 g, 90%) by addition of CN^tBu (98 μl, 0.86 mmol) to a solution of *cis*-6 (0.31 g, 0.43 mmol) in toluene (25 ml) following the procedure described ear-

lier. Anal. Found: C, 49.39; H, 6.58; N, 10.16%. $C_{34}H_{54}O_2Si_2N_6Mo_2$. Calc. C, 45.67; H, 6.15; N, 9.04%. IR (Nujol): $\nu(CN^iBu) = 2112vs, 1922s$ (broad); $\nu(NO) = 1576vs$. 1H NMR (500 MHz; C_6D_6 ; $20^\circ C$) $\delta = 5.71$ (2H, C_5H_3), 5.37 (1H, C_5H_3 , $^3J(HH) = 3$), 1.16 (s, 18H, CN^iBu), 0.86 (s, 3H, $SiMe_2$), 0.49 (s, 3H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz; C_6D_6 ; $20^\circ C$): $\delta = 195.44$ (CN^iBu), 105.88 (C_5H_3 , α to the $SiMe_2$ bridges), 100.57 (C_5H_3 , β to the $SiMe_2$ bridges), 97.35 (C_5H_3 , γ to the $SiMe_2$ bridges), 58.12 ($CNCMe_3$), 31.14 ($CNCMe_3$), 5.41 ($SiMe_2$), 2.40 ($SiMe_2$).

4.10. Preparation of *trans*- $\{[Mo(NO)(CN^iBu)_2]\}_2\{\mu-(\eta^5-C_5H_3)_2(SiMe_2)_2\}$ (*trans-8*)

A suspension of *trans-6* (0.34 g, 0.46 mmol) in toluene (20 ml) was prepared and then CN^iBu (107 μ l, 0.94 mmol) was added with a microsyringe. The mixture was heated to $80^\circ C$ and stirred until the solids were dissolved. Stirring was continued for 3 h. Then the solution was cooled to room temperature and hexane was slowly added to give *trans-8* as a red solid (0.37 g, 93%). The product was washed with hexane and toluene. *Trans-8* can also be prepared from *trans-3* (0.36 g, 0.59 mmol) with CN^iBu (268 μ l, 2.36 mmol) by the procedure described earlier (0.46 g, 90%). Anal. Found: C, 49.01; H, 6.83; N, 8.23%. $C_{34}H_{54}O_2Si_2N_6Mo_2$. Cal. C, 45.67; H, 6.15; N, 9.04%. IR (Nujol): $\nu(CN^iBu) = 2102s, 1966s$ (broad); $\nu(NO) = 1566w$. 1H NMR (500 MHz; $CDCl_3$; $20^\circ C$): $\delta = 5.61$ (2H, C_5H_3 , $^3J(HH) = 2.6$), 5.47 (1H, C_5H_3), 1.37 (s, 18H, $CNCMe_3$), 0.33 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz; $CDCl_3$; $20^\circ C$): $\delta = 188.38$ ($CNCMe_3$), 103.98 (C_5H_3 , β to the $SiMe_2$ bridges), 103.15 (C_5H_3 , α to the $SiMe_2$ bridges), 94.35 (C_5H_3 , γ to the $SiMe_2$ bridges), 58.15 ($CNCMe_3$), 31.19 ($CNCMe_3$), 4.81 ($SiMe_2$).

4.11. Preparation of *cis*- $\{[MoCl_2(NO)]_2\}_2\{\mu-(\eta^5-C_5H_3)_2(SiMe_2)_2\}$ (*cis-9*)

PCl_5 (0.46 g, 2.2 mmol) was added to an orange solution of *cis-3* (0.67 g, 1.1 mmol) in diethyl ether (50 ml), and the solution was stirred for 4 h at room temperature. A colour change from orange to green was observed and a red solid was deposited. The solid was isolated and washed three times with diethyl ether (3×25 ml) to remove any traces of PCl_3 . The solid was then dried under vacuum to obtain *cis-9* (0.66 g, 94%) as a red powder. Anal. Found: C, 26.99; H, 2.84; N, 4.69%. $C_{14}H_{18}O_2Si_2N_2Cl_4Mo_2$. Cal. C, 26.43; H, 2.83; N, 4.40%. IR (Nujol): $\nu(NO) = 1686vs$; $\nu(Mo-Cl) = 320m, 284w$. 1H NMR (500 MHz; CD_2Cl_2 ; $-80^\circ C$; I and II see Fig. 5): $\delta = 6.63$ (2H, I, C_5H_3 , β to the $SiMe_2$ bridges), 6.51 (2H, II, C_5H_3 , β to the $SiMe_2$ bridges), 6.41 (2H, I, C_5H_3 , β to the $SiMe_2$ bridges), 6.35 (2H, II, C_5H_3 , γ to the $SiMe_2$ bridges), 6.33. (2H,

I, C_5H_3 , γ to the $SiMe_2$ bridges), 6.29 (2H, II, C_5H_3 , β to the $SiMe_2$ bridges), 0.69 (s, I, 3H, $SiMe_2$); 0.58 (s, II, 6H, $SiMe_2$), 0.50 (s, I, 3H, $SiMe_2$), 0.46 (s, II, 6H, $SiMe_2$), 0.44 (s, I, 3H, $SiMe_2$), 0.42 (s, I, 3H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz; CD_2Cl_2 ; $-70^\circ C$; I and II see Fig. 5): $\delta = 136.66$ (I, C_5H_3 , γ to the $SiMe_2$ bridges), 135.43 (II, C_5H_3 , α to the $SiMe_2$ bridges), 134.28 (II, C_5H_3 , α to the $SiMe_2$ bridges), 131.18 (I, C_5H_3 , α to the $SiMe_2$ bridges), 118.32 (I, C_5H_3 , α to the $SiMe_2$ bridges), 103.88 (I, C_5H_3 , β to the $SiMe_2$ bridges), 102.97 (I, C_5H_3 , β to the $SiMe_2$ bridges), 102.25 (II, C_5H_3 , β to the $SiMe_2$ bridges), 102.23 (II, C_5H_3 , β to the $SiMe_2$ bridges), 100.99 (II, C_5H_3 , γ to the $SiMe_2$ bridges), 2.49, -5.33 (II, $SiMe_2$), 2.07, 1.86, -4.12 , -5.19 (I, $SiMe_2$).

4.12. Preparation of *trans*- $\{[MoCl_2(NO)]_2\}_2\{\mu-(\eta^5-C_5H_3)_2(SiMe_2)_2\}$ (*trans-9*)

This complex was obtained as a red powder (0.5 g, 74%) from *trans-3* (0.65 g, 1.07 mmol) by the procedure described for *cis-9*. Anal. Found: C, 27.09; H, 2.95; N, 4.25%. $C_{14}H_{18}O_2Si_2N_2Cl_4Mo_2$. Cal. C, 26.43; H, 2.83; N, 4.40%. IR (Nujol): $\nu(NO) = 1678m$; $\nu(Mo-Cl) = 322w, 298w$. 1H NMR (500 MHz; Acetone- d_6 ; $20^\circ C$): $\delta = 6.71$ (2H, C_5H_3 , $^3J(HH) = 3$), 6.69 (1H, C_5H_3), 0.76 (s, 6H, $SiMe_2$). $^{13}C\{^1H\}$ NMR (125.8 MHz; Acetone- d_6 ; $20^\circ C$): $\delta = 125.97$ (C_5H_3 , β to the $SiMe_2$ bridges), 118.59 (C_5H_3 , α to the $SiMe_2$ bridges), 112.29 (C_5H_3 , γ to the $SiMe_2$ bridges), -0.77 ($SiMe_2$).

4.13. Preparation of *cis*- $\{[Mo(CN^iBu)Cl_2(NO)]_2\}_2\{\mu-(\eta^5-C_5H_3)_2(SiMe_2)_2\}$ (*cis-10*)

PCl_5 (0.31 g, 1.49 mmol) was added to a solution of *cis-8* (0.66 g, 0.74 mmol) in toluene (40 ml) and the mixture was stirred at room temperature for 4 h. An orange solid appeared and the supernatant solution became colourless. This solution was filtered off and the solid was washed with toluene and diethyl ether. *cis-10* (0.5 g, 94%) was obtained as an orange solid. Anal. Found: C, 36.12; H, 4.73; N, 6.53%. $C_{24}H_{36}N_4O_2Si_2Cl_4Mo_2$. Cal. C, 35.92; H, 4.52; N, 6.98%. IR (Nujol): $\nu(CN^iBu) = 2214vs$; $\nu(NO) = 1681vs$; $\nu(Mo-Cl) = 314vs$. 1H NMR (300 MHz; CD_2Cl_2 ; $20^\circ C$; I, II and III see Scheme 7): $\delta = 7.20$ (4H, C_5H_3), 6.66 (2H, C_5H_3), 6.47 (4H, C_5H_3), 6.39 (1H, C_5H_3), 6.31 (2H, C_5H_3), 6.25 (4H, C_5H_3), 5.89 (1H, C_5H_3), 1.63 (s, 9H, III, $CNCMe_3$), 1.62 (s, 9H, III, $CNCMe_3$), 1.60 (s, 18H, I or II, $CNCMe_3$), 1.40 (s, 18H, I or II, $CNCMe_3$), 1.02 (s, 3H, III, $SiMe_2$), 0.81 (s, 3H, III, $SiMe_2$), 0.65 (s, 3H, III, $SiMe_2$), 0.57 (s, 3H, III, $SiMe_2$), 0.89 (s, 6H, I or II, $SiMe_2$), 0.62 (s, 6H, I or II, $SiMe_2$), 0.56 (s, 6H, I or II, $SiMe_2$), 0.10 (s, 6H, I or II, $SiMe_2$).

Table 5
Crystal Data, experimental data and structure refinement procedures for *cis*-3.5 and *trans*-6.8 compounds

| | <i>cis</i> -3 | <i>cis</i> -5 | <i>trans</i> -6 | <i>trans</i> -8 |
|--|---|--|---|--|
| Formula | C ₁₈ H ₁₈ Mo ₂ N ₂ O ₆ Si ₂ | C ₃₀ H ₂₇ Mo ₂ N ₃ O ₅ PSi ₂ | C ₂₆ H ₃₆ Mo ₂ N ₄ O ₄ Si ₂ | C ₄₈ H ₇₀ Mo ₂ O ₂ Si ₂ |
| Crystal habit | Prismatic | Prismatic | Prismatic | Prismatic |
| Color | Orange | Dark red | Red | Red |
| Crystal size (mm) | 0.35 × 0.29 × 0.26 | 0.30 × 0.25 × 0.15 | 0.20 × 0.15 × 0.12 | 0.28 × 0.22 × 0.15 |
| Symmetry | Orthorhombic, <i>Pbca</i> | Monoclinic, <i>P2₁/c</i> | Monoclinic, <i>P2₁/c</i> | Monoclinic, <i>P2₁/c</i> |
| <i>Unit cell dimensions</i> | | | | |
| <i>a</i> (Å) | 15.189(3) | 8.978(2) | 9.453(3) | 9.116(2) |
| <i>b</i> (Å) | 11.754(2) | 13.493(1) | 12.715(3) | 15.599(3) |
| <i>c</i> (Å) | 26.644(5) | 22.713(8) | 13.857(6) | 18.698(4) |
| α (deg) | 90.0 | 90.0 | 90.0 | 90.0 |
| β (deg) | 90.0 | 99.94(1) | 107.09(3) | 101.68(3) |
| γ (deg) | 90.0 | 90.0 | 90.0 | 90.0 |
| <i>V</i> (Å ³) | 4757(2) | 2710(1) | 1592.0(9) | 2603.8(9) |
| <i>Z</i> | 8 | 4 | 2 | 2 |
| <i>D</i> _{calc} (g cm ⁻³) | 1.694 | 1.604 | 1.495 | 1.290 |
| MW | 606.40 | 654.47 | 716.64 | 1011.16 |
| <i>F</i> (000) | 2400 | 1312 | 728 | 1056 |
| μ (cm ⁻¹) | 11.89 | 11.04 | 8.98 | 5.68 |
| scan mode | ω scans | ω scans | ω scans | ω scans |
| θ range | 2 < θ < 29 | 2 < θ < 30 | 2 < θ < 27 | 2 < θ < 27 |
| <i>no. of reflections</i> | | | | |
| measured | 4338 | 6194 | 3717 | 6110 |
| independent | 4063 | 5771 | 3450 | 5645 |
| observed | $F_o > 2\sigma(F_o)$ criterion | 3821 $F_o > 2\sigma(F_o)$ criterion | 1764 $F_o > 2\sigma(F_o)$ | 2681 $F_o > 4\sigma(F_o)$ criterion |
| range of <i>hkl</i> | -18 < <i>h</i> < 0; -13 < <i>k</i> < 0; -6 < <i>l</i> < -31 | -11 < <i>h</i> < 11; 0 < <i>k</i> < 17; 0 < <i>l</i> < 28 | 0 < <i>h</i> < 12; 0 < <i>k</i> < 16; -17 < <i>l</i> < 17 | 0 < <i>h</i> < 11; 0 < <i>k</i> < 19; -23 < <i>l</i> < 23 |
| standard reflections | three reflections 120 min ⁻¹ | no variation | | |
| <i>R</i> ₁ | 0.0340 | 0.0445 | 0.1138 | 0.0797 |
| <i>wR</i> ₂ | 0.0717 | 0.0951 | 0.3059 | 0.1750 |
| <i>Parameters for weighting scheme</i> | | | | |
| <i>x</i> , <i>y</i> | 0.0268, 7.5606 | 0.0219, 5.3753 | 0.3141, 79.8920 | 0.0878, 10.8511 |
| goodness of fit indicator | 1.155 | 1.249 | 1.040 | 1.114 |
| largest diff. peak | 0.466 and -0.429 | 0.576 and -1014 | 2.54 and -2.47 | 1.618 and -0.779 |
| and hole (e Å ⁻³) | | | | |

Details in common: cell dimensions from least-squares of 25 reflections; $R_1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR_2 = [(\sum (F_o^2 - F_c^2)^2) / \sum w(F_o^2)^2]^{1/2}$.
 Weighting scheme: $w = 1 / (s^2(F_o^2) + (xP)^2 + yP)$ where $P = (F_o^2 + 2F_c^2) / 3$. Temperature 293(2) K.

4.14. Preparation of *trans*-[Mo(CN^tBu)Cl₂(NO)]₂{μ-(η⁵-C₅H₃)₂(SiMe₂)₂}(*trans*-10)

PCl₅ (0.21 g, 1 mmol) was added to a suspension of *trans*-8 (0.42 g, 0.47 mmol) in toluene (25 ml) and stirred at room temperature for 3h. The suspension changed colour giving a yellow solid and a pale orange supernatant solution. The solution was filtered off and the precipitate was washed with toluene and diethyl ether to remove traces of PCl₃ formed. Complex *trans*-10 was obtained as a pale yellow powder (0.32 g, 84%). Anal. Found: C, 33.95; H, 4.66; N, 7.20%. C₂₄H₃₆N₄O₂Si₂Cl₄Mo₂. Calc. C, 35.92; H, 4.52; N, 6.98%. IR (Nujol): ν(CN^tBu) = 2212m; ν(NO) = 1676m; ν(Mo–Cl) = 308w, 262w. ¹H NMR (500 MHz; CD₂Cl₂; 20°C): δ = 6.66 (A part of an ABC spin system, 1H, C₅H₃), 6.42 (A part of an ABC spin system, 1H, C₅H₃), 6.46 (C parts of two ABC spin systems, 2H, C₅H₃), 6.37 (B parts of two ABC spin systems, 2H, C₅H₃), 1.61 (s, 36H, CNCMe₃), 0.75 (s, 6H, SiMe₂), 0.64 (s, 3H, SiMe₂), 0.63 (s, 3H, SiMe₂). ¹³C{¹H} NMR (125.8 MHz; CD₂Cl₂; 20°C): δ = 131.68–111.19 (10 signals to C₅H₃), 60.95 (CNCMe₃), 60.91 (CNCMe₃), 29.69 (CNCMe₃), 0.80, 0.56, 0.49, 0.45 (SiMe₂).

4.15. Reaction of *trans*-6 with PCl₅

The reaction between *trans*-6 (0.25 g, 0.349 mmol) and PCl₅ (0.145 g, 0.697 mmol) was carried out by the procedure described in Section 4.14. The ¹H NMR spectra showed a mixture of complexes *trans*-10 and *trans*-11.

Complex *trans*-11: IR (Nujol): ν(CN^tBu) = 2212m; ν(CO) = 1906w; ν(NO) = 1676m; ν(Mo–Cl) = 308w, 262w. ¹H NMR (500 MHz; CD₂Cl₂; 20°C): δ = 6.56, 6.53, 6.48, 6.45, 6.31, 6.25, 5.84, 5.77, 5.74, 5.57, 5.55 (C₅H₃), 1.47 (s, 36H, CNCMe₃), 0.70, 0.65, 0.58, 0.54, 0.52, 0.47, 0.43, 0.39 (SiMe₂).

4.16. Crystal structures of *cis*-3, *cis*-5, *trans*-6 and *trans*-8

Suitably sized orange crystals of *cis*-3 were obtained by crystallization from toluene; crystals of *cis*-5 were obtained from a mixture of toluene–hexane; *trans*-6 was crystallized at –40°C from a mixture of toluene–hexane and crystals of *trans*-8 were obtained from a mixture of toluene–C₆D₆. The crystals were mounted in sealed tubes under Argon in a Enraf-Nonius CAD-4 automatic four-circle diffractometer with bisecting geometry, using graphite-oriented monochromator and Mo-K_α (λ = 0.71073 Å) radiation. Crystallographic and experimental details are summarized in Table 5. Data were collected at room temperature. Intensities were corrected for Lorentz and polarization effects in the

usual manner. No absorption or extinction corrections were made. The structures were solved by a combination of heavy atoms, direct methods, and Fourier synthesis and refined on F² by full-matrix least-squares calculations by Shelx system [24,25]. All non-hydrogen atoms were refined anisotropically. In the last cycle of refinement hydrogen atoms were introduced from geometric calculations and fixed thermal parameters. All calculations were performed on an Alpha AXP Digital Workstation

5. Supplementary material available

Tables of atomic coordinates (Tables 1–3, 1 page; Tables 1–5, 1 page; Tables 1–6, 1 page; Tables 1–8, 1 page), complete bond distances and angles (Tables 2–3, 2 pages; Tables 2–5, 2 pages; Tables 2–6, 2 pages; Tables 2–8, 1 page), anisotropic displacement parameters (Tables 3–3, 1 page; Tables 3–5, 1 page; Tables 3–6, 1 page; Tables 3–8, 1 page), positional parameters of hydrogen atoms (Tables 4–3, 1 page; Tables 4–5, 1 page; Tables 4–6, 1 page; Tables 4–8, 1 page) and structure factors (Tables 5–3, 28 pages; Tables 5–5, 40 pages; Tables 5–6, 24 pages; Tables 5–8, 40 pages) for complexes *cis*-3, *cis*-5, *trans*-6 and *trans*-8 are available. Ordering information is given on any current masthead page.

Acknowledgements

We acknowledge financial support from DGICYT (Project 92-0178-C). R.G-G acknowledges CAM for a fellowship.

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