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Journal of Organometallic Chemistry 494 (1995) 187–193

Journal of Organometallic Chemistry

Synthesis and characterization of asymmetric C,N-cyclometallated complexes of Mo(II). X-ray crystal structures of $[(\eta^5\text{-}C_5H_5)Mo\{C_6H_2\text{-}(OCH_2O)\text{-}2,3\text{-}CH_2NMe_2\text{-}6\}(I)(NO)]$ and $[(\eta^5\text{-}C_5H_5)Mo\{S\text{-}C_6H_4CH(Me)NMe_2\text{-}2\}(I)(NO)]$

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Received 27 October 1994

Abstract

The reaction of $\{(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}I)(I)(NO)\}_2]$ with the Hg derivatives of substituted *N,N*-dimethylbenzylamines $[Hg(Q\ dmba)_2]$ (HQ = substituted *N,N*-dimethylbenzylamine affords the organomolybdenum complexes $[(\eta^5\text{-}C_5H_5)Mo(Qdmba)(I)(NO)]$ (**2a**–**2e**) in nearly quantitative yield as a racemic mixture of both enantiomers. When the reaction is carried out with $Hg\{S\text{-}C_6H_4C(H)(Me)NMe_2\}_2$, a 1:1 mixture of both diastereoisomers $[(\eta^5\text{-}C_5H_5)Mo\{S\text{-}C_6H_4C(H)(Me)NMe_2\text{-}2\}(I)(NO)]$ (**2f**–**2g**) is obtained. The resolution of this mixture can be accomplished by fractional crystallization in CH_2Cl_2/hexane. The X-ray crystal structure of the complexes (*SPY*-5-15-A,C)-$[(\eta^5\text{-}C_5H_5)Mo\{C_6H_2\text{-}(OCH_2O)\text{-}2,3\text{-}CH_2NMe_2\text{-}6\}(I)(NO)]$ (**2b**) and (*SPY*-5-15-C)-$[(\eta^5\text{-}C_5H_5)Mo\{S\text{-}C_6H_4C(H)(Me)NMe_2\text{-}2\}(I)(NO)]$ (**2f**) are reported.

Keywords: Molybdenum; Cyclometallation; Nitrosyl; Asymmetry; Iodide; Transmetallation

1. Introduction

Transition metal complexes have proved to be useful reagents in organic synthesis, due to the ability of the metal to activate its ligands. Thus cyclometallated amines with internal alkynes afford new synthetic pathways to carbo- and hetero-cyclic compounds [1a,b]. The reactions are strongly metal-dependent. For instance, a marked difference has been found in the reactivity of cyclopalladated or cycloruthenated complexes towards internal alkynes [1c]. Several reasons prompted us to investigate the synthesis of new cyclometallated complexes of transition metals, the main one being their potential applications in organic synthesis. We also sought to determine whether other cyclometallated complexes such as those of molybdenum might display behaviour analogous (or complementary) to that already described with Pd and/or Ru. This metal has already proved to be useful in synthesis. For example, 2,3-diphenylindols have been obtained by reaction of $[(\eta^5\text{-}C_5H_5)Mo(pap)(CO)_2]$ [pap = (phenylazo)phenyl] with diphenylacetylene [2].

However, few examples of cyclometallated Mo derivatives have been reported. Complexes such as $[(\eta^5\text{-}C_5H_5)Mo(C\text{–}N)(CO)_2]$ (C–N = cyclometallated 8-methylquinoline [3], (phenylazo)phenyl [4] or benzo-*H*-quinoline [5]) and $[(\eta^5\text{-}C_5Me_5)Mo(C\text{-}N)(CO)_2]$ (C-N = pap [4]) are known, but were obtained in very low yield (1–16%). The synthesis of this kind of complex has been accomplished by either direct C–H activation by $[(\eta^5\text{-}C_5H_5)Mo(Me)(CO)_3]$ or oxidative addition of a halo-derivative of the ligand to $Na[(\eta^5\text{-}C_5H_5)Mo(CO)_3]$.

Transmetallation reactions are also useful for the synthesis of cyclometallated complexes and have been a powerful synthetic tool in Ru(II) chemistry [1c]. We have investigated the synthesis of cyclometallated Mo(II) derivatives through a transmetallation process. $\{(\eta^5\text{-}C_5H_5)Mo(\mu\text{-}I)(I)(NO)\}_2]$ provides an ideal starting material because of its air-stability and easy accesibility. In this paper we report full details of the synthesis and characterization of the resulting Mo-complexes.

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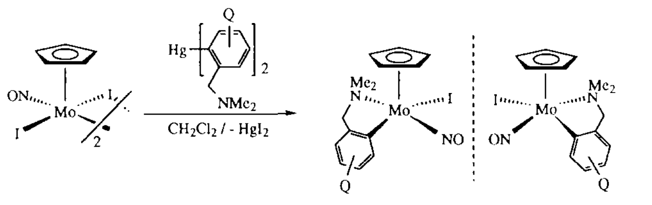
0022-328X/95/$09.50
SSDI 0022-328X(95)05429-4

2. Results and discussions

Attempts to obtain cyclometallated Mo-derivatives by intramolecular C–H activation did not meet with success: only coordination molybdenum amine species were detected in the reaction mixture.

However, [{CpMo(μ-I)(I)(NO)}$_2$] reacts slowly in CH_2Cl_2 at room temperature with the bis(aryl)mercury derivatives shown in Scheme 1 to give the corresponding organomolybdenum complexes **2a**–**2e**. They were isolated in nearly quantitative yield for compounds **2a**–**2d** but the yield of **2e** was only 15%. The general process is presented in Eq. 1.



Q = H (2a), (OCH2O)-2,3 (2b), Me-5 (2c), F-5 (2d), (OMe)-2,3 (2e)

(1)

The transmetallation always occurs with retention of the cyclometallation position and there is no influence of the amine substituents on the general process; good yields are obtained either with electron-withdrawing (F) or electron-donating substituents (Me, OCH_2O). The low yields of **2e** might be explained by steric repulsions between the *ortho*-OMe group and the neighbouring ligands on molybdenum, as shown by the shift of the C_5H_5 resonance to a slightly lower field when there are substituents *ortho* to the Mo–C bond (**2b**,**2e**).

The IR spectra of complexes **2a**–**e** in CH_2Cl_2 solution (see Section 4) show an intense absorption band around 1660 cm^{-1}, fairly typical of terminal nitrosyl bonded to molybdenum [6,7,8]. In addition, the single set of signals in the ^{1}H and ^{13}C{^{1}H} NMR spectra indicate that the reaction is stereoselective and, rather than two possible coordination isomers, only one was obtained. The ^{1}H NMR spectra of these complexes in the low field region (see Section 4) show the expected resonances for the cyclometallated ligands: a doublet of relative intensity 1 and a multiplet of intensity 3 for **2a**, an AB system for complexes **2b** and **2e**, a singlet and an AB system for **2c** and three complex resonances of relative intensity 1/1/1 for **2d**. A similar pattern of additional signals is observed for all complexes: the resonance attributed to the C_5H_5 appears as a sharp singlet, the protons of the CH_2N group appear as an AB system (the two protons are diastereotopic because of their location in an asymmetric environment) and the methyl groups of the NMe_2 unity appear as two singlet resonances. This last fact shows that the nitrogen is in a stable tetrahedral array, reflecting the chirality of the adjacent Mo.

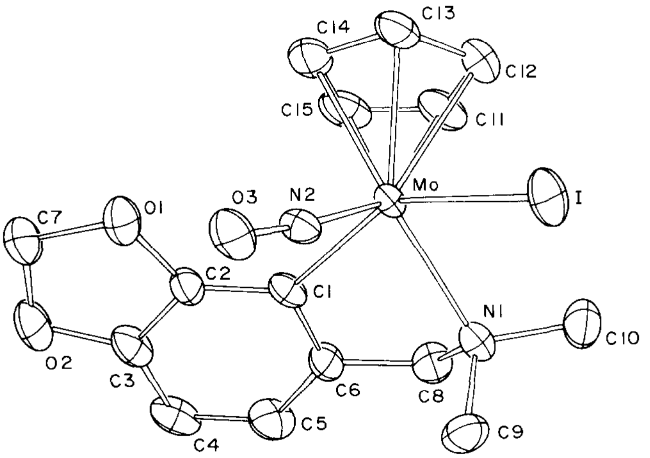


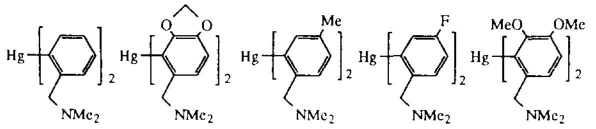
Fig. 1. X-ray crystal structure of (*SPY*-5-15-A,C)-[η^5-C_5H_5)-Mo($C_6H_2(OCH_2O)$-2,3-CH_2NMe_2-6)(I)(NO)] (**2b**).

In order to elucidate the stereochemistry around the molybdenum an X-ray structural analysis of **2b** was carried out. Suitable crystals of **2b** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **2b** at −30°C. An ORTEP drawing of **2b** is shown in Fig. 1 and selected bond distances and angles are given in Table 1. The X-ray structure shows that **2b** is a mononuclear molybdenum species with a "four-legged-piano-stool" geometry the η^5-cyolopentadienyl ligand being in the "seat" position, while the "legs" are comprised of the arylamine [bonded via C(1) and N(1)], the iodine atom and the *N*-bonded nitrosyl group. The Mo–N(2) (1.775(7) Å) and N(2)–O(3) (1.18(1) Å)

Table 1
Selected bond distances and angles for **2b**

Bond distances (Å)			
Mo–I	2.8705(9)	Mo–C(1)	2.184(7)
Mo–N(1)	2.343(8)	Mo–N(2)	1.775(7)
Mo–C(C_5H_5) [a]	2.35(1)	N(2)–O(3)	1.18(1)
Bond angles (°)			
N(2)–Mo–C(1)	84.4(3)	N(2)–Mo–I	81.8(2)
N(2)–Mo–N(1)	113.5(3)	C(1)–Mo–N(1)	73.7(3)
C(1)–Mo–I	145.9(2)	N(1)–Mo–I	83.6(2)
Mo–N(2)–O(3)	174.2(7)		

[a] Mean value; distances range from 2.28(1) to 2.43(1) Å.



(1a) (1b) (1c) (1d) (1e)

Scheme 1.

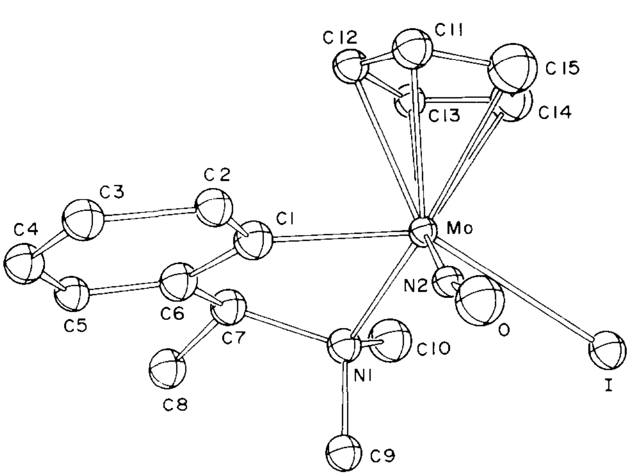
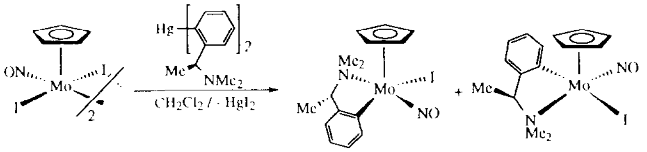


Fig. 2. X-ray crystal structure of (*SPY*-5-15-C)-[η^5-C_5H_5)Mo(*S*-C_6H_4CHMeNMe$_2$-2)(I)(NO)] (**2f**).

distances are similar to those found in the related complex [(η^5-C_5H_5)Mo(NO)(I)(η^3-allyl)] [9] (1.783(2) Å and 1.178(2) Å, respectively), though the Mo–I distance (2.8705(9) Å) is slightly longer (2.821(1) Å). The values found for the Mo–N(1) (2.343(8) Å) and Mo–C(1) (2.184(7) Å) distances are similar to those of related compounds [10]. Finally, the Mo–NO system is almost linear [Mo–N(2)–O(3) = 174.2(7)°].

In complexes **2a–2e**, the Mo atom is the only chiral centre and consequently they are obtained as a racemic mixture. When the reaction is carried out using Hg{*S*-C_6H_4CH(Me)NMe$_2$}$_2$, which contains a stereogenic centre resulting from methyl substitution at the benzyl carbon atom, and with a similar work-up, an orange-brown solid of stoichiometry [(C_5H_5)Mo(*S*-C_6H_4CH-(Me)NMe$_2$)(I)(NO)] is obtained in almost quantitative yield. The ^{1}H NMR spectrum of this compound shows the presence of the two diastereoisomers (**2f,g**) in 1/1 ratio, and the reaction is not diastereoselective. The process is represented in Eq. 2.



(2f) (2g)

(2)

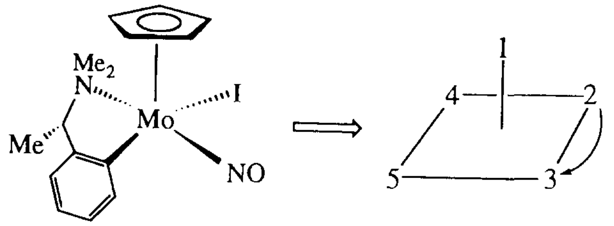
The resolution of this mixture of diastereoisomers can be accomplished by crystallization from CH_2Cl_2/hexane (see Section 4): complex **2f** crystallizes as deep-orange blocks (suitables for X-ray determination) while **2g** crystallizes as pale-orange plates which lose their transparency on exposure to air.

The purity of the separated complexes was checked by ^{1}H NMR; solutions of **2f** or **2g** did not show the presence of any of the other form. Moreover, when solutions of pure **2f** or **2g** were left stirring at room temperature for several days, no evidence of epimerization could be detected suggesting that both compounds are thermodynamically stable in solution.

Table 2
Selected bond distances and angles for **2f**

Bond distances (Å)			
Mo–I	2.857(1)	Mo–C(1)	2.161(9)
Mo–N(1)	2.360(7)	Mo–N(2)	1.770(8)
Mo–C(C_5H_5) [a]	2.35(1)	N(2)–O	1.18(1)
Bond angles (°)			
N(2)–Mo–C(1)	83.0(4)	N(2)–Mo–I	82.7(3)
N(2)–Mo–N(1)	116.7(3)	C(1)–Mo–N(1)	73.4(3)
C(1)–Mo–I	145.1(3)	N(1)–Mo–I	85.0(2)
Mo–N(2)–O(3)	170.9(7)		

[a] Mean value; distances range from 2.28(1) to 2.43(1) Å.



Scheme 2.

The X-ray crystal structure of **2f** was also determined. An ORTEP drawing of **2f** is shown in Fig. 2 and selected bond distances and angles are given in Table 2. The structure is similar to that of **2b**. The unit cell belongs to a noncentrosymmetric space group (in this case $P2_12_12_1$) showing, as expected, that it contains only one diastereoisomer. The Mo-complex has a local geometry analogous to that of **2b** and the most important distances and angles are similar to those found in complex **2b** within experimental error (see Tables 1 and 2). The most remarkable feature is that the methyl group at the chiral carbon atom of the *C,N*-cyclometalated *S*-$C_6H_4C^*$(H)(Me)NMe$_2$ is *exo* with respect to the η^5-C_5H_5, probably to minimize steric interactions. These data allow us to determine the absolute configuration of the Mo atom as C(clockwise) if the priority sequence C_5H_5 > I > NO > N(amine) > C (amine) is used [11] (see Scheme 2). The complete designation is then (*SPY*–5–15-C)-[(η^5-C_5H_5)Mo(*S*-C_6H_4CHMe-NMe$_2$-6)(I)(NO)].

3. Conclusion

The transmetallation reaction between Hg derivatives of the type Hg(Qdmba)$_2$ (HQ = substituted *N,N*-dimethylbenzylamine) and [{(η^5-C_5H_5)Mo(μ-I)(I)

$(NO)\}_2]$ to be an efficient method for the synthesis of *C,N*-cyclometallated complexes of Mo(II). When a chiral amine is present in the Hg-precursor the process is not diastereoselective. The separate diastereoisomers are thermodynamically stable and they do not epimerize in solution. Further work is now in progress to evaluate the synthetic potential of this class of compound.

4. Experimental section

4.1. General comments

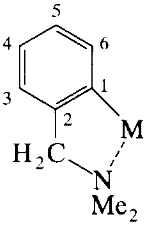
All reactions were performed in Schlenk flasks under oxygen and water-free nitrogen. Solvents were dried and distilled under nitrogen: diethyl ether over benzophenone ketyl, hexane over sodium, and dichloromethane over P_2O_5. IR spectra were recorded in CH_2Cl_2 solution on a Bruker IFS-66. Elemental analysis were performed by the Service Central d'Analyse du CNRS (Lyon). The ^1H NMR spectra were recorded at 300.13 MHz and ^{13}C NMR spectra at 75.47 MHz on a FT–Bruker instrument (AC-300) and externally referenced to TMS. $[\alpha]_D$ values were measured at room temperature on a Perkin Elmer Polarimeter at 589 nm. Column chromatography was performed under nitrogen by using Al_2O_3 as support (Aluminiumoxid 90, Merck). The starting materials $[(\eta^5\text{-}C_5H_5)Mo(\mu\text{-I})(I)(NO)\}_2]$ [12] and $Hg(dmba)_2$ **1a** [13] were prepared according to published methods. $Hg\{S\text{-}C_6H_4CH(Me)NMe_2\}_2$ was prepared using a procedure that slightly modified from that used for $Hg(dmba)_2$.

4.2. Synthesis of Hg compounds

4.2.1. $Hg\{C_6H_2(OCH_2O)\text{-}2,3\text{-}CH_2NMe_2\text{-}6\}_2$ *(1b)*

To a stirred solution of *N,N*-dimethylaminomethyl-1-dioxymethylene-3,4-benzene (3.00 g, 16.74 mmol) in hexane (20 ml) was added slowly a solution of 1.6 M *n*-butyllithium (11.0 ml, 17.6 mmol). The resulting white suspension was stirred for 14 h at room temperature and subsequently filtered off. The residue was washed with hexane (2 × 10 ml) and dried *in vacuo* leaving 3.09 g (16.7 mmol, 100% yield) of a white powder. This solid was suspended in Et_2O (100 ml) and solid $HgCl_2$ (2.27 g, 8.37 mmol) was added slowly, causing a gentle reflux of the solvent. After addition, the mixture was stirred for 2 h. and the solvent was then removed *in vacuo*. The residue was extracted with CH_2Cl_2 (50 ml) and filtered. Evaporation of the solvent to small volume and addition of hexane (20 ml) gave 3.45 g (74%) of **1b** as a white powder. Anal. Calc. for $C_{20}H_{24}HgN_2O_4$: C, 43.13; H, 4.34; N, 5.03. Found: C, 42.91; H, 4.36; N, 5.07%. ^1H NMR ($CDCl_3$): δ 6.74, 6.62 (AB system, H_4 and H_5, Ar, $^3J_{H_4-H_5} = 7.69$ Hz), 5.88 (s, 2H, O_2CH_2), 3.36 (s, 2H, CH_2N), 2.22 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 152.08, 145.56, 137.63, 121.38, 108.42, 100.31 (C_6H_2), 84.63 (O_2CH_2), 64.02 (CH_2N), 44.56 (NMe_2).

Throughout the experimental section, the numbering of the H and C, aromatic atoms of the dmba-chelate is according the following scheme



4.2.2. $Hg\{C_6H_3\text{-}CH_3\text{-}5\text{-}CH_2NMe_2\text{-}2\}_2$ *1c*

Complex **1c** was obtained using a work-up similar to that described for **1b** except that *N,N*-dimethylaminomethyl-1-methyl-4-benzene (3.00 g, 20.10 mmol) was allowed to react with t-butyllithium (13.0 ml, 22.0 mmol) (yield of the Li derivative: 14.24 mmol, 71%) and $HgCl_2$ (1.93 g, 7.12 mmol) giving 3.23 g (91%) of **1c** as a white powder. Anal. Calc. for $C_{20}H_{28}HgN_2$: C, 48.33; H, 5.68; N, 5.63. Found: C, 48.31; H, 5.72; N, 5.68%. ^1H NMR ($CDCl_3$): δ 7.34 (s, H_6, Ar), 7.16, 6.98 (AB system, H_3 and H_4, Ar, $^3J_{H_3-H_4} = 7.61$ Hz), 3.44 (s, 2H, CH_2N), 2.35 (s, 3H, Me), 2.28 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 170.37, 144.33, 139.06, 135.53, 128.44, 127.49 (C_6H_3), 67.07 (CH_2N), 45.24 (NMe_2), 21.41 (Me).

4.2.3. $Hg\{C_6H_3F\text{-}5\text{-}CH_2NMe_2\text{-}2\}_2$ *(1d)*

Complex **1d** was obtained using a work-up similar to that described for **1b** except that *N,N*-dimethylaminomethyl-1-fluoro-4-benzene (1.53 g, 10.0 mmol) was allowed to react with t-butyllithium (5.8 ml, 10 mmol) (yield of the Li derivative: 7.60 mmol, 76%) and $HgCl_2$ (1.03 g, 3.80 mmol) to obtain **1d** as a white powder (1.59 g, 83%). Anal. Calc. for $C_{18}H_{22}F_2HgN_2$: C, 42.81; H, 4.39; N, 5.54. Found: C, 43.11; H, 4.46; N, 5.37%. ^1H NMR ($CDCl_3$): δ 7.23 (dd, H_6, Ar, $^3J_{H_6-F} = 7.82$ Hz, $^4J_{H_4-H_6} = 2.79$ Hz), 7.20 (dd, H_3, Ar, $^3J_{H_3-H_4} = 8.39$ Hz, $^4J_{H_3-F} = 5.29$ Hz), 6.81 (ddd, H_4, Ar, $^3J_{H_4-F} = 8.39$ Hz), 3.41 (s, 2H, CH_2N), 2.28 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 172.46, 155.54 ($^1J_{C-F} = 237.73$ Hz), 142.72, 129.32 ($^3J_{C-F} = 6.56$ Hz), 124.29 ($^2J_{C-F} = 17.28$ Hz), 113.21 ($^2J_{C-F} = 21.13$ Hz) (C_6H_3), 66.35 (CH_2N), 45.09 (NMe_2).

4.2.4. $Hg\{C_6H_2(OCH_3)_2\text{-}2,3CH_2NMe_2\text{-}6\}_2$ *(1e)*

Complex **1e** was obtained using a work-up similar to that described for **1b** except that *N,N*-dimethylaminomethyl-1-dimethoxy-3,4-benzene (4.48 g, 23 mmol) was reacted with n-butyllithium (15.6 ml, 25 mmol) (yield of the Li derivative: 20.3 mmol, 89%) and $HgCl_2$ (2.76 g, 10.15 mmol) giving **1e** as white crystals

(4.36 g, 73%). Anal. Calc. for $C_{22}H_{32}HgN_2O_4$: C, 44.85; H, 5.47; N, 4.75. Found: C, 45.33; H, 5.72; N, 4.73%. ^{1}H NMR ($CDCl_3$): δ 7.02, 6.73 (AB system, H_4 and H_5, Ar, $^3J_{H_4-H_5}$ = 8.00 Hz), 3.86 (s, 6H, OMe), 3.38 (s, 2H, CH_2N), 2.21 (s, 6H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 160.90, 153.98, 151.58, 139.82, 124.15, 110.59 (C_6H_2), 66.41 (CH_2N), 60.65, 55.61 (OMe), 45.03 (NMe_2).

4.3. Synthesis of the Mo complexes

4.3.1. *[(η^5-C_5H_5)Mo($C_6H_4CH_2NMe_2$-2)(I)(NO)] (2a)*

To a suspension of 2.00 g (2.24 mmol) of [{(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] in 50 ml of CH_2Cl_2, Hg(dmba)$_2$ (1.06 g, 2.24 mmol) was added. The mixture was stirred for 3 d at room temperature and then filtered. The resulting dark red filtrate was concentrated (3 ml) and then hexane (40 ml) was added, precipitating of **2a** an orange solid, which was filtered off and dried *in vacuo*. The yield was quantitative (2.03 g). Anal. Calc. for $C_{14}H_{17}IMoN_2O$: C, 37.19; H, 3.79; N, 6.19. Found: C, 37.04; H, 3.68; N, 6.03%. IR (CH_2Cl_2): 1664 cm^{-1} (vs. N≡O). ^{1}H NMR ($CDCl_3$): δ 7.46 (d, H_6, Ar, $^3J_{H-H}$ = 6.90 Hz), 7.18–7.05 (m, 3H, Ar), 5.70 (s, C_5H_5), 4.29, 3.70 (AB system, CH_2N, $^2J_{H-H}$ = 13.40 Hz), 3.19 (s, 3H, NMe_2), 2.68 (s, 3H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.12, 143.69, 140.32, 127.25, 125.32, 123.84 (C_6H_4), 102.06 (C_5H_5), 74.86 (CH_2N), 57.75, 52.76 (NMe_2).

4.3.2. *[(η^5-C_5H_5)Mo{C_6H_2-(OCH_2O)-2,3-CH_2NMe_2-6}(I)(NO)] (2b)*

Complex **2b** was obtained using a work-up similar to that used for **2a**: 1.00 g (1.12 mmol) of {(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] reacts with 0.626 g (1.12 mmol) of Hg{C_6H_2-(OCH_2O)-2,3-CH_2NMe_2}$_2$ to give **2b** as an orange solid. The yield was 1.02 g (95%). Anal. Calc. for $C_{15}H_{17}IMoN_2O_3$: C, 36.31; H, 3.45; N, 5.64. Found: C, 36.21; H, 3.54; N, 5.35%. IR (CH_2Cl_2): 1663 cm^{-1} (vs, N≡O). ^{1}H NMR ($CDCl_3$): δ 6.69 (dd, H_5, Ar, $^3J_{H_4-H_5}$ = 7.61 Hz, $^4J_{H_5-CH_2N}$ = 0.97 Hz), 6.56 (d, H_4, Ar), 5.95 and 5.92 (AB system, O_2CH_2, $^2J_{H-H}$ = 1.35 Hz), 5.83 (C_5H_5), 4.19, 3.63 (AB system, CH_2N, $^2J_{H-H}$ = 13.02 Hz), 3.18 (s, 3H, NMe_2), 2.73 (s, 3H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 154.94, 144.25, 137.59, 116.76, 105.74, 103.76 (C_6H_2), 102.12 (C_5H_5), 99.98 (O_2CH_2), 74.93 (CH_2N), 57.80, 52.76 (NMe_2).

4.3.3. *[(η^5-C_5H_5)Mo-{C_6H_3-(Me)-5-CH_2NMe_2-2}-(I)(NO)] (2c)*

Complex **2c** was obtained using a work-up similar to that used for **2a**: 1.00 g (1.12 mmol) of [(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] reacts with 0.56 g (1.12 mmol) of Hg{C_6H_3-(Me)-3-CH_2NMe_2}$_2$ to give **2c** as an orange solid. The yield was quantitative. Anal. Calc. for $C_{15}H_{19}IMoN_2O$: C, 38.64; H, 4.11; N, 6.01. Found: C, 38.53; H, 4.19; N, 5.73%. IR (CH_2Cl_2 solution): 1656 cm^{-1} (vs, N≡O). ^{1}H NMR ($CDCl_3$): δ 7.27 (s, 1H, H_6), 7.05 (d, 1H, H_4, $^3J_{H_4-H_3}$ = 7.48 Hz), 6.87 (dd, 1H, H_3, $^4J_{H_3-CH_2N}$ = 0.66 Hz), 5.70 (C_5H_5), 4.25 and 3.66 (AB system, CH_2N, $^2J_{H-H}$ = 13.35 Hz), 3.17 (s, 3H, NMe_2), 2.67 (s, 3H, NMe_2), 2.31 (s, 3H, Me-5). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 167.12, 140.96, 140.52, 136.56, 126.19, 123.42 (C_6H_3), 101.92 (C_5H_5), 74.62 (CH_2N), 57.69, 52.64 (NMe_2), 21.36 (Me-5).

4.3.4. *[(η^5-C_5H_5)Mo(C_6H_3F-5-CH_2NMe_2-2)(I)(NO)] (2d)*

Complex **2d** was obtained using a work-up similar to that used for **2a**: 1.00 g (1.12 mmol) of [{(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] [2] reacts with 0.57 g (1.12 mmol) of Hg{C_6H_3F-3-CH_2NMe_2}$_2$ to give **2d** as an orange solid. The yield was 0.95 g (94%). Anal. Calc. for $C_{14}H_{16}FIMoN_2O$: C, 35.76; H, 3.43; N, 5.95. Found: C, 36.23; H, 3.53 N, 5.72%. IR (CH_2Cl_2): 1658 cm^{-1} (vs. N≡O). ^{1}H NMR ($CDCl_3$): δ 7.18 (dd, H_6, 1H, $^3J_{H_6-F}$ = 8.64 Hz, $^4J_{H_6-H_4}$ = 2.53 Hz), 7.13 (ddd, H_3, 1H, $^3J_{H_3-H_4}$ = 8.35 Hz, $^4J_{H_3-F}$ = 5.21 Hz, $^4J_{H_3-CH_2N}$ = 0.86 Hz), 6.74 (dt, 1H, H_4, $^3J_{H_4-F}$ = 8.35 Hz), 5.70 (C_5H_5), 4.24, 3.69 (AB system, CH_2N, $^2J_{H-H}$ = 13.38 Hz), 3.18 (s, 3H, NMe_2), 2.67 (s, 3H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.61, 139.05, 126.11 ($^2J_{C-F}$ = 18.24 Hz), 124.49 ($^3J_{C-F}$ = 6.96 Hz), 112.16 ($^2J_{C-F}$ = 22.33 Hz) (C_6H_3), 102.11 (C_5H_5), 74.18 (CH_2N), 57.77, 52.67 (NMe_2).

4.3.5. *[(η^5-C_5H_5)Mo{$C_6H_2(OCH_3)_2$-2,3-CH_2NMe_2-6}(I)(NO)] (2e)*

To a suspension of 0.89 g (1 mmol) of [{(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] [2] in 50 ml of CH_2Cl_2, 0.59 g (1.12 mmol) of Hg{$C_6H_2(OCH_3)_2$-2,3-CH_2NMe_2}$_2$ was added, the mixture was stirred for 4 d at room temperature and then filtered. The resulting dark-red solution was evaporated to small volume (2 ml) and chromatographed over Al_2O_3 using CH_2Cl_2 as eluant. A deep red band developed, which was collected, evaporated to small volume and layered with hexane. Red crystals of (**2e**)–0.5CH_2Cl_2 were obtained after 7 d at −30°C. The yield was 0.154 g (15%). Anal. Calc. for $C_{16}H_{21}IMoN_2O_3 \cdot 0.5CH_2Cl_2$: C, 35.72; H, 3.99; N, 5.05. Found: C, 35.97; H, 4.00; N, 4.81. IR (CH_2Cl_2): 1662 cm^{-1} (vs. N≡O). ^{1}H NMR ($CDCl_3$): δ 6.90 (dd, 1H, H_5, $^3J_{H_4-H_5}$ = 8.00 Hz, $^4J_{H_5-CH_2N}$ = 0.68 Hz), 6.70 (d, 1H, H_4), 5.80 (C_5H_5), 4.21, 3.68 (AB system, CH_2N, $^2J_{H-H}$ = 13.29 Hz), 4.00 (s, 3H, OMe), 3.85 (s, 3H, OMe), 3.18 (s, 3H, NMe_2), 2.77 (s, 3H, NMe_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 158.47, 155.57, 151.28, 136.58, 118.60, 110.43 (C_6H_2), 102.57 (C_5H_5), 74.87 (CH_2N), 61.82 (OMe), 57.80 (NMe_2), 55.57 (OMe), 52.71 (NMe_2).

4.3.6. (SPY-5-15-C)-[(η^5-C_5H_5)Mo{S-C_6H_4CH(Me)-NMe_2-2}(I)(NO)] (2f) and (SPY5-15-A)-[(η^5-C_5H_5)-Mo{S-C_6H_4CH(Me)NMe_2-2}(I)(NO)] (2g)

To a suspension of 2.00 g (2.24 mmol) of [{(η^5-C_5H_5)Mo(μ-I)(I)(NO)}$_2$] [2] in 40 ml of CH_2Cl_2 was added Hg{S-C_6H_4CH(Me)NMe_2-2}$_2$ (1.12 g, 2.24 mmol). The mixture was stirred at room temperature for 4 d and then filtered. The resulting dark-red solution was concentrated to small volume (5 ml). Addition of hexane (40 ml) afforded a mixture (**2f**/**2g** 1 : 1 ratio) as an orange solid which was filtered off and dried in vacuo. The yield quantitative (2.09 g). Anal. Calc. For $C_{15}H_{19}IMoN_2O$: C, 38.64; H, 4.11; N, 6.01). Found: C, 38.60; H, 4.04; N, 6.28%.

4.4. Resolution of complexes 2f and 2g

The mixture was dissolved in the minimal amount of CH_2Cl_2. The resulting solution was carefully layered with hexane and kept at −30°C. After 1 week, complex **2f** crystallized as deep-orange blocks, while complex **2g** crystallized as pale orange plates, which quickly lost their transparency on exposure to air.

Table 3
Crystal data and details for the structure determinations of complexes **2b**

Crystal data		
Formula	$C_{15}H_{18}IMoN_2O_3$ (**2b**)	$C_{15}H_{19}IMoN_2O$ (**2f**)
Molecular wt.	497.2	466.2
Colour	Orange	Orange
Cryst. Syst.	Orthorhombic	Orthorhombic
Space Group	$Pca2_1$ (n° 29)	$P2_12_12_1$ (n° 19)
a (Å)	20.258(6)	10.590(3)
b (Å)	7.706(2)	10.614(3)
c (Å)	10.762(3)	14.495(4)
V (Å^3)	1680.1	1629.3
Z	4	4
D_{calc} (g cm^{-3})	1.965	1.900
μ (cm^{-1})	25.928	26.588
Cryst. size (mm)	0.24×0.24×0.20	0.30×0.25×0.20
Data collection		
T (K)	293	293
θ_{min}, θ_{max}	2, 30	2, 27
Radiation	MoKα [a]	MoKα [a]
Wavelength (Å)	0.7107	0.7107
$\Delta\omega$ (deg)	0.97+0.34 tan θ	1.25+0.34 tan θ
Total n° of data	2914	2051
Observed data	2098 [$I > 3\sigma(I)$]	1566 [$I > 3\sigma(I)$]
Octants	$+h$ $+k$ $+l$	$+h$ $+k$ $+l$
Refinement		
Final R (F), R_w (F)	0.036, 0.057	0.031, 0.055
GOF	1.140	1.154
p	0.08	0.08
min/max abs	0.93/1.00	0.84/1.00

[a] Graphite monochromated.

Table 4
Atomic coordinates for compound **2b** [a]

Atom	x	y	z	B (Å^2)
I	0.98345(3)	0.68773(9)	0.754	4.03(1)
Mo	0.86881(3)	0.76970(8)	0.8996(1)	2.282(8)
O1	0.6979(3)	0.6536(9)	0.9187(8)	4.2(1)
O2	0.6008(4)	0.807(1)	0.9096(9)	4.7(2)
O3	0.8042(4)	0.532(1)	0.7227(6)	4.1(1)
N1	0.8881(4)	1.052(1)	0.8270(7)	3.0(1)
N2	0.8303(4)	0.633(1)	0.7884(6)	2.9(1)
C1	0.7736(3)	0.9024(9)	0.9034(9)	2.7(1)
C2	0.7124(4)	0.829(1)	0.908(1)	3.0(1)
C3	0.6540(4)	0.918(1)	0.903(1)	3.6(2)
C4	0.6539(4)	1.096(1)	0.886(1)	4.2(2)
C5	0.7155(5)	1.175(1)	0.883(1)	4.2(2)
C6	0.7732(4)	1.0810(9)	0.8906(9)	3.0(1)
C7	0.6278(4)	0.639(2)	0.928(1)	4.3(2)
C8	0.8407(5)	1.165(1)	0.892(1)	3.7(2)
C9	0.8744(6)	1.065(1)	0.690(1)	4.0(2)
C10	0.9563(6)	1.118(1)	0.850(1)	4.7(2)
C11	0.8987(6)	0.845(2)	1.111(1)	4.6(2)
C12	0.9431(5)	0.717(1)	1.067(1)	3.7(2)
C13	0.9064(5)	0.569(1)	1.038(1)	3.9(2)
C14	0.8394(6)	0.599(2)	1.0674(9)	4.1(2)
C15	0.8361(6)	0.773(2)	1.108(1)	5.0(2)

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

4.4.1. (SPY-5-15-C)-[(η^5-C_5H_5)Mo{S-C_6H_4CH(Me)-NMe_2-2}(I)(NO)] (2f)

IR (CH_2Cl_2): 1654 cm^{-1} (vs. N≡O). ^{1}H NMR ($CDCl_3$): δ 7.50 (dd, H_6, 1H, $^3J_{H_6-H_5}$ = 7.23 Hz,

Table 5
Atomic coordinates for compound **2f** [a]

Atom	x	y	z	B (Å^2)
Mo	0.77807(7)	0.78391(7)	0.15900(5)	2.77(1)
I	0.55782(6)	0.62915(8)	0.14815(5)	4.95(1)
C1	0.9696(8)	0.7964(9)	0.2097(7)	3.5(2)
C2	1.0764(9)	0.7884(9)	0.1542(8)	4.3(2)
C3	1.1994(9)	0.794(1)	0.1893(9)	4.7(2)
C4	1.2154(9)	0.812(1)	0.2832(9)	4.7(2)
C5	1.115(1)	0.8192(9)	0.3397(8)	4.4(2)
C6	0.988(1)	0.810(1)	0.3054(7)	4.0(2)
C7	0.874(1)	0.819(1)	0.3626(6)	4.2(2)
C8	0.897(1)	0.791(1)	0.4671(6)	6.3(3)
N1	0.7695(8)	0.7415(8)	0.3187(5)	3.6(2)
C9	0.792(1)	0.604(1)	0.3338(6)	4.4(2)
C10	0.646(1)	0.775(1)	0.3607(7)	5.3(3)
N2	0.8428(7)	0.6646(7)	0.0880(5)	3.2(1)
O	0.882(1)	0.5957(7)	0.0307(6)	6.0(2)
C11	0.827(1)	0.946(1)	0.0622(8)	5.3(3)
C12	0.826(1)	1.0018(9)	0.1498(9)	4.6(2)
C13	0.703(1)	0.9978(9)	0.1839(9)	5.2(2)
C14	0.630(1)	0.942(1)	0.117(1)	6.9(3)
C15	0.704(1)	0.908(1)	0.0432(8)	6.5(3)

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

${}^4J_{H_6-H_4} = 1.64$ Hz), 7.20–7.05 (m, 3H, Ar), 5.69 (C_5H_5), 4.18 (q, 1H, **CH**(Me)N, ${}^3J_{H-H} = 6.58$ Hz), 3.33 (s, 3H, NMe_2), 2.51 (s, 3H NMe_2), 1.50 (d, 3H, CH(**Me**)N) ${}^{13}C\{{}^1H\}$ NMR ($CDCl_3$): δ 167.96, 147.24, 140.18, 127.52, 125.29, 124.65 (C_6H_4), 101.95 (C_5H_5), 72.80 (**C**H(Me)N), 53.76, 43.84 (NMe_2), 10.76 (CH(**Me**)N). $[\alpha]_D = +510°C$ ($c = 2.51$ mg ml^{-1} in CH_2Cl_2).

4.4.2. *(SPY-5-15-A)-[(η^5-C_5H_5)Mo{S-C_6H_4CH(Me)-NMe_2-2}(I)(NO)] (2g)*

IR (CH_2Cl_2): 1658 cm^{-1} (vs, N≡O). ${}^1H$ NMR ($CDCl_3$): δ 7.27 (dd, H_6, 1H, ${}^3J_{H_6-H_5} = 7.41$ Hz, ${}^4J_{H_6-H_4} = 1.30$ Hz), 7.12–7.04 (m, 3H, Ar), 5.79 (C_5H_5), 3.74 (q, 1H, **CH**(Me)N, ${}^3J_{H-H} = 6.78$ Hz), 3.09 (s, 3H, NMe_2), 2.95 (s, 3H NMe_2), 1.43 (d, 3H, CH(**Me**)N). ${}^{13}C\{{}^1H\}$ NMR ($CDCl_3$): δ 164.83, 150.34, 140.79, 126.90, 125.20, 123.59 (C_6H_4), 102.42 (C_5H_5), 79.56 (**C**H(Me)N), 56.58, 55.20 (NMe_2), 21.19 (CH(**Me**)N). $[\alpha]_D = -582°$ ($c = 2.75$ mg ml^{-1} in CH_2Cl_2).

4.5. *Structure determination and refinement for compounds **2b** and **2f***

Crystal data and numerical details of the structure determination are given in Table 3 while atomic coordinates are given in Tables 4 and 5. The crystals were mounted on a rotation-free goniometer head and transferred to an Enraf–Nonius CAD4-F automatic diffractometer for data collection at 293 K. The resulting data sets were transferred to a VAX computer, and for all the subsequent calculations the MOLEN / VAX package was used [14]. Three standard reflections measured every 1 h during the entire data collection periods showed no significant decay. The raw data were converted to intensities and corrected for Lorentz, polarization and absorption factors, the latter computed from the Ψ-scans of four reflections. The structures were solved using the heavy-atom method. Refinement were carried out by full least-squares techniques; $\sigma^2(F^2) = \sigma^2_{\text{counts}} + (pI)^2$. The absolute structures were determined by comparing (x, y, z) and $(-x, -y, -z)$ refinements. Final difference maps revealed no significant maxima. The scattering factor coefficients and anomalous dispersion coefficients come from Refs. [15a] and [15b], respectively.

5. Supplementary material available

Tables of atomic coordinates, bond lengths and angles and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Structure factors are available from the authors.

Acknowledgment

E.P.U. thanks the Comision Mixta, Caja de Ahorros de la Immaculada, Diputacion General de Aragon for a fellowship (ref. CB12/94).

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