



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].

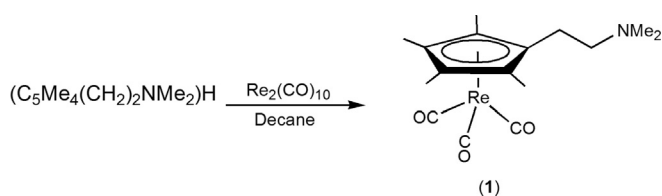
Results and discussion

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 $(\eta^5\text{-C}_5\text{Me}_4(\text{CH}_2)_2\text{L})\text{Re}(\text{CO})_3$ (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].

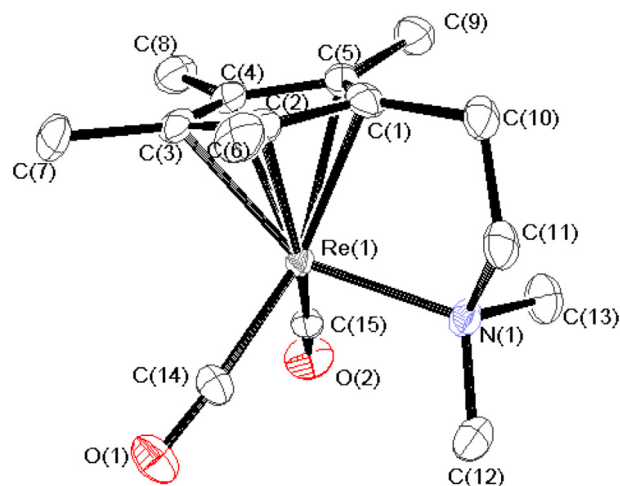


Fig. 1. ORTEP plot of complex **2** at 50% probability level. Hydrogen atoms are omitted for clarity.

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