



Synthesis, structure, and reactivity of $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$. Electron transfer behavior of a nitrosyl derivative

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ABSTRACT

The UV irradiation of a hexane solution of the complex $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_3$ (**1**) afforded the chelated species $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$ (**2**). The molecular structure of **2** has been determined by X-ray crystallography. The reaction of **2** with two-electron donor ligands yields $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2(\text{L})$ (**1**, L = CO; **3**, L = PMe₃). The chelated species **2** also reacts with MeOTf, HBF₄, and I₂ to form the cationic compounds *trans*- $[(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2\text{X}]^+$ (**[4]**)⁺, X = Me; **[5]**)⁺, X = H; **[6]**)⁺, X = I). The *trans* stereochemistry of **4–6** have been assigned on the basis of $\nu(\text{CO})$ IR intensities and ¹³C NMR spectroscopy. Also, complex **2** reacts with nitrosyl tetrafluoroborate to yield $[(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2\text{NO})\text{Re}(\text{CO})_2(\text{NO})\text{BF}_4]$ (**[7]**)²⁺. The redox behavior of the {ReNO}⁶ complex **[7]**²⁺ was studied and the products obtained after two-electron reduction were characterized by IR. DFT calculations were done to optimize the structure of **[7]**²⁺ and to study the effect of the sidearm coordination on the electronic structure of a cyclopentadienyl {ReNO}⁸ complex.

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Introduction

Transition-metal complexes with an amino group tethered on the cyclopentadienyl and tetramethylcyclopentadienyl ligands have been widely studied [1]. The amino-functionalized lateral side chain, under appropriate conditions, can intramolecularly stabilize electron-deficient metal centers in a reversible or an irreversible way, since the binding strength between the metal and the nitrogen donor ligand can be controlled sterically or electronically [2]. Complexes with pendant amino as well as amido groups attached to pentagonal rings have attracted considerable attention from a biological point of view [3] and in catalysis (olefin polymerization [4]). For example, the system CpTiCl₃/MAO (MAO = methylaluminoxane) is an almost inactive catalyst precursor for ethylene or propylene polymerization. However Rausch and col. [5] demonstrated that the

complex $(\eta^5:\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{NMe}_2)\text{TiCl}_3$ in the presence of MAO, is an efficient catalyst for the polymerization reactions mentioned above. On the other hands, Okuda and col. reported the synthesis of the amido-cyclopentadienyl complex $[(\eta^5:\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NCMe}_3)\text{Y}(\text{CH}_2\text{SiMe}_3)(\text{THF})]$ and its use as catalyst for polymerization of *tert*-butyl acrylate to give poly-*tert*-butyl acrylate in high yields [6]. Also this type of complexes containing Fe, Mo, Ca, Sm, etc. [7] were described in the literature. Regarding the group 7 metals, Wang and col. have reported the synthesis and reactions of some complexes of manganese [8] and rhenium [9]. As part of an ongoing research on substituted cyclopentadienyl rhenium complexes, in this work we describe the synthesis and reactivity of the unreported tetramethylcyclopentadienyl rhenium complex containing a dimethylaminoethyl sidearm $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_3$, the photochemical reaction of this compound leading to the chelate species $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$, the reactions of the latter with CO and PMe₃ to form Re(I) complexes $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2(\text{L})$ (L = CO, PMe₃) and the formation of oxidative addition products $[(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2(\text{R})]^+$ (R = Me, H, I). The analogous complexes without the

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methyl substituents in the cyclopentadienyl ring, $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_3$ and $(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$, were reported by Wang and col. [9a]. We are also including in this work the reaction of the chelated species with nitrosyl tetrafluoroborate to yield $[(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2\text{NO})\text{Re}(\text{CO})_2(\text{NO})]^{2+}[\text{BF}_4]^{-2}$, a $\{\text{ReNO}\}^6$ complex according to the Ene-mark–Feltham notation [10]. The analogous nitrosyl complex without the methyl substituents in the cyclopentadienyl ring was also reported by Wang and col. [9b]. However, the rather interesting electron transfer behavior was not studied. The interest in the $\{\text{ReNO}\}^6 \rightarrow \{\text{ReNO}\}^{7/8}$ conversion arises due to the presence of the amine, which leaves room for the possibility of complexes with different coordination number (depending on whether the amine arm is coordinated or not) that could lead to different electronic structures of the ReNO moiety [10].

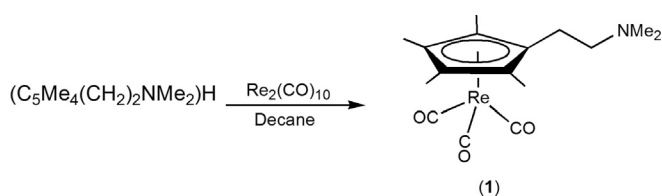
Results and discussion

Synthesis and characterization of $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$ (**2**)

Refluxing a decane solution of $\text{Re}_2(\text{CO})_{10}$ and $(\text{C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{H}$ under nitrogen atmosphere leads to the formation of the tricarbonyl complex $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_3$ (**1**) (Scheme 1), which can be isolated as a yellow oily solid in a moderate yield (55%).

This complex was stable in air and soluble in most organic solvents. The IR spectrum of **1** in hexane solution showed two absorption bands (in the carbonyl region) at 2013 and 1923 cm^{-1} . Identical frequencies have been reported for $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ [11] and $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)\text{L})\text{Re}(\text{CO})_3$ (L = PPh₂ [12], CH₂ [13], 2-C₄H₃S [14]); the presence of the dimethylaminoethyl sidearm does not alter the electron density on the rhenium. As expected, these absorption bands are shifted to lower wavenumbers when compared with those measured by Wang for the cyclopentadienyl analogs [9a]. The ¹H and ¹³C NMR spectra showed the expected resonances for the $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)$ ligand, which are similar to those reported for the complexes $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Co}(\text{CO})_2$ [15], $[(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Mo}(\text{CO})_2]_2$ [7] and $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{M}(\text{CO})_2$ (M = Rh, Ir) [16]. The fragmentation pattern observed in the mass spectrum is in good agreement with the proposed structure and resemble to the ones observed in related complexes [12–14].

Irradiation of complex **1** in hexane solution (room temperature and $\lambda = 300$ nm) gave the chelated complex $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$ (**2**) in moderate yield (44%), while a similar percentage of the starting tricarbonyl complex **1** remained unreacted. Much longer irradiation times did not increase the yield of the product; instead, significant amounts of an unidentified carbonyl-containing product was observed in the IR spectrum. Complex **2** was obtained as yellow needles soluble in polar solvents and stable in air as the solid and in solution. The IR spectrum showed two absorption bands (1880(s) and 1806(s) cm^{-1} corresponding to ν_{CO}), which are shifted to lower energy compared with



Scheme 1.

the precursor complex **1**, which is consistent with an increase of the electron density on rhenium due to the replacement of the acceptor ligand CO by the donor amino ligand. The $\Delta\nu$ is quite similar with that seen for the closely related complexes $(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_3$ and $(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$ reported by Wang et al. [9a].

The most significant feature of the ¹H NMR spectrum of **2** is a singlet at δ 3.32 assigned to the protons of the methyl groups of the *N,N*-dimethyl moiety, which appears 1.06 ppm downfield relative to those of complex **1**, a shift ($\Delta\delta$) that is almost identical with that reported for the cyclopentadienyl analogs [9a]. The ¹³C NMR spectrum of **2** showed, in addition to the signals of the C₅Me₄ and CO groups, resonances at δ : 25.2 and 80.0 assigned to methylene protons of the CH₂CH₂NMe₂ fragment, which were confirmed by 2D NMR (HMBC and HSQC). Both values are almost the same as those reported for the chelated complex of the cyclopentadienyl derivative [9a] and $[(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Fe}(\text{CO})_2]\text{BF}_4$ [7]. Further characterization of complex **2** was carried out by X-ray crystallography: the molecular structure of $(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})_2$ (**2**) is shown in Fig. 1 and the most relevant bond distances and angles are given in Table 1.

This mononuclear complex, exhibits a three-legged piano-stool type structure, where the two basal positions are occupied by carbonyl groups and the third is used for the nitrogen atom of the *N,N*-dimethylamino-ethyl-sidearm.

The Re–N bond length (2.223(4) Å) of **2** is similar to that measured in the complex $[(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMeH})\text{Re}(\text{CO})(\text{H})(\text{N}^t\text{BuH}_2)]^+$ (2.21 Å) [9f], but slightly longer than that found in $(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^{2+}$ (2.177 Å) [9b], $(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\eta^2\text{-CO}_2)$ (2.165 Å) [9d], and $[(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMeCH}_2\text{PPh}_2)\text{Re}(\text{CO})(\text{H})]^{2+}$ (2.146 Å) [9g].

The alkyl tether is bent down 11.1° from the cyclopentadienyl ring toward rhenium, an angle close to those reported for $[(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMeH})\text{Re}(\text{CO})(\text{H})(\text{N}^t\text{BuH}_2)]^+$ and $(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^{2+}$, 8.2° and 13.7°, respectively [9f,b]. The torsion angle $-2.1(4)^\circ$ of N(1)–Re–C(1)–C(10) is similar to that reported for $[(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^{2+}$, and it indicates that the Re–N(1) and C(1)–C(10) bonds are coplanar. Both the Re–C bond distances (1.897(6) and 1.875(6) Å) and Re–C–O angles (175.27° and 177.26°) are in good agreement with those reported for other dicarbonyl rhenium(I) complexes with a coordinated functionality [12–15].

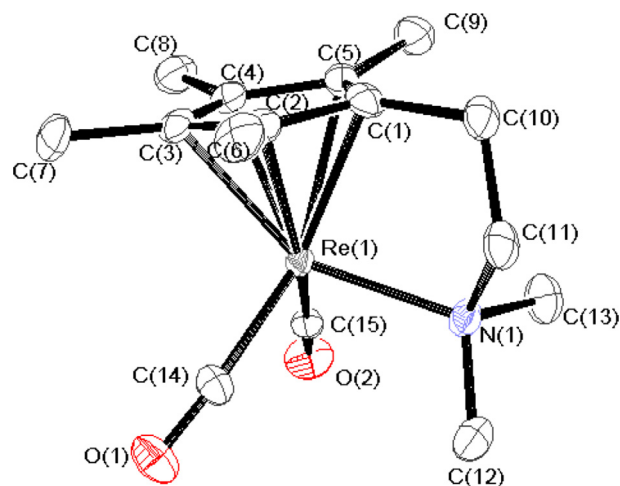


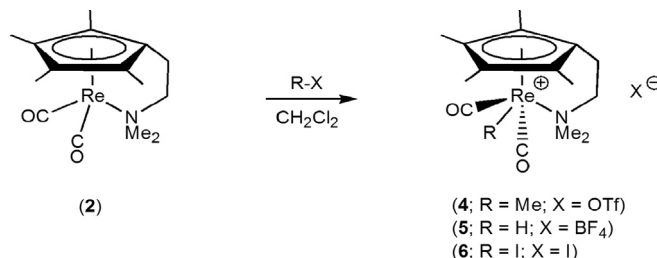
Fig. 1. ORTEP plot of complex **2** at 50% probability level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (deg) for complex **2**.

Re(1)–N(1)	2.223(4)
Re(1)–C(14)	1.897(6)
Re(1)–C(15)	1.875(6)
Re(1)–C ^a	1.931(2)
C(14)–O(1)	1.160(7)
C(15)–O(2)	1.185(7)
C(1)–C(10)	1.505(8)
C(10)–C(11)	1.514(8)
C(11)–N(1)	1.511(6)
C(14)–Re(1)–C(15)	88.2(2)
Re(1)–N(1)–C(11)	106.4(3)
N(1)–C(11)–C(10)	112.0(5)
C(1)–C(10)–C(11)	110.8(5)

Bold signifies bond distances.

^a G = centroid (C₅Me₄CH₂).



Scheme 3.

respect to thermal isomerization. The presence of the dimethylaminoethyl-tetramethylcyclopentadienyl ligand coordinated to rhenium in an $\eta^5:\eta^1$ -fashion was unequivocally established by ¹H, ¹³C and 2D NMR spectroscopy.

The IR spectra of compounds [**4–6**]⁺ showed two $\nu(\text{CO})$ absorptions in the CO region. The relative intensity of these absorptions is typical for a *trans* arrangement of the two CO groups in a four-legged piano-stool type of structure *i.e.* the higher wavenumber absorption being much less intense than the other. As expected, the two $\nu(\text{CO})$ absorption bands are shifted to much higher frequencies when compared to those observed for the precursor compound **2**, as a result of reduction of the electron density at the Re(III) center in complexes [**4–6**]⁺. Similar features were observed for the complexes [($\eta^5:\eta^1$ -C₅H₄(CH₂)₂NMe₂)Re(CO)₂] and [($\eta^5:\eta^1$ -C₅H₄(CH₂)₂NMe₂)Re(CO)₂Br]⁺ [9d].

The ¹³C NMR spectra of [**4–6**]⁺ exhibited only one singlet for the CO groups magnetically equivalent around 200 ppm, in good agreement with the *trans* stereochemistry proposed.

The ¹H NMR spectra of the methyl derivative [**4**]⁺ exhibit one singlet at 0.76 ppm, attributed to the methyl group bound to the rhenium fragment, this chemical shift is quite similar to those reported for the complexes *trans*-[($\eta^5:\eta^1$ -C₅Me₄CH₂PPh₂)Re(CO)₂(Me)]⁺ [11] and *trans*-(η^5 -C₅Me₅)Re(CO)₂(Me)(I) [18].

The ¹H NMR spectra of the hydride complex [**5**]⁺ showed a singlet at –8.31 ppm for the hydride ligand, which is also in agreement with those reported for related functionalized cyclopentadienyl rhenium complexes [12,9g].

Synthesis and characterization of [($\eta^5:\eta^1$ -C₅Me₄(CH₂)₂NMe₂NO)Re(CO)₂(NO)]²⁺ (**7**)²⁺

The chelated species **2** reacts with two equivalents of NOBF₄ in acetonitrile under nitrogen atmosphere to give [**7**]²⁺. As had been reported previously for the reaction of (η^5 -C₅H₄(CH₂)₂NMe₂)Re(CO)₃ with nitrosyl tetrafluoroborate [9b], two equivalents are required. It is not unlikely that the amino group is partially uncoordinated in **2** when dissolved in a coordinating solvent as acetonitrile. Then one equivalent of NOBF₄ presumably reacts with the free amino group to form an N-nitrosonium adduct and the second equivalent reacts with the rhenium fragment to give the nitrosyl derivative [(η^5 -C₅Me₄(CH₂)₂NMe₂(NO))Re(CO)₂(NO)]²⁺[BF₄]^{–2}. The IR spectrum in solid state (film) showed the presence of two strong absorption bands shifted to higher frequency, at 2098 and 2041 cm^{–1}, assigned to ν_{CO} , and one strong and broader band at 1796 cm^{–1}, assigned to ν_{NO} . This values are very similar to those reported for the pentamethyl complex [(η^5 -C₅Me₅)Re(CO)₂(NO)]⁺PF₆[–] [19], and they are 15–20 cm^{–1} lower than the frequencies reported for [(η^5 -C₅H₄(CH₂)₂NMe₂(NO))Re(CO)₂(NO)]²⁺[BF₄]₂ [9b], which is consistent with the greater donation ability of the tetramethyl ring in complex [**7**]²⁺, as compared to the unsubstituted analogous. The assignment of the NO stretching band was confirmed by preparing the ¹⁵N enriched

Reaction of the complex ($\eta^5:\eta^1$ -C₅Me₄(CH₂)₂NMe₂)Re(CO)₂ (**2**) with two-electron donor ligands

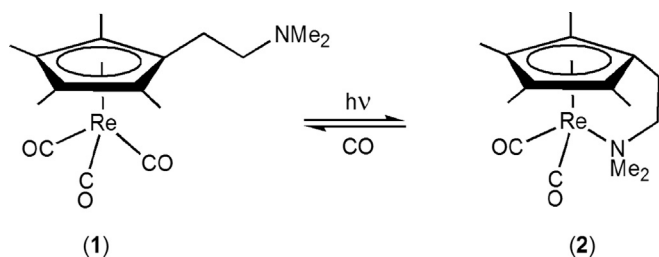
With the aim to explore the lability of the dimethylamino group coordinated to the rhenium fragment, we decided to study the reaction of complex **2** with CO (500 psi), the unchelated compound **1**, was the only product formed in quantitative yield (Scheme 2).

The lability of the amino ligand in compound **2** is not surprising, since it has been previously observed in the complexes ($\eta^5:\eta^1$ -C₅Me₄(CH₂)₂NMe₂)M(I)₂ (M = Co, Rh, Ir) which under carbon monoxide atmosphere form the carbonyl complexes (η^5 -C₅Me₄(CH₂)₂NMe₂)M(I)₂(CO) [15,16]. Furthermore complex **2** was treated with excess of PMe₃ to afford the species (η^5 -C₅Me₄(CH₂)₂NMe₂)Re(CO)₂(PMe₃) (**3**) quantitatively. The IR spectra of **3** showed two absorption bands, shifted to higher frequencies when compared to those of the starting material. The trimethylphosphine derivative **3** showed almost the same IR (in the carbonyl region) and ³¹P NMR spectra as those reported for their unsubstituted analog (η^5 -C₅Me₅)Re(CO)₂PMe₃ [17] and related functionalized complexes (η^5 -C₅Me₄CH₂L)Re(CO)₂(PMe₃) (L = CH₂CH(CH₂), 2-C₄H₃S, PPh₂) [12,13]. On the other hand, when a solution of complex **2** in chloroform-d₃ was loaded with ethylene at 150 psi (Wilmad[®] quick pressure valve NMR tube), the ¹H NMR spectrum did not show displacement of the coordinated sidearm after 4 h and complex **2** was recovered.

Oxidative addition reactions to ($\eta^5:\eta^1$ -C₅Me₄(CH₂)₂NMe₂)Re(CO)₂ (**2**)

While the reaction of **2** with two electron donor ligands produced Re(I) complexes, reaction of this complex with MeOTf, HBF₄ and I₂ yielded Re(III) cationic complexes *trans*-[($\eta^5:\eta^1$ -C₅Me₄(CH₂)₂NMe₂)Re(CO)₂(R)]⁺ (**4**)⁺ R = Me; **5**)⁺ R = H; **6**)⁺ R = I) (Scheme 3).

These complexes are insoluble in non polar solvents, but dissolve in CHCl₃, CH₂Cl₂ and CH₃CN, in which they are stable with



Scheme 2.

compound, which shows the NO band at 1763 cm^{-1} , with the expected isotope shift. The IR spectra of **2** and $[7]^{2+}$ are shown in Fig. S1 (Supporting information). As a side product of this reaction, which is obtained in variable amounts from 5 to 30%, there is a complex with only one ν_{CO} at 1980 cm^{-1} and ν_{NO} at 1710 cm^{-1} , which was tentatively identified as the complex $[(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^+$, **[8]**⁺. The much lower frequencies as compared with $[7]^{2+}$ are consistent with the more electron rich rhenium center in **[8]**⁺, due to the replacement of the acceptor ligand CO by the donor amino ligand. The analogous complex with the cyclopentadienyl ligand, $[(\eta^5:\eta^1\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^+$, shows bands at 2006 and 1743 cm^{-1} in CH_3CN [9b], at higher frequencies than **[8]**⁺, which is consistent with the greater donation ability of the tetramethyl ring in complex **[8]**⁺.

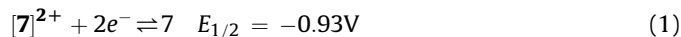
As the reported $\{\text{ReNO}\}^6$ complex $[(\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2\text{NMe}_2(\text{NO}))\text{Re}(\text{CO})_2(\text{NO})]^{2+}(\text{BF}_4^-)_2$ was only characterized by IR [9b], we decided to further characterize the analogous complex $[7]^{2+}$. Since suitable crystals of $[7]^{2+}$ for X-ray analysis could not be obtained, we performed DFT calculations (Fig. 2).

The lineal arrangement of the ReNO moiety is typical of $\{\text{MNO}\}^6$ complexes and is consistent with a predominant Re^1NO^+ character, as have been observed for similar $\{\text{ReNO}\}^6$ complexes with cyclopentadienyl ligands [9b,20]. The N–N distance between the amine and the nitrosonium group is 1.948 \AA . For the structure shown in Fig. 2, four IR bands of equal intensity are predicted; 2093 and 2039 cm^{-1} , due to ν_{CO} (in excellent agreement with the experimental data) and 1956 and 1887 cm^{-1} , due to ν_{NO} . For other optimized structure of $[7]^{2+}$, in which the NO moiety linked to the amine is closer to the metal center, only one NO band is predicted, at 1892 cm^{-1} . That structure is only 3 kcal/mol higher in energy than the structure in Fig. 2, so it cannot be ruled out as a stable form of $[7]^{2+}$, and is consistent with the experimental IR data that shows only one NO band. Anyway, DFT calculations generally fail to accurately reproduce the electronic distribution in MNO moieties and so reliable ν_{NO} frequencies are difficult to obtain. On the other hand, the experimental NO band at 1796 cm^{-1} is quite broad and could be the result of two close modes. Moreover, the ^{15}N NMR spectrum shows two signals at $+1.8$ and $+4.6\text{ ppm}$ vs CH_3NO_2 , values that are in the range expected for NO moieties with NO^+ character, as the ones in $[7]^{2+}$ [21]. The spectrum also shows a signal at $+119.8\text{ ppm}$, that was assigned to complex **[8]**⁺, obtained always as an impurity in the syntheses of $[7]^{2+}$. Also we can confirm the divalent nature of $[7]^{2+}$ (that indicates the presence of two NO^+ fragments) from the ^1H NMR of $[7]^{2+}(\text{BARF}^-)_2$ ($\text{BARF}^- = \text{Tetrakis}(3,5\text{-trifluoromethyl})$

phenylborate) (Fig. S2), in which the integral relation between the $[\text{BARF}]^-$ signals and the ones of the cyclopentadienyl ligand indicates the presence of two counterions $[\text{BARF}]^-$ per complex.

Redox behavior of $[7]^{2+}$

Fig. 3 shows a typical voltammogram of $[7]^{2+}$, with a first quasi-reversible reduction at -0.93 V . The separation of only 30 mV between the cathodic and the anodic waves indicates a two-electron process, represented by Equation (1).



The next two observed processes could be due to further reductions of **7**, or reductions of products generated after the electron transfer, since the couple $[7]^{2+}/7$ is not fully reversible.

In line with the two-electron reduction at $E_{1/2} = -0.93\text{ V}$, when a solution of $[7]^{2+}$ in CH_3CN reacts with only one equivalent of the one-electron reductant cobaltocene ($E_{1/2} = -1.33\text{ V}$), only partial conversion is observed by IR (Fig. 4). On the other hand, when two equivalents of the reductant are added, the bands attributed to $[7]^{2+}$ disappear. Moreover, the EPR spectrum recorded after the addition of one equivalent of reductant shows no signal, consistent with the absence of paramagnetic products that would arise from a one-electron reduction.

All bands observed in Fig. 4 were assigned to products of decomposition of the two-electron reduction product **7** and none of them were attributed to **7**, in spite of the quasi-reversibility observed in the cyclic voltammetry.

The bands at 2097 , 2042 (ν_{CO}) and 1802 cm^{-1} (ν_{NO}) are due to the presence of $[7]^{2+}$ in solution showing that with 1 equivalent of reductant the reaction is not complete. The bands at 1880 and 1803 cm^{-1} are assigned to the non-nitrosyl complex **2**, that could be a decomposition product of **7** by loss of two NO molecules. Then, the bands at 2005 and 1910 cm^{-1} are attributed to the tricarbonyl complex **1**. The formation of the tricarbonyl complex **1** from the dicarbonyl **7** implies that a complex with less than two CO ligands should also be formed, to account for the mass balance. In fact, the bands at 1980 and 1710 cm^{-1} in Fig. 4 are the same as the ones observed for the byproduct of the reaction of **2** with NOBF_4 , that was identified as the complex with only one CO and one NO, $[(\eta^5:\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{NMe}_2)\text{Re}(\text{CO})(\text{NO})]^+$ (**[8]**⁺).

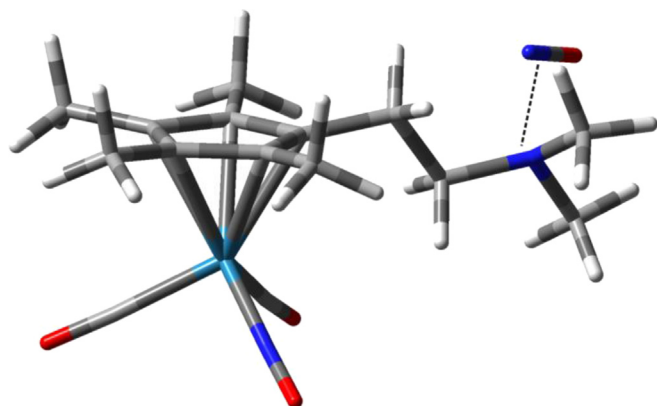


Fig. 2. DFT optimized structure of complex $[7]^{2+}$.

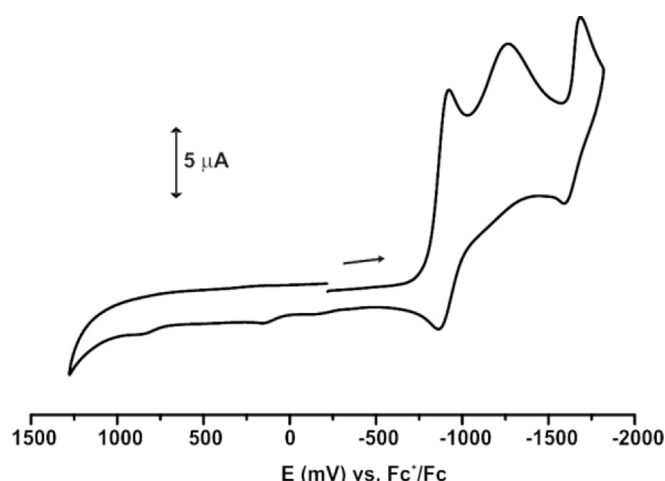


Fig. 3. Cyclic voltammogram of 7^{2+} in $\text{CH}_3\text{CN}/0.1\text{ M Bu}_4\text{NPF}_6$ at 100 mV/s scan rate.

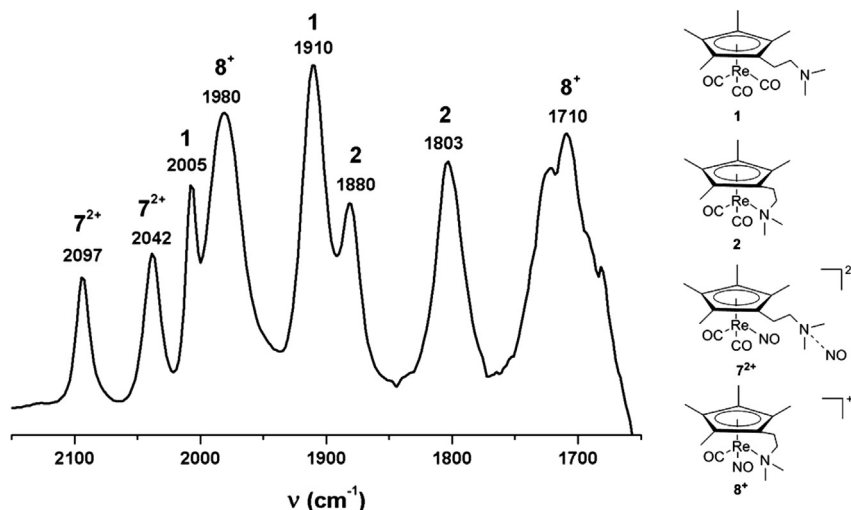


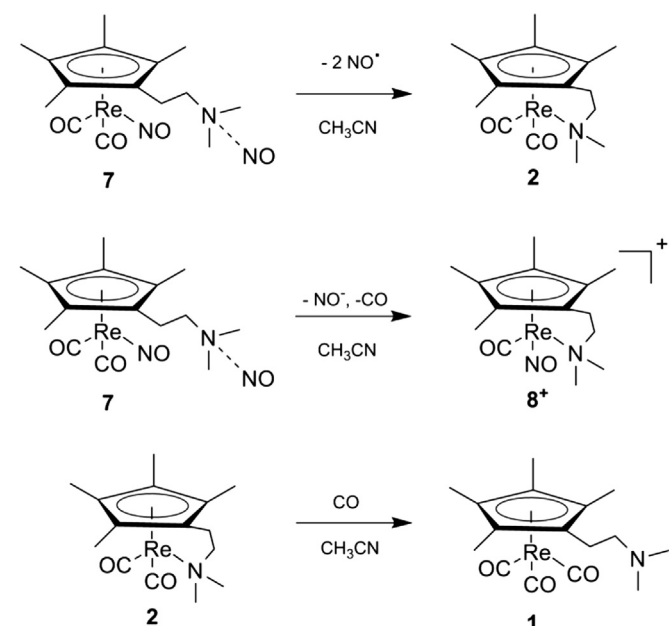
Fig. 4. IR spectrum obtained after the addition of 1 equivalent of cobaltocene to an acetonitrile solution of $[7]^{2+}$.

The presence of complexes **1** and **2** was also confirmed by NMR. The proposed reactions explaining the formation of **1**, **2** and $[8]^+$ after the electron transfer are shown in Scheme 4.

We also performed an IR spectroelectrochemistry experiment in the same solvent at a potential lower than -0.93 V (Fig. 5), observing the same spectral changes as in the chemical reduction.

DFT calculations on a $\{ReNO\}^8$ complex: different electronic structures depending on the sidearm coordination

One of the most interesting aspects of $\{MNO\}^n$ complexes is the ability to adopt very different electronic structures between the three limiting (M^n-NO , $M^{n+1}-NO^-$, and $M^{n-1}-NO^+$) and countless intermediate states. It is known that the coordination number of the $\{MNO\}^n$ complex plays an important role and, for example, the addition of a ligand to bipyramidal five-coordinate [22] or square-planar four-coordinate [23] $\{MNO\}^8$ complexes induces a



Scheme 4.

dramatic change in the electronic structure from $M^{n-1}-NO^+$ to $M^{n+1}-NO^-$. In this sense, it is particularly interesting to explore the influence of the coordination of the sidearm on the electronic structure of a cyclopentadienyl $\{ReNO\}^8$ complex. To do this we performed DFT calculations on the $\{ReNO\}^8$ complex $[8]^-$, since as it bears only one CO ligand, it leaves room for the sidearm coordination. In fact, the $\{ReNO\}^6$ precursor, $[8]^+$, would present the amine sidearm coordinated to fulfill the 18-electron rule. The question is if the amine remains coordinated in the $\{ReNO\}^8$ form. Fig. 6 shows the DFT optimized structures for the $\{ReNO\}^6$ complex $[8]^+$ and for two isomers of the $\{ReNO\}^8$ form $[8]^-$ (with and without amine coordination).

As with other $\{MNO\}^8$ complexes, the electronic structure of $[8]^-$ is highly sensitive to the presence of the amine ligand. The form without amine coordination shows a lineal $ReNO$ moiety (Table 2) and is best described as $Re^{-1}NO^+$. On the other hand, when the amine is coordinated, the complex shows a highly bent $ReNO$ unit, with typical parameters of NO^- complexes (longer $Re-N$ and $N-O$ bonds, and much lower ν_{NO} frequency, Table 2), so the complex is best described as $Re^{+1}NO^-$.

In the case of the $\{ReNO\}^6$ complex, there was not considerable change in the electronic structure due to the amine coordination: both forms (with and without amine) are described as $Re^{+1}NO^+$ and the ν_{NO} frequencies differ only by 20 cm^{-1} . In this case, the most stable form is the one with amine coordination (by 43 kcal/mol) and is the one shown in Fig. 6. This is not surprising since the complex without amine coordination is unsaturated (16-electron). Conversely, in the case of the $\{ReNO\}^8$ complex, the most stable form is the one without amine coordination (by 25 kcal/mol), which means that the sidearm would be expelled in the $\{ReNO\}^6 \rightarrow \{ReNO\}^8$ conversion, reflecting the hemilability of the $C_5R_4(CH_2)_2NMe_2$ ligand.

Conclusions

The tricarbonyl complex **1** reacts photochemically (in solution) to form the chelated dicarbonyl derivative **2**. The amine ligand in **2** can be displaced by CO or PMe_3 . The chelated species **2** also reacts with $MeOTf$, HBF_4 , and I_2 to form the cationic compounds $trans-[(\eta^5-C_5Me_4(CH_2)_2NMe_2)Re(CO)_2X]^+$ (**[4]**) $^+$, $X = Me$; **[5]**) $^+$, $X = H$; **[6]**) $^+$, $X = I$). Finally, a new $\{ReNO\}^6$ was prepared and characterized and the redox behavior was studied. Even though the complex shows a quasi-reversible reduction in

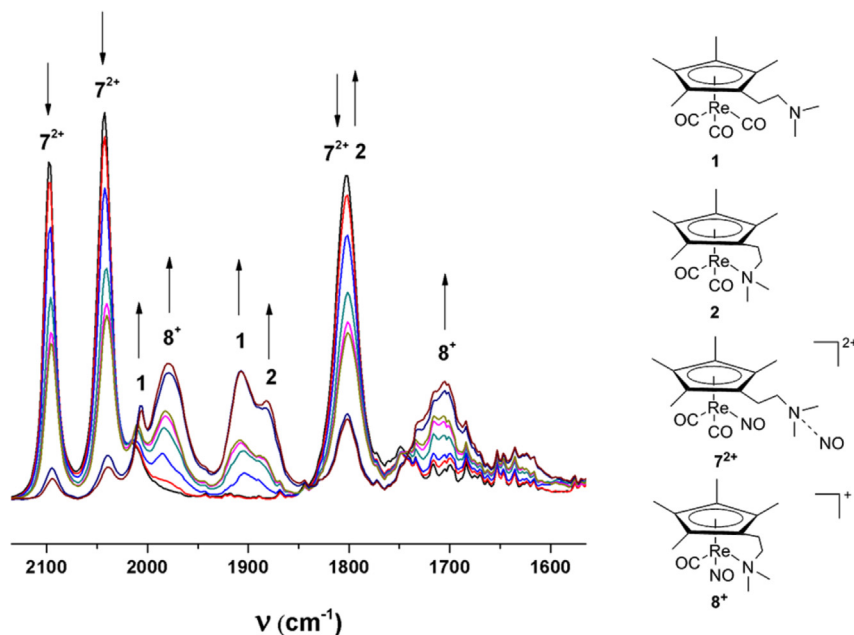


Fig. 5. IR spectral changes observed during the electrochemical reduction of $[7]^{2+}$ in $\text{CH}_3\text{CN}/0.1 \text{ M Bu}_4\text{NPF}_6$.

the CV, the $\{\text{ReNO}\}^{7/8}$ complexes were not observed. The decomposition products were identified through IR and NMR spectroscopies. DFT calculations on the related $\{\text{ReNO}\}^3$ complex $[8]^-$ showed that the most stable form is the one without the coordinated amine sidearm, and is best described as a rhenium(-1) center coordinated to NO^+ .

Experimental

General methods

The reactions were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glovebox equipped with a MO

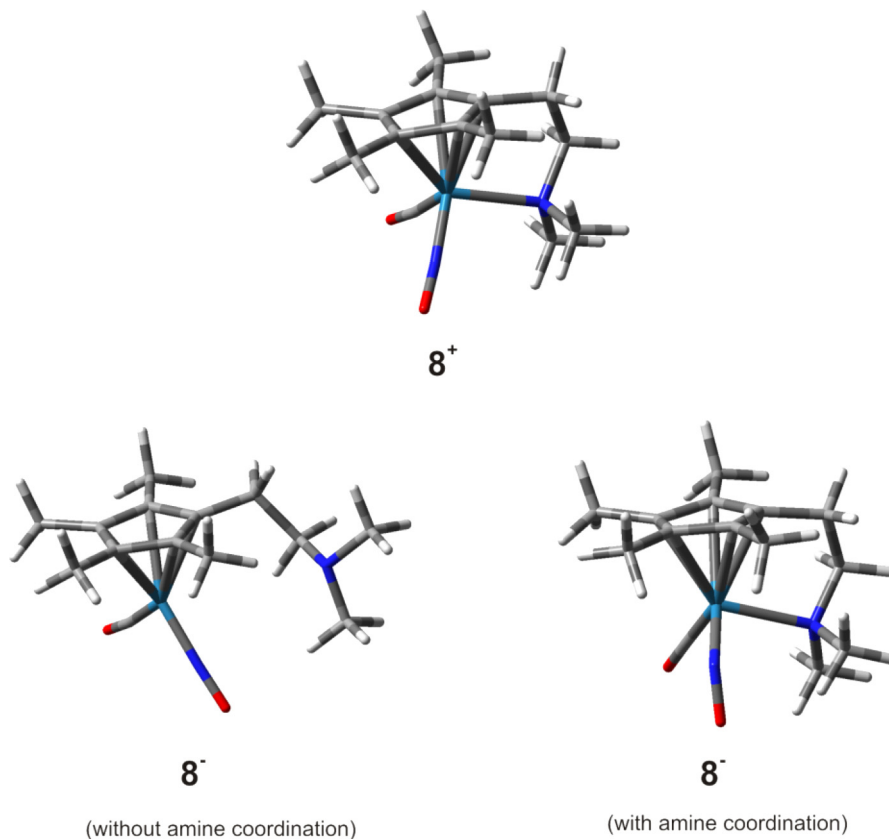


Fig. 6. DFT optimized structures for complexes $[8]^+$ and $[8]^-$.

Table 2
Bonding parameters of the ReNO moiety and IR frequencies for complex **[8]⁺** and both isomers of complex **[8]⁻**.

	[8]⁺	[8]⁻ (without amine)	[8]⁻ (with amine)
∠Re–N–O (deg)	175.1	177.4	134.4
d(N–O) (Å)	1.184	1.222	1.265
d(Re–N) (Å)	1.809	1.793	1.887
ν _{CO} (cm ⁻¹)	2004	1876	1808
ν _{NO} (cm ⁻¹)	1827	1662	1370

40–2 inert gas purifier (only when cobaltocene was used) or using standard Schlenk techniques. All solvents were purified and dried by conventional methods, and distilled under nitrogen prior to use. Commercially available reagents were used as received, except Cp₂Co that were purified by sublimation. The ligand (C₅Me₄(CH₂)₂NMe₂)H was prepared according to known procedures [24].

Infrared spectra were recorded in solution or as films on a Perkin–Elmer FT-1605 spectrophotometer or a Nicolet Avatar FTIR spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AC 400 instrument. All ¹H NMR chemical shifts were referenced using the chemical shifts of residual solvent resonances. ¹³C NMR chemical shifts were referenced to solvent peaks. Mass spectra were recorded on GCMS-QP5050A Shimadzu instrument and electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument. Cyclic voltammetry was carried out at 100 mV/s scan rate in dry and deoxygenated CH₃CN/0.1 M Bu₄NPF₆ using a three-electrode configuration (glassy carbon or Pt working electrode, Pt counter electrode, Ag wire pseudoreference electrode) and a TEQ 03 potentiostat. The ferrocenium/ferrocene (Fc⁺⁰/Fc⁰) couple served as internal reference. All the potentials are expressed against Fc⁺⁰. Spectroelectrochemistry was performed by use of an OTTL cell, in dry and deoxygenated CH₃CN/0.1 M Bu₄NPF₆.

Computational methodology

All calculations were carried out with the program package Gaussian 03 [25]. The structures of all molecules were fully geometry optimized at DFT level, using the PBE exchange-correlation functional. The LANL2DZ basis set and pseudo potential were used for the rhenium atom. For the H, N, O and C 6-31G** basis set was used. The vibrational frequencies were calculated on optimized structures using the same functional and basis set.

Preparation

(η⁵-C₅Me₄(CH₂)₂NMe₂)Re(CO)₃ (**1**)

The Re₂(CO)₁₀ complex (1.000 g, 1.533 mmol), was dissolved in decane (100 mL), and (C₅Me₄H(CH₂)₂NMe₂)H (600 mg, 3.109 mmol) was added, nitrogen was bubbled through the reaction mixture, which was refluxed for 4 h. After this time, the IR spectrum showed the complete disappearance of the starting material and the presence of two new CO absorption bands at 2013 and 1923 cm⁻¹, attributed to the (η⁵-C₅Me₄(CH₂)₂NMe₂)Re(CO)₃ (**1**) complex. The solvent was removed under reduced pressure and the oily solid was dissolved in hexane (3 × 15 mL) and filtered through Celite. Complex **1** was obtained as a yellow oily solid after evaporation of the solvent (779 mg, 1.685 mmol, 55% yield). IR [hexane, ν(CO), cm⁻¹]: 2013 (s) 1923 (s); ¹H NMR (CDCl₃) δ: 2.16 (s, 6H, C₅Me₄), 2.17 (s, 6H, C₅Me₄), 2.30 (s, 6H, NMe₂), 2.39 (m, 2H, CH₂N), 2.58 (t, J_{HH} = 7.8 Hz, 2H, CH₂). ¹H NMR (C₆D₆) δ: 1.80 (s, 6H, C₅Me₄), 1.93 (s, 6H, C₅Me₄), 2.11 (s, 6H, NMe₂), 2.18 (m, 2H, CH₂N), 2.40 (t, J_{HH} = 7.6 Hz, 2H, CH₂). ¹³C{¹H} NMR (C₆D₆) δ: 10.4 (s, C₅Me₄), 24.1 (s,

CH₂N), 45.3 (s, NMe₂), 61.8 (s, CH₂), 98.4 (s, C₅Me₄), 99.5 (s, C₅Me₄), 101.2 (s, C₅Me₄), 198.2 (s, Re–CO). MS (EI, based on ¹⁸⁷Re) *m/z*: 463 [M⁺]; 435 [M⁺ – CO]; 407 [M⁺ – 2CO].

(η⁵:η¹-C₅Me₄(CH₂)₂NMe₂)Re(CO)₂ (**2**)

Complex **1** (100 mg, 0.216 mmol) was dissolved in dry hexane (15 mL) in a quartz tube. The solution was irradiated for 2 h (λ = 300 nm) under nitrogen. After this time a yellow solid was formed, and the reaction mixture showed absorption bands due to the starting material and two new CO bands shifted to lower energy at 1880 and 1806 cm⁻¹. The mixture was cooled at –18 °C and filtered through Celite. The solid residue was dissolved in CH₂Cl₂ and crystallized from CH₂Cl₂/hexane (9:1). The (η⁵:η¹-C₅Me₄(CH₂)₂NMe₂)Re(CO)₂ (**2**) complex was obtained as yellow crystals, 41 mg (0.094 mmol, 44% yield). IR [CH₂Cl₂, ν(CO), cm⁻¹]: 1880 (s) 1806 (s). ¹H NMR (CDCl₃) δ: 1.61 (s, 6H, C₅Me₄), 2.51 (s, 6H, C₅Me₄), 2.81 (t, J_{HH} = 6.5 Hz, 2H, CH₂), 3.36 (s, 6H, NMe₂), 4.03 (t, J_{HH} = 6.5 Hz, 2H, CH₂N). ¹³C{¹H} NMR (CDCl₃) δ: 9.8 (s, C₅Me₄), 10.6 (s, C₅Me₄), 21.7 (s, CH₂N), 60.8 (s, NMe₂), 81.9 (s, CH₂), 95.4 (s, C₅Me₄), 98.9 (s, C₅Me₄), 99.7 (s, C_{ipso}, C₅Me₄), 206.2 (s, Re–CO). MS (IE, based on ¹⁸⁷Re) *m/z*: 435 [M⁺]; 407 [M⁺ – CO]; 379 [M⁺ – 2CO]. Anal. Calc. for C₁₅H₂₂O₂NRe: C, 41.36; H, 5.10. Found: C, 42.06; H, 4.98%.

(η⁵-C₅Me₄(CH₂)₂NMe₂)Re(CO)₂(PMe₃) (**3**)

Complex **2** (100 mg, 0.230 mmol) was dissolved in CH₂Cl₂ (15 mL) and PMe₃ was added (40 μL, 0.375 mmol, *d* = 0.735, 97%), the reaction mixture was stirred overnight and the IR spectrum showed the complete disappearance of **2** and the presence of two strong bands at 1908 and 1849 cm⁻¹. The solvent was pumped off and the residue was extracted with hexane (3 × 10 mL) and filtered through Celite. **3a** was obtained as a pale brown oily solid after pumping off the solvent, 103 mg (0.202 mmol, 88%). IR [hexane, ν(CO), cm⁻¹]: 1924 (s) 1856 (s). ¹H NMR (CDCl₃) δ: 1.58 (d, J_{PH} = 8.9 Hz, 9H, PMe₃), 2.07 (s, 6H, C₅Me₄), 2.10 (s, 6H, C₅Me₄), 2.28 (t, J_{HH} = 8.0 Hz, 2H, CH₂), 2.30 (s, 6H, NMe₂), 2.54 (t, J_{HH} = 8.0 Hz, 2H, CH₂N). ¹³C{¹H} NMR (CDCl₃) δ: 11.2 (s, C₅Me₄), 11.3 (s, C₅Me₄), 22.7 (d, J_{PC} = 35.1 Hz, PMe₃), 23.8 (s, CH₂N), 44.9 (s, NMe₂), 61.3 (s, CH₂N), 95.6 (s, C₅Me₄), 96.2 (s, C₅Me₄), 97.0 (s, C₅Me₄), 206.1 (d, J_{PC} = 7.6 Hz, Re–CO). ³¹P NMR (CDCl₃) δ: –27.07 (s, Re–PMe₃). MS (IE, based on ¹⁸⁷Re) *m/z*: 511 [M⁺]; 483 [M⁺ – CO]; 407 [M⁺ – CO – PMe₃].

trans-[(η⁵:η¹-C₅Me₄(CH₂)₂NMe₂)Re(CO)₂Me]⁺ [OTf]⁻ (**4**)⁺

To a solution of **2** (100 mg, 0.230 mmol) in CH₂Cl₂ (15 mL) was added MeOTf (26 μL, 0.230 mmol, *d* = 1.45 g/mL; 98%) and the reaction mixture was stirred overnight under nitrogen atmosphere. After this time, the IR spectrum showed the complete disappearance of **2** and the presence of two bands at 2025(s) and 1954(vs) cm⁻¹. The solvent was removed under reduced pressure and the solid washed twice with diethyl ether (5 mL). Complex **4**⁺ was crystallized from CH₃CN/diethyl ether. Yield: 121 mg (0.202 mmol, 88%). IR [CH₂Cl₂, ν(CO), cm⁻¹]: 2025 (s) and 1954 (vs). ¹H NMR (CDCl₃) δ: 0.76 (s, 3H, Re-Me), 1.61 (s, 6H, C₅Me₄), 2.51 (s, 6H, C₅Me₄), 2.81 (t, J_{HH} = 6.6 Hz, 2H, CH₂), 3.36 (s, 6H, NMe₂), 4.06 (t, J_{HH} = 6.6 Hz, 2H, CH₂N). ¹³C{¹H} NMR (CDCl₃) δ: –16.2 (s, broad, Re–Me), 8.2 (s, C₅Me₄), 10.2 (s, C₅Me₄), 22.7 (s, CH₂), 64.0 (s, NMe₂), 84.3 (s, CH₂N), 80.1 (s, C₅Me₄), 95.6 (s, C₅Me₄), 98.3 (s, C₅Me₄), 200.4 (s, Re–CO). Mass Spectrum (ESI, based on ¹⁸⁷Re) *m/z*: 450 [M⁺]; 435 [M⁺ – Me]; 422 [M⁺ – CO].

trans-[(η⁵:η¹-C₅Me₄(CH₂)₂NMe₂)Re(CO)₂H]⁺ [BF₄]⁻ (**5**)⁺

To a solution of **2** (30 mg, 0.069 mmol) in chloroform-*d*₃ was added HBF₄ (10 μL; 0.072 mmol, *d* = 1.180 g/mL, 54%, in Et₂O). The reaction was monitored by ¹H NMR spectroscopy. After 5 min at

0 °C, the spectrum showed the complete disappearance of **2** and the presence of **[5]⁺**. This compound could not be isolated and was only identified *in situ* by spectroscopic techniques. IR [CH₂Cl₂, $\nu(\text{CO})$, cm⁻¹]: 2033 (s), 1963 (vs). ¹H NMR (CDCl₃) δ : -8.31 (s, 1H, Re-H), 1.61 (s, 6H, C₅Me₄), 2.51 (s, 6H, C₅Me₄), 2.79 (t, $J_{\text{HH}} = 6.6$ Hz, 2H, CH₂), 3.29 (s, 6H, N-Me₂), 4.03 (t, $J_{\text{HH}} = 6.5$, 2H, CH₂N). ¹³C{¹H} NMR (CDCl₃) δ : 10.0 (s, C₅Me₄), 12.43 (s, C₅Me₄), 22.4 (s, CH₂), 63.0 (s, NMe₂), 84.2 (s, CH₂-N), C_{ipso} of C₅H₄ not seen, 94.9 (s, C₅Me₄), 100.8 (s, C₅Me₄), 198.4 (s, Re-CO).

trans-[(η^5 : η^1 -C₅Me₄(CH₂)₂NMe₂)Re(CO)₂l]⁺ [l]⁻ (**[6]⁺**)

To a solution of **2** (100 mg, 0.230 mmol) in diethyl ether (15 mL) was added iodine (59 mg, 0.232 mmol). Immediately a brown reddish solid precipitated, the reaction mixture was stirred by 1 h. After this time, the solid residue was washed with diethyl ether (2 × 10 mL) and dried under reduced pressure. Complex **[6]⁺** was obtained as a brown reddish solid, yield: 148 mg (0.215 mmol, 94%). IR [CH₂Cl₂, $\nu(\text{CO})$, cm⁻¹]: 2038 (s) 1974 (vs). ¹H NMR (CDCl₃) δ : 1.74 (s, 6H, C₅Me₄), 2.55 (s, 6H, C₅Me₄), 2.96 (t, $J_{\text{HH}} = 6.4$, 2H, CH₂), 3.45 (s, 6H, NMe₂), 4.19 (t, $J_{\text{HH}} = 6.4$, 2H, CH₂). ¹³C{¹H} RMN (CDCl₃) δ : 9.4 (s, C₅Me₄), 11.1 (s, C₅Me₄), 22.7 (s, CH₂), 63.8 (s, NMe₂), 86.2 (s, N-CH₂), 193.4 (s, CO). Mass Spectrum (ESI, based on ¹⁸⁷Re) *m/z*: 562 [M⁺]; 534 [M⁺ - CO]; 506 [M⁺ - 2CO].

[(η^5 -C₅Me₄(CH₂)₂NMe₂NO)Re(CO)₂NO]²⁺ ([BF₄]⁻)₂ (**[7]²⁺**)

To a solution of **2** (100 mg, 0.230 mmol) in CH₃CN (15 mL) was added NOBF₄ (56 mg, 0.480 mmol, 95%) the reaction mixture was stirred at 0 °C under nitrogen atmosphere. After two hours, the solution turned brown reddish and the IR spectrum showed the complete disappearance of **2** and the presence of three bands. The solvent was removed under reduced pressure and the oily residue was washed twice with diethyl ether (5 mL). Complex **[7]²⁺**, was crystallized from CH₃CN/diethyl ether. Yield: 116 mg (0.211 mmol, 92%). IR [CH₃CN, cm⁻¹]: 2096 (vs), 2042 (vs) and 1802 (s, ν_{NO}) cm⁻¹. ¹H NMR (CD₃CN) δ : 2.30 (s, 6H, C₅Me₄), 2.36 (s, 6H, C₅Me₄), 2.91 (s, 6H, NMe₂), 2.91 (m, 2H, CH₂N), 3.10 (m, 2H, CH₂). ¹³C{¹H} NMR (CD₃CN) δ : 10.0 (s, C₅Me₄), 10.2 (s, C₅Me₄), 20.9 (s, CH₂N), 43.8 (s, NMe₂), 56.9 (s, CH₂), 100.7 (s, C₅Me₄), 103.1 (s, C₅Me₄), 186.0 (s, Re-CO). MS (ESI-MS, Positive ion, based on ¹⁸⁷Re) *m/z*: 465 [M⁺ - NO⁺]; 437 [M⁺ - NO⁺ - CO].

Structural determination of complex **2**

Crystals of **2** suitable for X-ray diffraction studies were obtained by recrystallization from CH₂Cl₂/hexane diffusion at room temperature followed by slow cooling to -18 °C. A summary of crystal data, data collection, and refinement parameters for the structural analyses is provided as shown in Table S3 (Supporting information). A pale yellow crystal **2** was glued to a glass fiber and mounted on a Bruker SMART APEX diffractometer, equipped with a CCD area detector. Data collection computed with SMART-NT [26]. Both data were integrated with the Bruker SAINTPLUS program [27] and absorption corrections were applied using the SADABS routine. The structure was solved by the Patterson method, was completed by difference Fourier techniques, and was refined by full-matrix leastsquares on F² (SHELXL-97) [28] with initial isotropic, but subsequent anisotropic thermal parameters. Hydrogen atoms in **2**, were obtained from difference Fourier maps and were refined with isotropic thermal parameters.

Crystal data for compound **2**: C₁₅H₂₂NO₂Re, *M* = 434.55; monoclinic, *P* 2(1)/c; *a* = 18.5013(9), *b* = 11.6771(6), *c* = 14.8544(8) Å, β = 112.8400(10)°, *Z* = 8; *V* = 2957.5(3) Å³; *D_c* = 1.952 g/cm³; μ = 8.215 mm⁻¹, min. and max. transmission factors 0.0864 and 0.0192; 16,090 reflections collected, 6290 unique [*R*_{int} = 0.0304]; number of data/restraints/parameters 6290/

0/355; final *GoF* 1.060, Final *R* indices [*I* > 2σ(*I*)] (*R*1 = 0.0371, *wR*2 = 0.1038); *R* indices (all data) *R*1 = 0.0405, *wR*2 = 0.1062.

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Appendix A. Supplementary material

CCDC 705099 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jorganchem.2014.04.019>.

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