



Reactions of cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3\text{I}]^+$ with primary amines leading to cyclic carbamoyl complexes

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ABSTRACT

The reaction of cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3\text{I}]^+$ with aliphatic and aromatic primary amines unexpectedly produced the chelated carbamoyl species *trans*- $(\eta^5\text{-C}_5\text{Me}_4\text{CH}_2\text{NRC}(=\text{O}))\text{Re}(\text{CO})_2(\text{I})$ (**1**, R = Me; **2**, R = Pr; **3**, R = Ph; **4**, R = *p*-tolyl). The η^1 -coordination of carbamoyl moiety linkages to a methylene group of tetramethylcyclopentadienyl ligand was confirmed by X-ray crystallography of complex **3**. All the complexes were isolated as pure samples and fully characterized by IR, ^1H and ^{13}C NMR spectroscopies, mass spectrometry and elemental analysis.

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1. Introduction

Although carbamoyl (carboxamide) complexes of transition metals have received considerable attention over many years [1], the topic remains of interest, especially owing to their recognition as intermediates in several important catalytic processes such as carbonylation of amines leading to the formation of carbamates [2], ureas [3], isocyanates [4] and allylic amination of olefins [5]. These compounds have usually been synthesized by the reaction of a variety of metal carbonyl complexes (especially cationic complexes) with primary and secondary amines [6]. An alternative method has also been used for the preparation of carbamoyl derivatives which involves the reaction of metal complexes with external CO and amines [7].

A large number of complexes containing carbamoyl ligands coordinated in η^1 - and η^2 -fashions to metal fragments have been prepared. Some recent examples are: $\text{CpW}[\text{CH}=\text{CH}(\text{t-Bu})](\text{NO})(\eta^2\text{-CONR}_2)$ [8], $\text{M}(\eta^2\text{-CON}^i\text{Pr}_2)\text{I}(\text{CO})_3(\text{PPh}_3)$ M = Mo, W, [9] $\text{Pt}(\text{Cl})(\text{CONHR})(\text{PPh}_3)_2$ [10], $\text{Fe}[\text{CON}^i\text{Pr}_2]_2(\text{CO})_4$ [11], $(\text{PN})\text{PdCl}(\text{CONHC}_6\text{H}_4\text{OH})$ [2] and $[\text{Fe}(\eta^2\text{-OCNi-Pr}_2)(\text{X})(\text{CO})_2(\text{PPh}_3)]$ (X = Br, I) [12].

Rare examples of carbamoyl complexes are those where the carbamoyl ligand is part of a side chain of a cyclopentadienyl group coordinated to a same metal fragment. According to our knowledge only few examples of this type of chelated complexes have been reported in literature e.g. $(\eta^5\text{-}\eta^1\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{C}(=\text{O}))\text{Re}(\text{CO})_2\text{R}$,

$[\eta^5\text{-}\eta^2\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{N}(\text{Me})\text{C}(=\text{O})]\text{Re}(\text{CO})\text{R}$ formed via carbonylation of a cyclic imido precursor [13], and $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{N}(\text{Ph})\text{C}(=\text{O}))\text{Fe}(\text{CO})_2$, unexpectedly formed in the reaction of the dimer $[\text{Cp}^*\text{Fe}(\text{CO})_2]_2$ with nitrobenzene under CO atmosphere [5].

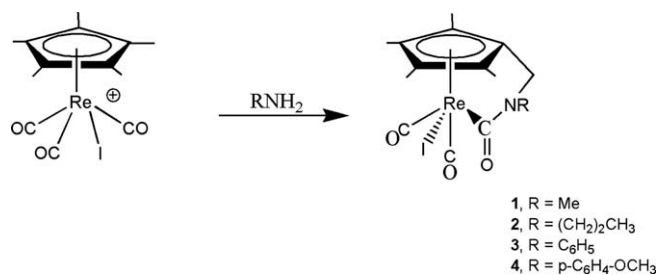
In this paper we would like to report the reaction of the cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3\text{I}]^+$ with aliphatic and aromatic primary amines leading to the unexpected chelated carbamoyl derivatives *trans*- $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{N}(\text{R})\text{C}(=\text{O}))\text{Re}(\text{CO})_2$, (**1**, R = Me; **2**, R = Pr; **3**, R = Ph; **4**, R = *p*-tolyl). The structure of complex **3** was authenticated by X-ray crystallography.

2. Results and discussion

The reaction of the cationic complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3\text{I}]^+$ with aliphatic and aromatic primary amines in CH_2Cl_2 solution, afforded the neutral species *trans*- $(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{CH}_2\text{NRC}(=\text{O}))\text{Re}(\text{CO})_2(\text{I})$ (**1**, R = Me; **2**, R = Pr; **3**, R = Ph; **4**, R = *p*-tolyl) in low to moderate yields (Scheme 1); also the complexes $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{I})_2$ were isolated in low percentage. The latter species probably are formed by partial decomposition of $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3\text{I}]^+ \text{I}_3^-$ in solution, as was observed previously [14]. It is important to note, that attempts to react the cationic complex with secondary amines such as dimethyl and diisopropylamine and lithium diisopropylamide (LDA) did not produce any acyclic carbamoyl complex as expected, instead decomposition products were formed from which $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and *trans*- $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{I})_2$ were identified by IR spectroscopy.

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Scheme 1.

In all cases, the chelated carbamoyl complexes were obtained analytically pure as orange or orange–red crystalline solids after crystallization from CH₂Cl₂–hexanes mixture. The compounds resisted air and moisture stable in solid state and in solution.

The IR spectra of these complexes (in CH₂Cl₂ solution) showed two $\nu(\text{CO})$ absorptions around 2032 and 1963 cm⁻¹, attributed to the terminal carbonyl groups. The intensity pattern of these bands (the higher wavenumber band ($\nu(\text{CO})_{\text{asym}}$) is the less intense of the pair) and the correspondence between our IR values and those reported for *trans*-(η^5 -C₅Me₅)Re(CO)₂(I)₂ [14], *trans*-(η^5 -C₅Me₅)Re(CO)₂(I)(COOR) [15] and *trans*-(η^5 -C₅Me₄CH₂I)Re(CO)₂(C₆F₅)I [16], we consider that these new compounds are also the *trans* isomer [17]. In addition, the IR spectra also showed a weak absorption band around 1612 cm⁻¹ assigned to the $\nu(\text{CO})$ of the carbamoyl fragment, which is in good agreement with the data reported for the analogous carbamoyl complexes (η^5 : η^1 -C₅-Me₄CH₂N(Ph)C(=O))Fe(CO)₂, (1602 cm⁻¹) [5] and *trans*-(η^5 : η^1 -C₅H₄(CH₂)₂NMeC(=O))Re(CO)₂(X) [X = Br (1569 cm⁻¹); X = I (1570 cm⁻¹)] [13].

These complexes possessing a four-legged piano-stool type of structure, with a *trans* orientation of the CO groups, are stable with respect to thermal isomerization as solids and in solution of organic solvents at room temperature. No isomerization was observed even in boiling chloroform or benzene, though the complexes do not survive for long at these temperatures.

The ¹H and ¹³C NMR exhibit just the resonances expected for a single isomer and the data clearly established the presence of the chelated ligand C₅Me₄CH₂N(R)C(=O) coordinated to Re. The two distinct resonances observed for the methyl groups of the cyclopentadienyl as well as the resonances of the CH₂ of the side arm resemble the resonances measured for several complexes containing these groups prepared in our laboratory [18]. In addition the ¹H and ¹³C chemical shift of the methylene group (δ about 4.0 and 43.0, respectively), are both almost identical to those reported for the complex (η^5 : η^1 -C₅Me₄CH₂N(Ph)C(=O))Fe(CO)₂ [5]. The low field region of the ¹³C NMR spectra exhibited two different resonances at $\delta \sim 170$ assigned to the carbamoyl group and around 190 ppm for the two magnetically equivalent CO ligands.

The mass spectra of these compounds showed the presence of the molecular ion and fragments corresponding to the successive loss the one and two CO groups. The elemental analyses of all complexes are consistent with the proposed structure.

The pathway leading to the formation of these cyclic carbamoyl complexes remains to be established, however, we believe that the first step of the reaction involve a nucleophilic addition of the amine to one activated CO ligand of the cation [(η^5 -C₅Me₅)Re(CO)₃I]⁺ forming the complex [(η^5 -C₅Me₅)Re(CO)₂(I)(CONHR)] with the carbamoyl ligand coordinated in a classic monohapto fashion. Support for the above assumption comes from the reaction of the same cation with alkoxides leading to the stable alkoxycarbonyl *trans*-(η^5 -C₅Me₅)Re(CO)₂(I)(COOR) [15]. The intramolecular cyclization is more speculative and it may involve an intramolecular nucleophilic attack of the N-carbamoyl to a carbon atom of a

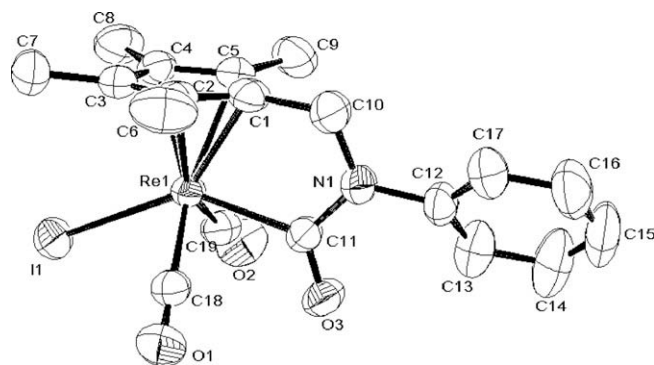


Fig. 1. Molecular structure of cyclic carbamoyl complex *trans*-(η^5 : η^1 -C₅Me₄CH₂NC₆H₅C(=O))Re(CO)₂(I) (**3**).

methyl group with simultaneous H₂ lost. Unfortunately at present time, we do not have any experimental evidence to support the above assumption. Efforts are currently in progress to probe the mechanism of formation of these complexes.

2.1. X-ray structure of **3**

The structure of *trans*-(η^5 : η^1 -C₅Me₄CH₂N(Ph)C(=O))Re(CO)₂(I) (**3**) confirms the presence of the chelated ligand tetramethylcyclopentadienyl substituted with a carbamoyl side arm (Fig. 1). Table 1 collects the most relevant bond distances and angles. Complex **3** exists as discrete molecules in the unit cell, with no unusually short intermolecular contacts. The rhenium atom is formally in a III oxidation state and is seven coordinated if the η^5 -C₅Me₄ portion of the substituted cyclopentadienyl ligand is considered as three coordinate and the overall geometry is that of a four-legged piano-stool type of structure with two CO, one iodine and the carbamoyl moiety occupying the basal positions. The Re–C(CO) bond distances (1.952(7) and 1.933(7) Å) are in range 1.89–2.03 Å reported for *trans*-(η^5 -C₅Me₅)Re(CO)₂I₂ [14], and *trans*-(η^5 -C₅Me₅)Re(CO)₂(R)I (R = Ph, Me) [17b]. The interbond angle relating the carbonyl groups C(18)–Re–C(19) of 102.0(2)° is in the range for the complexes mentioned above, for which the *trans* orientation of the CO ligands has been confirmed by X-ray crystallography. The *trans* I and the η^1 -carbamoyl define an angle of 140.04(13)° close to the one measured for *trans*-(η^5 : η^1 -C₅H₄(CH₂)₂NMeC(=O))Re(CO)₂(Br) (138.7(3)°) [13]. The bond distances Re–C(11) 2.190(5) Å, C(11)–O(3) 1.209(6) Å and C(11)–N(1) 1.393(6) Å and the angles Re(1)–C(11)–N(1) 117.5(3)°, Re(1)–C(11)–O(3) 122.4(4)° correlate well with those reported for *trans*-(η^5 : η^1 -C₅H₄(CH₂)₂NMeC(=O))Re(CO)₂(Br) indicating a *sp*² hybridization at both C(11) and N(1). It is worth noting that the atoms attached to the carbamoyl group, namely C(12), N(1), C(11), O(3) and the rhenium atom are essentially planar.

3. Experimental

3.1. General methods

All reactions were carried out using standard Schlenk techniques under nitrogen. All solvents were dried and purified by conventional methods, and distilled under nitrogen prior to use. Methylamine solution 2.0 M in THF, propylamine, aniline and *p*-anisidine (Aldrich) were used as received. The cationic complex [(η^5 -C₅Me₅)Re(CO)₂(I)]⁺I₃⁻ was prepared according to known procedure [14]. Infrared spectra were recorded in solution (CaF₂ cell) on a Perkin–Elmer FT-1605 spectrophotometer. ¹H and ¹³C NMR spectra were measured on a Bruker AC 400 instrument. All ¹H NMR chemical shifts were referenced using the chemical shifts of

Table 1
Selected bond lengths (Å) and angles (deg) for complex **3**.

Re(1)–C(18)	1.957(5)
Re(1)–C(19)	1.925(6)
Re(1)–C(11)	2.190(5)
Re(1)–I(1)	2.7784(5)
C(1)–C(10)	1.501(8)
C(10)–N(1)	1.459(7)
N(1)–C(12)	1.440(6)
N(1)–C(11)	1.393(6)
C(18)–O(1)	1.116(6)
C(19)–O(2)	1.139(7)
C(11)–O(3)	1.209(6)
C(18)–Re(1)–C(19)	102.0(2)
I(1)–Re(1)–C(11)	140.04(13)
C(1)–C(10)–N(1)	109.5(5)
C(10)–N(1)–C(11)	118.1(4)
Re(1)–C(11)–O(3)	122.4(4)
C(10)–N(1)–C(12)	118.1(4)
Re(1)–C(11)–N(1)	117.5(3)

residual solvent resonances. ^{13}C NMR chemical shifts were referenced to solvent peaks. Mass spectra were recorded on GCMS-QP5050A Shimadzu instrument. Elemental analyses were obtained at the Centro de Instrumentación, Pontificia Universidad Católica de Chile, Santiago, Chile.

3.2. General procedure

3.2.1. *Trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NRC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**)

The complex $[(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{I})]^+\text{I}_3^-$ (225 mg, 0.246 mmol) was dissolved in CH_2Cl_2 (15 mL) at room temperature under nitrogen, and stirred for 5 h with the corresponding primary amine (3 equivalent excess). After this time, the IR spectrum of the reaction mixture showed the disappearance of the starting material (2100 and 2142 cm^{-1}) and the presence of two intense absorption bands in the $2040\text{--}1970\text{ cm}^{-1}$ infrared region, attributed to carbamoyl complexes *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NRC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**). In addition, small absorptions corresponding to $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and *trans*-(η^5 - C_5Me_5) $\text{Re}(\text{CO})_2\text{I}_2$ were also observed. The solvent was pumped off and solid residues were chromatographed on an alumina column (prepared in hexane). In all cases, elution with hexane moved $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$, and hexane- CH_2Cl_2 mixture (9:1) moved a red-brownish band of *trans*-(η^5 - C_5Me_5) $\text{Re}(\text{CO})_2\text{I}_2$. Further elution with hexanes- CH_2Cl_2 (1:1) moved an red-orange band from which the complexes *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{-NRC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) were obtained.

3.2.2. *Trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NMeC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**)

In this reaction were obtained 8.0 mg (0.020 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and 9.0 mg (0.014 mmol) of *trans*-(η^5 - C_5Me_5) $\text{-Re}(\text{CO})_2\text{I}_2$. The chelated complex *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{-NMeC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) was isolated as an orange solid after removal of solvents under vacuum. The solid residue was dissolved in the minimum amount of CH_2Cl_2 and crystallized by diffusion in a hexanes layer. Complex **1** was obtained as reddish microcrystals (24 mg, 0.043 mmol, yield 17.4%). IR (CH_2Cl_2 , $\nu(\text{CO})\text{ cm}^{-1}$): 2032 (s), 1963 (vs), 1611 (s). ^1H NMR (CDCl_3) δ : 2.28 (s, 12H, C_5Me_4), 2.91 (s, 3H, NMe), 3.64 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 10.2 (s, C_5Me_4), 11.6 (s, C_5Me_4), 31.3 (s, NMe), 42.7 (s, CH_2), 99.8 (s, C_5Me_4), 103.1 (s, C_5Me_4), 105.6 (s, C_5Me_4), 170.9 (s, $\text{C}(=\text{O})$), 190.8 (s, CO). MS (IE, based on ^{187}Re) m/z : 561 [M^+], 533 [$\text{M}^+ - \text{CO}$], 505 [$\text{M}^+ - 2\text{CO}$]. Anal. Calc. for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{NRe}$: C, 30.01; H, 3.06. Found: C, 29.97; H, 2.99%.

3.2.3. *Trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{N}(\text{CH}_2)_2\text{MeC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**)

In this reaction were obtained 8.0 mg (0.020 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and 9.0 mg (0.014 mmol) of *trans*-(η^5 - C_5Me_5) $\text{-Re}(\text{CO})_2\text{I}_2$. The chelated complex *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{N}(\text{CH}_2)_2\text{MeC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) was isolated as an orange-red solid in 51.0% (78 mg, 0.125 mmol): IR (CH_2Cl_2 , $\nu(\text{CO})\text{ cm}^{-1}$): 2036 (s), 1968 (vs), 1612 (s). ^1H NMR (CDCl_3) δ : 2.32 (s, 6H, C_5Me_4), 2.39 (s, 6H, C_5Me_4), 4.14 (s, 2H, CH_2), 7.36 (m, 5H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 10.2 (s, C_5Me_4), 11.6 (s, C_5Me_4), 43.4 (s, CH_2), 99.7 (s, C_5Me_4), 102.8 (s, C_5Me_4), 103.4 (s, C_5Me_4), 124.9, 125.8, 129.0, 140.8 (s, C_6H_5), 171.2 (s, $\text{C}(=\text{O})$), 190.5 (s, CO). MS (IE, based on ^{187}Re) m/z : 623 [M^+], 595 [$\text{M}^+ - \text{CO}$], 567 [$\text{M}^+ - 2\text{CO}$]. Anal. Calc. for $\text{C}_{19}\text{H}_{19}\text{O}_3\text{NRe}$: C, 36.60; H, 3.05. Found: C, 36.55; H, 3.04%.

Table 2

Crystal data and structure refinement for *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NC}_6\text{H}_5\text{C}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) (**3**).

Empirical formula	$\text{C}_{19}\text{H}_{19}\text{O}_3\text{NRe}$
Formula weight	622.46
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	
<i>a</i> (Å)	12.102(2)
<i>b</i> (Å)	25.896(5)
<i>c</i> (Å)	13.507(2)
β (°)	107.297(3)
<i>V</i> (Å ³)	4041.5(12)
<i>Z</i>	4
D_{calcd} (g cm ⁻³)	2.124
Absorption coefficient (mm ⁻¹)	7.625
<i>F</i> (0 0 0)	2428
Crystal size (mm)	0.36 × 0.35 × 0.27
θ Range for data collection (°)	1.276–27.90
Index ranges	$-15 \leq h \leq 15$, $-32 \leq k \leq 32$, $-17 \leq l \leq 17$
Reflections collected	33460
Independent reflections	8940 [$R_{\text{int}} = 0.0258$]
Completeness to $\theta = 26.00$	99.6%
Absorption corrections	Semi-empirical from equivalents
Minimum/maximum transmission	0.128 and 0.080
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8940/0/477
Goodness-of-fit on F^2	1.035
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R1 = 0.0308$, $wR2 = 0.0741$
<i>R</i> indices (all data)	$R1 = 0.0383$, $wR2 = 0.0778$
Largest difference peak and hole (e Å ⁻³)	2.159 and -2.046

$\text{Re}(\text{CO})_2\text{I}_2$. The complex *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{N}(\text{CH}_2)_2\text{MeC}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) (**2**) was isolated as a pale red solid in 19.4% yield (28 mg, 0.048 mmol): IR (CH_2Cl_2 , $\nu(\text{CO})\text{ cm}^{-1}$): 2037 (s), 1969 (vs), 1611 (s). ^1H NMR (CDCl_3) δ : 0.92 (t, 3H, $(\text{CH}_2)_2\text{CH}_3$), 1.62 (m, 2H, $(\text{CH}_2)_2\text{CH}_3$), 2.27 (s, 6H, C_5Me_4), 2.29 (s, 6H, C_5Me_4), 3.31 (t, 2H, $(\text{CH}_2)_2\text{CH}_3$), 3.64 (s, 2H, CH_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 10.2 (s, $(\text{CH}_2)_2\text{CH}_3$), 10.6 (s, C_5Me_4), 11.9 (s, C_5Me_4), 21.5 (s, $(\text{CH}_2)_2\text{CH}_3$), 41.2 (s, CH_2), 46.4 (s, $(\text{CH}_2)_2\text{CH}_3$), 99.9 (s, C_5Me_4), 103.6 (s, C_5Me_4), 105.5 (s, C_5Me_4), 170.7 (s, $\text{C}(=\text{O})$), 191.4 (s, CO). MS (IE, based on ^{187}Re) m/z : 589 [M^+], 561 [$\text{M}^+ - \text{CO}$], 533 [$\text{M}^+ - 2\text{CO}$]. Anal. Calc. for $\text{C}_{16}\text{H}_{21}\text{O}_3\text{NRe}$: C, 32.66; H, 3.60. Found: C, 32.36; H, 3.54%.

3.2.4. *Trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NC}_6\text{H}_5\text{C}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) (**3**)

In this reaction were obtained 4.2 mg (0.010 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and 7.0 mg (0.011 mmol) of *trans*-(η^5 - C_5Me_5) $\text{-Re}(\text{CO})_2\text{I}_2$. The chelated complex *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{NC}_6\text{H}_5\text{-C}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) (**3**) was isolated as an orange-red solid in 51.0% (78 mg, 0.125 mmol): IR (CH_2Cl_2 , $\nu(\text{CO})\text{ cm}^{-1}$): 2036 (s), 1968 (vs), 1612 (s). ^1H NMR (CDCl_3) δ : 2.32 (s, 6H, C_5Me_4), 2.39 (s, 6H, C_5Me_4), 4.14 (s, 2H, CH_2), 7.36 (m, 5H, C_6H_5). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 10.2 (s, C_5Me_4), 11.6 (s, C_5Me_4), 43.4 (s, CH_2), 99.7 (s, C_5Me_4), 102.8 (s, C_5Me_4), 103.4 (s, C_5Me_4), 124.9, 125.8, 129.0, 140.8 (s, C_6H_5), 171.2 (s, $\text{C}(=\text{O})$), 190.5 (s, CO). MS (IE, based on ^{187}Re) m/z : 623 [M^+], 595 [$\text{M}^+ - \text{CO}$], 567 [$\text{M}^+ - 2\text{CO}$]. Anal. Calc. for $\text{C}_{19}\text{H}_{19}\text{O}_3\text{NRe}$: C, 36.60; H, 3.05. Found: C, 36.55; H, 3.04%.

3.2.5. *trans*-(η^5 : η^1 - $\text{C}_5\text{Me}_4\text{CH}_2\text{-}p\text{-C}_6\text{H}_4\text{-OCH}_3\text{C}(=\text{O})$) $\text{Re}(\text{CO})_2$ (**1**) (**4**)

In this reaction were obtained 4.0 mg (0.010 mmol) of $(\eta^5\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_3$ and 7.0 mg (0.011 mmol) of *trans*-(η^5 - C_5Me_5) $\text{-Re}(\text{CO})_2\text{I}_2$. Complex **4**, was isolated as a pale red solid in 52.4% yield (84 mg, 0.129 mmol): IR (CH_2Cl_2 , $\nu(\text{CO})\text{ cm}^{-1}$): 2036 (s), 1968 (vs), 1612 (s). ^1H NMR (CDCl_3) δ : 2.35 (s, 6H, C_5Me_4), 2.44 (s, 6H, C_5Me_4), 3.81 (s, 3H, OCH_3), 4.16 (s, 2H, CH_2), 6.89 (d, $J = 9.0$ Hz, 2H, C_6H_4), 7.23 (d, $J = 9.0$ Hz, 2H, C_6H_4). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3) δ : 10.4 (s, C_5Me_4), 11.8 (s, C_5Me_4), 43.7 (s, CH_2), 55.7 (s, OCH_3), 99.8

(s, C₅Me₄), 103.1 (s, C₅Me₄), 104.5 (s, C₅Me₄), 114.5 (s, C₆H₄), 126.9 (s, C₆H₄), 171.5 (s, C(=O)), 190.7 (s, CO). MS (IE, based on ¹⁸⁷Re) *m/z*: 653 [M⁺], 625 [M⁺–CO], 597 [M⁺–CO]. Anal. Calc. for C₂₀H₂₁O₄NiRe: C, 36.81; H, 3.24. Found: C, 36.75; H, 3.25%.

3.3. Structure determination of complex **3**

Crystals of **3** for X-ray diffraction studies were obtained by recrystallization from CH₂Cl₂/hexanes 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 given in Table 2. An orange crystal of **3** was glued to a glass fiber and mounted on a BRUKER SMART-APEX diffractometer, equipped with a CCD area detector. Data collection was collected with SMART-NT [19]. Both data sets were integrated with the Bruker SAINT-PLUS program [20] and absorption corrections were applied using the SADABS routine. The structures were solved by Patterson, completed by difference Fourier techniques, and refined by full-matrix least-squares on *F*² (SHELXL-97) [21] with initial isotropic, but subsequent anisotropic 40 thermal parameters. Hydrogens in **3** were introduced from observed positions and refined as isotropic atoms.

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Appendix A. Supplementary material

CCDC 736043 contains the supplementary crystallographic data for **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/

[data_request/cif](#). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.07.035](https://doi.org/10.1016/j.jorganchem.2009.07.035).

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