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Dirhenium carbonyl complexes bearing 2-vinylpyridine, morpholine and 1-methylimidazole ligands

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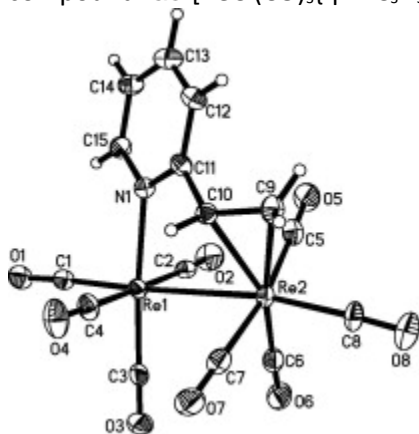
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Abstract

Treatment of the labile compound $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 2-vinylpyridine in refluxing benzene affords exclusively the new compound $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)]$ (**1**) in 39% yield in which the $\mu\text{-}\eta^1\text{:}\eta^2\text{-}$ vinylpyridine ligand is coordinated to one Re atom through the nitrogen and to the other Re atom via the olefinic double bond. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with morpholine in refluxing benzene furnishes two compounds, $[\text{Re}_2(\text{CO})_9(\eta^1\text{-NC}_4\text{H}_9\text{O})]$ (**2**) and $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**) in 5% and 29% yields, respectively. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 1-methylimidazole gives $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3))_2]$ (**4**) and the mononuclear compound *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**) in 18% and 26% yields, respectively. In the disubstituted compounds **2** and **4**, the heterocyclic ligands occupy equatorial coordination sites. The mononuclear compound **5** consists of three CO groups, two N coordinated $\eta^1\text{-1}$ -methylimidazole ligands and a terminal Cl ligand. The XRD structures of complexes **1**, **3** and **5** are reported.

Graphical abstract

The synthesis and characterization of the dirhenium complexes $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)]$ (**1**), $[\text{Re}_2(\text{CO})_9(\eta^1\text{-NC}_4\text{H}_9\text{O})]$ (**2**), $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**) and $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3))_2]$ (**4**) and the mononuclear compound *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**) are described.



Keywords

Rhenium carbonyl, 2-Vinylpyridine, Morpholine, 1-Methylimidazole, X-ray structures

1. Introduction

Nitrogen containing aromatic heterocycles such as pyridines and related compounds are an important class of ligands in organometallic and coordination chemistry [1]. Such ligands offer new possibilities for the synthesis of bi- and polynuclear complexes with application in catalysis and materials sciences [1], [2], [3], [4], [5], [6]. The synthesis and reactivity of the dirheniumpyridyl compound $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-C}_5\text{H}_4\text{N})(\mu\text{-H})]$ were investigated by Brown and co-workers in 1982 [7]. Arce et al. [4] reported the bipyridyldirhenium complexes $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_{10}\text{N}_2)]$, $[\text{Re}_2(\text{CO})_7(\mu\text{-}\eta^3\text{-C}_{12}\text{H}_9\text{N}_2)(\mu\text{-H})]$, $[\text{Re}_2(\text{CO})_6(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_9\text{N}_2)(\mu\text{-H})]$, $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^4\text{-C}_{12}\text{H}_{10}\text{N}_2)]$ and $[\text{Re}_2(\text{CO})_6(\mu\text{-}\eta^6\text{-C}_{24}\text{H}_{18}\text{N}_4)]$ from the reactions of *trans*-1,2-bis(2-pyridyl)ethene with $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$. Recently we have reported the dirhenium cyclometalated compounds

$[\text{Re}_2(\text{CO})_7\{\mu\text{-}2,3\text{-}\eta^2\text{-C}_3\text{H}(4\text{-R})\text{NS}\}\{\eta^1\text{-NC}_3\text{H}_2(4\text{-R})\text{S}\}(\mu\text{-H})]$ and $[\text{Re}_2(\text{CO})_6\{\mu\text{-}2,3\text{-}\eta^2\text{-C}_3\text{H}(\text{R})\text{NS}\}\{\eta^1\text{-NC}_3\text{H}_2(4\text{-R})\text{S}\}_2(\mu\text{-H})]$ together with the mononuclear *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_2(4\text{-R})\text{S}\}_2]$ (R = H, CH₃) from the reactions of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with thiazole and 4-methylthiazole [8].

2-Vinylpyridine is a versatile ligand, widely used to stabilize transition metal–carbon bonds in chelating coordination mode; this coordination mode may play the key role in catalysis. The reactivity of 2-vinylpyridine with a variety of mononuclear complexes has been studied extensively in recent years [9], [10], [11], [12], [13], [14], [15], [16], [17]. In particular C–H oxidative-addition reaction of both vinyl and pyridyl functionalities in the ligand has been observed. In comparison to the extensive cyclometalation chemistry of 2-vinylpyridine with mononuclear complexes its reactivity with polynuclear compounds is comparatively less developed. Deeming and co-workers [18] were the first to demonstrate the reactivity of organometallic clusters with 2-vinylpyridine in which they showed that $[\text{Os}_3(\text{CO})_{10}(\mu\text{-H})_2]$ and $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ react with 2-vinylpyridine with C–H bond cleavage at the vinyl carbon atom to give the triosmium cluster $[\text{Os}_3(\text{CO})_{10}(\eta^1\text{:}\eta^2\text{:}\eta^1\text{-NC}_5\text{H}_4\text{CH}=\text{CH})(\mu\text{-H})]$ with an open structure. A similar bonding mode of $\text{NC}_5\text{H}_4\text{CH}=\text{CH}$ has been reported in $[\text{Os}_6(\text{CO})_{20}(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-NC}_5\text{H}_4\text{CH}=\text{CH})(\mu\text{-H})]$ [19], $[\text{Os}_4\text{Rh}(\text{CO})_{13}(\mu\text{-}\eta^1\text{:}\eta^2\text{:}\eta^1\text{-NC}_5\text{H}_4\text{CH}=\text{CH})(\mu\text{-H})_4]$ [20] and in the mononuclear carbonyl complex $[\text{Re}(\text{NC}_5\text{H}_4\text{CH}=\text{CH})(\text{CO})_4]$ [21]. In contrast with the rich 2-vinylpyridine chemistry with most of the transition metals, noted above, morpholine has far less been investigated except for our recent report on the reaction of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ to afford the C–H oxidative-addition product $[\text{Os}_3(\text{CO})_{10}(\mu\text{-}\eta^2\text{-NC}_4\text{H}_6\text{O})(\mu\text{-H})]$ [22]. As a continuation of our studies on the reactivity of dirhenium carbonyl complexes with heterocyclic ligands we have now investigated the reactions of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 2-vinylpyridine, morpholine and 1-methylimidazole.

2. Experimental

All the reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried and distilled prior to use by standard methods. 2-Vinylpyridine, morpholine and 1-methylimidazole were purchased from Aldrich and used as received. $\text{Me}_3\text{NO} \cdot 2\text{H}_2\text{O}$ was purchased from Lancaster and water from it was removed and a Dean-Stark apparatus using benzene as a solvent. The starting compound $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ was prepared according to the published procedure [23]. Infrared spectra were recorded on a Shimadzu FTIR 8101 spectrophotometer. ¹H NMR spectra were recorded on Bruker DPX 400 spectrometer. Elemental analysis was performed by BCSIR Laboratories, Dhaka. Fast atom bombardment mass spectra were obtained on a JEOL SX-102 spectrometer using 3-nitrobenzyl alcohol as matrix and CsI as calibrant.

2.1. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 2-vinylpyridine

A benzene solution (50 mL) of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ (150 mg, 0.22 mmol) and 2-vinylpyridine (116 mg, 1.10 mmol) was heated to reflux for 4.5 h. The solvent was removed by rotary evaporation and the residue chromatographed by TLC on silica gel. Elution with hexane/ CH_2Cl_2 (7:3, v/v) afforded several very minor and one major bands. The minor bands were too small for complete characterization. The major band afforded $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)]$ (**1**) (61 mg, 39%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -4°C . Anal. Calc. for $\text{C}_{15}\text{H}_7\text{N}_1\text{O}_8\text{Re}_2$: C, 25.68; H, 1.01. Found: C, 25.89; H, 1.20%. IR (νCO , CH_2Cl_2): 2044 w, 2025 w, 1988 vs, 1955 m, 1917 m cm^{-1} . ^1H NMR (CDCl_3): δ 8.59 (d, $J = 5.2$ Hz, 1H), 7.58 (t, $J = 7.8$ Hz, 1H), 7.06 (d, $J = 7.8$ Hz, 1H), 6.93 (t, $J = 5.2$ Hz, 1H), 4.77 (dd, $J = 9.2, 11.4$ Hz, 1H_a), 2.08 (dd, $J = 1.6, 9.2$ Hz, 1H_b), 1.87 (dd, $J = 1.6, 11.4$ Hz, 1H_c). MS (FAB): m/z 701 (M^+).

2.2. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with morpholine

To a benzene solution (50 mL) of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ (150 mg, 0.22 mmol) was added morpholine (39 mg, 0.45 mmol) and refluxed for 2.5 h. After removal of the solvent under reduced pressure, the residue was chromatographed as above to develop two bands. The first band gave $[\text{Re}_2(\text{CO})_9(\eta^1\text{-NC}_4\text{H}_9\text{O})]$ (**2**) (8 mg, 5%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -4°C . Anal. Calc. for $\text{C}_{13}\text{H}_9\text{N}_1\text{O}_{10}\text{Re}_2$: C, 21.94; H, 1.27. Found: C, 22.09; H, 1.45%. IR (νCO , CH_2Cl_2): 2100 w, 2040 m, 1980 vs, 1955 m, 1917 m cm^{-1} . ^1H NMR (CDCl_3): δ 3.81 (m, 2H), 3.40 (m, 2H), 3.15 (m, 4H), 2.95 (br s, 1H). MS (FAB): m/z 711 (M^+). The second band gave $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**) (49 mg, 29%) as orange crystals after recrystallization from hexane/ CH_2Cl_2 at -4°C . Anal. Calc. for $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_{10}\text{Re}_2$: C, 24.93; H, 2.35. Found: C, 25.15; H, 2.49%. IR (νCO , CH_2Cl_2): 2064 w, 2003 vs, 1953 vs, 1942 vs, 1908 s cm^{-1} . ^1H NMR (CDCl_3): δ 3.71 (m, 8H), 3.38 (m, 8H), 3.10 (br s, 2H). MS (FAB): m/z 770 (M^+).

2.3. Reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 1-methylimidazole

A mixture of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ (150 mg, 0.22 mmol), 1-methylimidazole (91 mg, 1.11 mmol) and benzene (50 mL) was refluxed for 3 h. The solvent was removed under reduced pressure and the solid residue chromatographed as above to give three bands. The first band gave $[\text{Re}_2(\text{CO})_8\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**4**) (30 mg, 18%) as yellow crystals after recrystallization from hexane/ CH_2Cl_2 at -4°C . Anal. Calc. for $\text{C}_{16}\text{H}_{12}\text{N}_4\text{O}_8\text{Re}_2$: C, 25.26; H, 1.59. Found: C, 25.31; H, 1.63%. IR (νCO , CH_2Cl_2): 2070 m, 2001 vs, 1951 vs, 1900 s cm^{-1} . ^1H NMR (CDCl_3): δ 7.96 (s, 2H), 7.11 (s, 2H), 6.88 (s, 2H), 2.78 (s, 6H). MS (FAB): m/z 760 (M^+). The second band gave *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**) (22 mg, 26%) as colorless crystals after recrystallization from hexane/ CH_2Cl_2 at -4°C . Anal. Calc. for $\text{C}_{11}\text{H}_{12}\text{ClN}_4\text{O}_3\text{Re}$: C, 28.12; H, 2.57. Found: C, 28.04; H, 2.65%. IR (νCO , CH_2Cl_2): 2020 vs, 1908 s, 1887 s cm^{-1} . ^1H NMR

(CDCl₃): δ 8.03 (s, 2H), 7.15 (s, 2H), 6.55 (s, 2H), 3.68 (s, 6H). MS (FAB): m/z 470 (M⁺). The third band was too small for complete characterization.

2.4. X-ray structure determination compounds **1**, **3** and **5**

Single crystals of compounds of **1**, **3** and **5**, obtained as described above, were mounted on a Nylon fiber with a mineral oil, and diffraction data were collected at 100(2) K on a Bruker AXS SMART diffractometer equipped with an APEX CCD detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å for **1** and **3**, and 1.54178 Å for **5**). Integration of intensities and data reduction was performed using SAINT program [24]. Multi-scan absorption correction was applied using SADABS procedure [25].

The structures were solved by direct methods [26] and refined by full-matrix least squares on F^2 [27]. All non-hydrogen atoms were refined anisotropically. Positions of hydrogen atoms were calculated geometrically and were included into refinement with B(iso) = 1.2B(iso/eq) of an adjacent carbon atom using a riding model. All pertinent crystal data and other experimental conditions and refinement details are summarized in Table 1.

Table 1. Crystallographic data and structure refinement^a for **1**, **3** and **5**

	1	3	5
Empirical formula	C ₁₅ H ₇ NO ₈ Re ₂	C ₁₆ H ₁₈ N ₂ O ₁₀ Re ₂	C ₁₁ H ₁₂ ClN ₄ O ₃ Re
Formula weight	701.62	770.72	469.90
Wavelength (Å)	0.71073	0.71073	1.54178
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P2₁/c</i>	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	7.8918(8)	14.6169(14)	13.0082(2)
<i>b</i> (Å)	13.8882(14)	12.7458(12)	7.59120(10)
<i>c</i> (Å)	16.0788(17)	13.2940(14)	14.8491(3)
α (°)	90	90	90
β (°)	99.910(2)	120.0260(10)	92.5490(10)
γ (°)	90	90	90
Volume (Å ³)	1736.0(3)	2144.3(4)	1464.87(4)
<i>Z</i>	4	4	4
<i>D</i> _{calc} (Mg/m ³)	2.684	2.387	2.131
μ (Mo K α) (mm ⁻¹)	13.976	11.334	18.033
<i>F</i> (0 0 0)	1272	1432	888

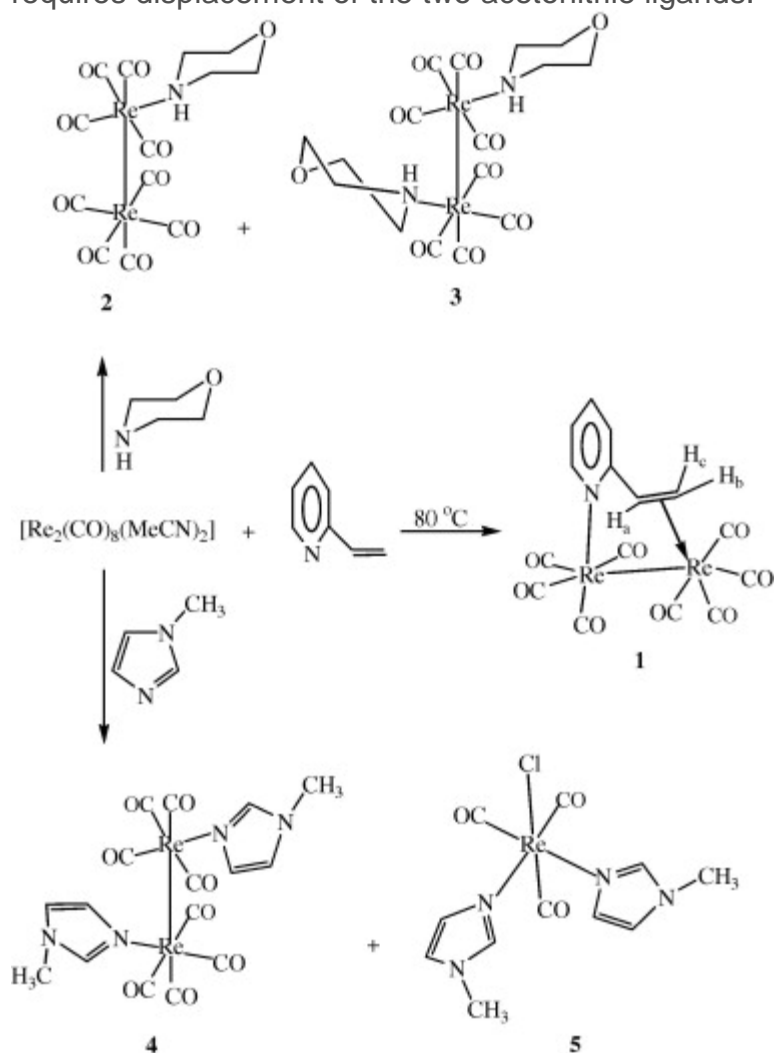
	1	3	5
Crystal size (mm ³)	0.45 × 0.14 × 0.07	0.40 × 0.25 × 0.15	0.47 × 0.23 × 0.05
θ Range (°)	1.95–31.86	2.27–31.81	5.97–61.40
Index ranges	-11 ≤ h ≤ 11 0 ≤ k ≤ 20 0 ≤ l ≤ 23	-21 ≤ h ≤ 18 0 ≤ k ≤ 18 0 ≤ l ≤ 19	-14 ≤ h ≤ 14 0 ≤ k ≤ 8 0 ≤ l ≤ 16
Reflections collected	27 974	17 248	12 186
Independent reflections (<i>R</i> _{int})	5644 (0.0368)	3495 (0.0236)	2203 (0.0246)
Maximum and minimum transmissions	0.4412 and 0.0617	0.2812 and 0.0928	0.4658 and 0.0431
Data/restraints/parameters	5644/0/248	3495/0/172	2203/0/248
Goodness-of-fit on <i>F</i> ²	1.034	0.927	1.238
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0287 <i>wR</i> ₂ = 0.0747	<i>R</i> ₁ = 0.0154 <i>wR</i> ₂ = 0.0401	<i>R</i> ₁ = 0.0179 <i>wR</i> ₂ = 0.0445
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0364 <i>wR</i> ₂ = 0.0778	<i>R</i> ₁ = 0.0169 <i>wR</i> ₂ = 0.0409	<i>R</i> ₁ = 0.0180 <i>wR</i> ₂ = 0.0445
Largest difference in peak and hole (e Å ⁻³)	3.559 and -0.907	1.525 and -1.283	0.811 and -0.618

aDetails in common: X-radiation, temperature (K) 100(2), refinement method: full-matrix least-squares on *F*².

3. Results and discussion

Reaction of [Re₂(CO)₈(MeCN)₂] with 5 equiv. of 2-vinylpyridine in refluxing benzene afforded the new compound [Re₂(CO)₈(μ-η¹:η²-NC₅H₄CH=CH₂)] (**1**) in 39% yield (Scheme 1). This is the first example of a dinuclear complex of this type to our knowledge. An example of this coordination mode of 2-vinylpyridine has recently been reported in the mononuclear ruthenium compound, [RuCl₂(2-CH₂=CHC₅H₃N)] [9]. Compound **1** has been characterized by a combination of IR, ¹H NMR, mass spectral data, elemental analysis and single crystal X-ray diffraction studies. The molecular structure of **1** is depicted in Fig. 1 and selected bond distances and angles are listed in the caption. The molecule consists of a dirhenium core with eight terminal carbonyl ligands and a four electron donor 2-vinylpyridine ligand. An intriguing structural feature of **1** is the coordination of 2-vinylpyridine ligand in a μ-η¹:η²-fashion to one Re atom through the nitrogen and to the other Re atom via the ethylenic double bond. Each Re atom attains a slightly distorted octahedral coordination sphere through the terminal carbonyl ligands and the organic ligand. The Re–Re bond distance of 3.0331(3) Å clearly corresponds to a single bond which is in accordance with the 18-electron count for each metal. This bond length is comparable to the Re–Re bond distance of 3.041(1) Å in [Re₂(CO)₁₀] [28], 3.036(1) Å in [Re₂(CO)₈(μ-η³-C₁₂H₁₀N₂)] [4] and 3.084(1) Å in [Re₂(CO)₈(μ-η³-C₁₄H₁₀N₂)] [2b]. The three

equatorial CO ligands bonded to Re(1) have torsion angles of the order $81(1)^\circ$ to $155(4)^\circ$ with respect to Re(2)–C(8) which is typical of $[M_2(CO)_{10-x}L_x]$ compounds [29]. The nitrogen atom of 2-vinylpyridine ligand is axially coordinated to Re(1) and the Re–N bond length of 2.208(4) Å is comparable to the Re–N bond distances of 2.20(2) Å in $[Re(CO)_3\{\eta^2-H_2B(tim^{Me})\}_2(4-NMe_2py)]$ (tim^{Me} = 2-mercapto-1-methylimidazolyl) [30] and 2.211(6) Å in $[Re_2(CO)_8(\mu-\eta^3-C_{12}H_{10}N_2)]$ [4]. An asymmetric triangle is formed by C(9), C(10) and Re(2) atoms [Re(2)–C(9) = 2.325(5), Re(2)–C(10) = 2.287(4) Å], and as a consequence of the η^2 -coordination of the ethylenic moiety; the distance C(9)–C(10) [1.418(6) Å] closely resembles to that observed for the corresponding distance of 1.38(2) Å in $[Re_2(CO)_8(\mu-\eta^3-C_{12}H_{10}N_2)]$ and is longer than an uncoordinated C–C double bond lengths [4]. The formation of **1** from $[Re_2(CO)_8(MeCN)_2]$ and 2-vinylpyridine simply requires displacement of the two acetonitrile ligands.



Scheme 1.

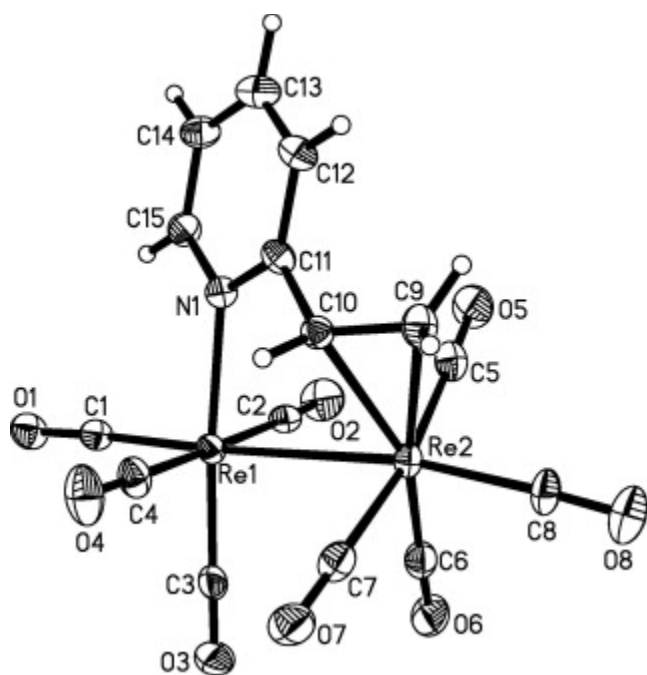


Fig. 1. Molecular structure of complex $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)]$ (**1**). Selected bond distances (Å) and angles ($^\circ$): $\text{Re}(1)\text{-C}(1) = 1.911(4)$, $\text{Re}(1)\text{-C}(3) = 1.921(5)$, $\text{Re}(1)\text{-C}(2) = 1.997(5)$, $\text{Re}(1)\text{-C}(4) = 1.998(5)$, $\text{Re}(1)\text{-N}(1) = 2.208(4)$, $\text{Re}(1)\text{-Re}(2) = 3.0331(3)$, $\text{Re}(2)\text{-C}(6) = 1.949(5)$, $\text{Re}(2)\text{-C}(8) = 1.949(5)$, $\text{Re}(2)\text{-C}(5) = 1.992(5)$, $\text{Re}(2)\text{-C}(7) = 1.990(5)$, $\text{Re}(2)\text{-C}(10) = 2.287(4)$, $\text{Re}(2)\text{-C}(9) = 2.325(5)$, $\text{N}(1)\text{-Re}(1)\text{-Re}(2) = 83.1(1)$, $\text{C}(6)\text{-Re}(2)\text{-Re}(1) = 79.8(1)$, $\text{C}(8)\text{-Re}(2)\text{-Re}(1) = 170.5(2)$, $\text{C}(5)\text{-Re}(2)\text{-Re}(1) = 87.6(1)$, $\text{C}(7)\text{-Re}(2)\text{-Re}(1) = 82.5(1)$, $\text{C}(10)\text{-Re}(2)\text{-Re}(1) = 72.4(1)$, $\text{C}(9)\text{-Re}(2)\text{-Re}(1) = 107.9(1)$.

The solid-state structure of **1** is supported by the solution spectroscopic data. The $\nu(\text{CO})$ absorption spectrum indicates that all the carbonyl groups are terminal. In particular, the ^1H NMR spectrum of **1** in the aromatic region contains two doublets at δ 8.59 ($J = 5.2$ Hz), 7.06 ($J = 7.8$ Hz) and two triplets at δ 7.58 ($J = 7.8$ Hz), 6.93 ($J = 5.2$ Hz) (integrating for 1H) assignable to the C–H protons of the ring. The most noticeable are the resonances corresponding to coordinated olefinic protons which appear as three doublet of doublets at δ 4.77 ($J = 9.2, 11.4$ Hz), 2.08 ($J = 1.6, 9.2$ Hz) and 1.87 (1.6, 11.4 Hz) (integrating for 1H) and significantly shifted to higher field with regard to the free ligand. Thus the ^1H NMR spectrum consists of four signals for the ring protons and three signals for the olefinic group and hence remains intact. The mass spectrum of **1** exhibits molecular ion peak at m/z 701 and fragmentation peaks due to the sequential loss of eight carbonyl groups are also observed. To gain insight into the reactivity of secondary aliphatic heterocyclic amines toward rhenium carbonyl complexes, we have investigated the reaction of morpholine with $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ to isolating the η^1 -coordinated compound $[\text{Re}_2(\text{CO})_8(\text{MeCN})(\eta^1\text{-NC}_4\text{H}_9\text{O})]$ and converting it to the cyclometalated product $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^2\text{-NC}_4\text{H}_8\text{O})(\mu\text{-H})]$. As expected the reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 2 equiv of morpholine in refluxing benzene gave the disubstituted compound $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**) in 29% yield along with the mono-substituted compound $[\text{Re}_2(\text{CO})_9(\eta^1\text{-NC}_4\text{H}_9\text{O})]$ (**2**) in 5% yield (Scheme 1). Most probably, the mono-substituted

compound **2** results from the $[\text{Re}_2(\text{CO})_9(\text{MeCN})]$ impurity in $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$. Both compounds **2** and **3** have been characterized by elemental analysis, IR, ^1H NMR and mass spectral data together with single crystal X-ray diffraction analysis for **3**. The pattern of the IR spectrum of **2** in the carbonyl stretching region is very similar to those of the mono-substituted compounds of the type $[\text{Re}_2(\text{CO})_9\text{L}]$ ($\text{L} = \text{tBuNC}$, $\text{P}(\text{CH}_2\text{C}_6\text{H}_5)_3$, RCN) indicating that they are isostructural [31]. The mass spectrum of **2** exhibits a molecular ion peak at m/z 711 and sequential loss of nine carbonyl groups were observed. The ^1H NMR spectrum of **2** shows three multiplets at δ 3.81, 3.40 and 3.15 due to the C–H protons of the ring and a singlet at δ 2.95 assigned to the N–H proton of the ligand with the relative intensities of 2:2:4:1, respectively.

The molecular structure of **3** is shown in Fig. 2 and selected bond distances and angles are in the caption. The molecule contains two mutually bonded rhenium atoms with the Re–Re distance of 3.0337(3) Å which closely resembles to that found in **2**. The overall structure of **3** is similar to that of $[\text{Re}_2(\text{CO})_{10}]$ [28], in which two square-pyramidal $\text{Re}(\text{CO})_5$ groups are joined by a Re–Re single bond with the equatorial ligands adopting a staggered arrangement on the two metal atoms. The two morpholine ligands are coordinated through the “amino” nitrogen atoms and occupy equatorial coordination sites. The Re–N bond distance {2.278(2) Å} is longer compared to the Re–N bond distances in previously reported η^1 -coordinated aromatic nitrogen heterocycles [4], [30]. This is due to the fact that the “amino” nitrogen atoms possess sp^3 hybridization rather than sp^2 hybridization observed for “imino” nitrogen atoms and thus the presence of hydrogen atoms cause steric hindrance to push the nitrogen atoms away from the rhenium atoms. Furthermore, because of this sp^3 hybridization the morpholine ligands are slightly tilted from the dirhenium metal plane and shows eclipsed arrangement with the N–Re–Re–N dihedral angle of 133.1(1)°.

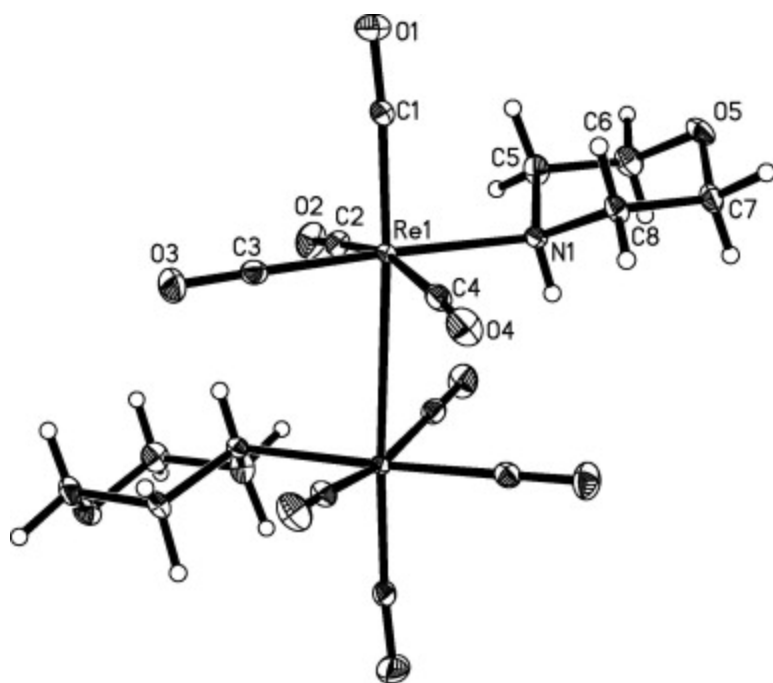


Fig. 2. Molecular structure of complex $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**). Selected bond distances (Å) and angles (°): $\text{Re}(1)\text{-C}(3) = 1.918(2)$, $\text{Re}(1)\text{-C}(1) = 1.924(2)$, $\text{Re}(1)\text{-C}(2) = 1.980(2)$, $\text{Re}(1)\text{-C}(4) = 1.992(2)$, $\text{Re}(1)\text{-N}(1) = 2.278(2)$, $\text{Re}(1)\text{-Re}(1)\#1 = 3.0337(3)$, $\text{C}(3)\text{-Re}(1)\text{-C}(1) = 91.88(9)$, $\text{C}(3)\text{-Re}(1)\text{-C}(2) = 90.58(9)$, $\text{C}(3)\text{-Re}(1)\text{-N}(1) = 177.74(7)$, $\text{C}(1)\text{-Re}(1)\text{-N}(1) = 90.38(8)$, $\text{C}(2)\text{-Re}(1)\text{-N}(1) = 89.01(8)$, $\text{C}(4)\text{-Re}(1)\text{-N}(1) = 92.41(8)$, $\text{C}(3)\text{-Re}(1)\text{-Re}(1)\#1 = 85.40(6)$, $\text{C}(1)\text{-Re}(1)\text{-Re}(1)\#1 = 176.84(7)$, $\text{C}(2)\text{-Re}(1)\text{-Re}(1)\#1 = 82.02(7)$, $\text{C}(4)\text{-Re}(1)\text{-Re}(1)\#1 = 85.33(6)$, $\text{N}(1)\text{-Re}(1)\text{-Re}(1)\#1 = 92.34(4)$.

The spectroscopic data in solution for **3** are consistent with the structure observed in solid-state. The pattern of the IR spectrum of **3** in the carbonyl stretching region is very similar to that of $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_5\text{H}_4)_2]$ indicating that they have a very similar distribution of the carbonyl ligands. The ^1H NMR spectrum of **3** shows two multiplets at δ 3.71 and 3.38 assigned to C–H protons of the rings and a singlet at δ 3.10 due to the N–H protons. The mass spectrum of **3** exhibits a molecular ion peak at m/z 770 and fragmentation peaks due to the sequential loss of eight carbonyl groups.

The reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 5 equiv. of 1-methylimidazole in refluxing benzene gave the dinuclear compound $[\text{Re}_2(\text{CO})_8\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**4**) and the mononuclear compound *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**) in 18% and 26% yields, respectively (Scheme 1). Compounds **4** and **5** have been characterized by elemental analysis, infrared, ^1H NMR and mass spectroscopic data together with single crystal X-ray diffraction analysis for **5**. The pattern for the infrared spectrum of **4** in the carbonyl region is very similar to that of **3** indicating that they are isostructural. The mass spectrum of **4** exhibits a molecular ion peak at m/z 760 and sequential loss of eight carbonyl groups were observed. The ^1H NMR spectrum of **4** shows three singlets at δ 7.96, 7.11 and 6.88 assigned to the imidazole ring protons and the aliphatic region exhibits a singlet at δ 2.78 due to the methyl protons of the ligands.

The molecular structure of **5** is shown in Fig. 3 and selected bond distances and angles are in the caption. The X-ray structure clearly reveals that compound consists of a single rhenium atom with three carbonyl groups, two N coordinated η^1 -methylimidazole ligands and a terminally coordinated Cl ligand which was contributed by the solvent (CH_2Cl_2) [8]. The coordination geometry at the Re atom is a distorted octahedron with three carbonyl ligands arranged in a *facial* fashion. The distortion from octahedral coordination geometry is evident from reduction of the N–Re–N angles from 90° in the idealized polyhedron to $85.0(1)^\circ$ in **5**. The basic structure of **5** is very similar to that of the recently reported thiazole analog *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ [8]. The *trans* angles about rhenium range from $175.4(1)$ to $179.0(1)^\circ$ which are comparable to the corresponding angles in *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ {range from $175.4(1)$ to $179.3(2)^\circ$ } [21]. The Re–N bond distances {Re(1)–N(3) 2.186(3); Re(1)–N(1) 2.201(3) Å} are comparable to the Re–N bond distances in *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ {2.185(6)–2.210(6) Å} [21] and $[\text{Re}(\text{CO})_3(\eta^2\text{-dpp})\text{Cl}]$ {1.178(5)–2.175(5) Å} [32]. The carbonyl groups assume a *fac* geometry with an average Re–CO bond distance of 1.917(3) similar to the average Re–CO bond distances in *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ {1.914(7) Å} [29] and $[\text{Re}(\text{CO})_3(\eta^2\text{-dpp})\text{Cl}]$ {1.915(7) Å} [32].

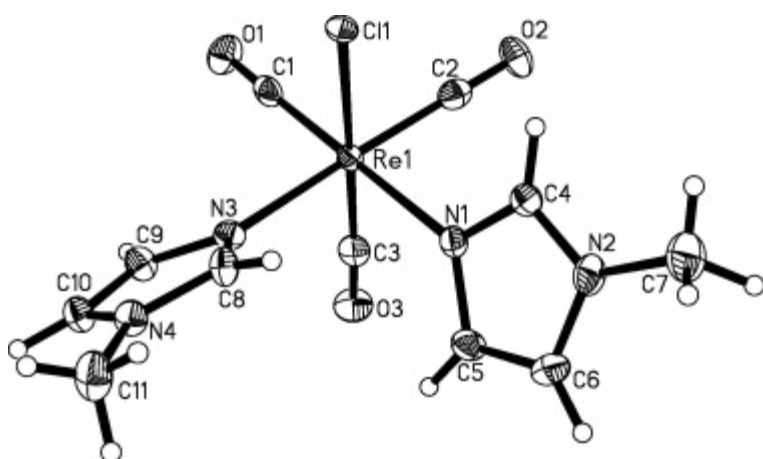


Fig. 3. Molecular structure of complex *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**). Selected bond distances (Å) and angles ($^\circ$): Re(1)–C(3) = 1.91(1), Re(1)–C(1) = 1.921(4), Re(1)–C(2) = 1.922(4), Re(1)–N(3) = 2.186(3), Re(1)–N(1) = 2.201(3), Re(1)–Cl(1) = 2.453(3), C(3)–Re(1)–C(1) = $86.2(3)$; C(3)–Re(1)–C(2) = $90.2(3)$, C(1)–Re(1)–C(2) = $88.5(2)$, C(3)–Re(1)–N(3) = $92.3(3)$, C(1)–Re(1)–N(3) = $95.5(1)$, C(2)–Re(1)–N(3) = $175.4(1)$, C(3)–Re(1)–N(1) = $92.9(3)$, C(1)–Re(1)–N(1) = $179.0(1)$, C(2)–Re(1)–N(1) = $91.0(1)$, N(3)–Re(1)–N(1) = $85.0(1)$, C(3)–Re(1)–Cl(1) = $177.3(3)$, C(1)–Re(1)–Cl(1) = $95.5(1)$, C(2)–Re(1)–Cl(1) = $92.0(1)$, N(3)–Re(1)–Cl(1) = $85.43(9)$, N(1)–Re(1)–Cl(1) = $85.44(9)$.

The spectroscopic data of **5** are consistent with the solid-state structure. The infrared spectrum displays three bands in the carbonyl stretching region similar to those observed for *fac*- $[\text{Re}(\text{CO})_3(\text{Cl})\{\eta^1\text{-NC}_3\text{H}_3\text{S}\}_2]$ [21], $[\text{Re}(\text{CO})_3(\text{tpy})\text{Cl}]$ [33], $[\text{Re}(\text{CO})_3(\text{ph-tpy})\text{Br}]$ [34] and $[\text{Re}(\text{CO})_3(\text{diimine})\text{Cl}]$ [35]. The ^1H NMR spectrum of **5** displays three singlets at δ 8.03, 7.15 and 6.55 due to the C–H protons of the rings and a singlet δ 3.68 for the methyl protons of the

rings. This data indicates that the two coordinated rings are magnetically equivalent due to the Cs point group of the molecule. The mass spectrum of **5** exhibits molecular ion peak at m/z 470, corresponding to its formulation and ions due to the successive loss of three carbonyl groups.

In summary, we have shown that the products obtained from the reactions of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with heterocyclic ligands are remarkably sensitive to the structure of the heterocycles used. For example, the reaction of $[\text{Re}_2(\text{CO})_8(\text{MeCN})_2]$ with 2-vinylpyridine leads not to the expected product $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_5\text{H}_5\text{CH}=\text{CH}_2)_2]$ or $[\text{Re}_2(\text{CO})_8(\mu, \eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)(\mu\text{-H})]$ but instead to $[\text{Re}_2(\text{CO})_8(\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2)]$, a unique example of a dirhenium compound containing $\mu\text{-}\eta^1\text{:}\eta^2\text{-NC}_5\text{H}_4\text{CH}=\text{CH}_2$ ligand whereas morpholine affords simple substitution products $[\text{Re}_2(\text{CO})_8(\eta^1\text{-NC}_4\text{H}_9\text{O})_2]$ (**3**) and $[\text{Re}_2(\text{CO})_8\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**4**). In sharp contrast, 1-methylimidazole furnishes the mononuclear compound *fac*- $[\text{ReCl}(\text{CO})_3\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**5**) as the major product together with $[\text{Re}_2(\text{CO})_8\{\eta^1\text{-NC}_3\text{H}_3\text{N}(\text{CH}_3)\}_2]$ (**4**) as the minor product, again demonstrating the sensitivity of the heterocyclic ring on product formation.

4. Supplementary material

CCDC 607488, 607489 and 621649 contain the supplementary data for **1**, **3** and **5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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