Dirhenium Carbonyl Complexes Bearing 2-Vinylpyridine, Morpholine and 1-Methylimidazole Ligands

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

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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 \([\text{Re}_2(\text{CO})_8(\mu-\eta^1:\eta^2-\text{NC}_5\text{H}_4\text{CH}==\text{CH}_2)]\) (1) in 39% yield in which the \(\mu-\eta^1:\eta^2\)-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, \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{O})]\) (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 \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{N}(\text{CH}_3))_2]\) (4) and the mononuclear compound \(\text{fac-}[\text{ReCl}(\text{CO})_3(\eta^1-\text{NC}_4\text{H}_9\text{N}(\text{CH}_3))_2]\) (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 \(\eta^1\)-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 \([\text{Re}_2(\text{CO})_8(\mu-\eta^1-\text{NC}_4\text{H}_9\text{CH}==\text{CH}_2)]\) (1), \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{O})]\) (2), \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{O})_2]\) (3) and \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{N}(\text{CH}_3))_2]\) (4) and the mononuclear compound \(\text{fac-}[\text{ReCl}(\text{CO})_3(\eta^1-\text{NC}_4\text{H}_9\text{N}(\text{CH}_3))_2]\) (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 \([\text{Re}_2(\text{CO})_8(\mu-\eta^1-\text{C}_2\text{H}_4\text{N})(\mu-\text{H})]\) were investigated by Brown and co-workers in 1982 [7]. Arce et al. [4] reported the bipyridyldirhenium complexes \([\text{Re}_2(\text{CO})_8(\mu-\eta^1-\text{C}_12\text{H}_{10}\text{N}_2)]\), \([\text{Re}_2(\text{CO})_8(\mu-\eta^1-\text{C}_12\text{H}_{10}\text{N}_2)(\mu-\text{H})]\), \([\text{Re}_2(\text{CO})_8(\mu-\eta^4-\text{C}_12\text{H}_{10}\text{N}_2)(\mu-\text{H})]\), \([\text{Re}_2(\text{CO})_8(\mu-\eta^4-\text{C}_12\text{H}_{10}\text{N}_2)]\) and \([\text{Re}_2(\text{CO})_8(\mu-\eta^6-\text{C}_24\text{H}_{18}\text{N}_4)]\) from the reactions of \(\text{trans-1,2-bis(2-pyridyl)}\text{ethene}\) with \([\text{Re}_2(\text{CO})_8(\text{MeCN})_2]\). Recently we have reported the dirhenium cyclometalated compounds
[Re₂(CO)₇{μ-2,3-η²-C₃H(4-R)NS}{η¹-NC₅H₂(4-R)S}{μ-H}] and [Re₂(CO)₈{μ-2,3-η²-C₃H(R)NS}{η¹-NC₅H₂(4-R)S}₂{μ-H}] together with the mononuclear fac-[Re(CO)₅(Cl){η¹-NC₅H₂(4-R)S}] (R = H, CH₃) from the reactions of [Re₂(CO)₈(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 [Os₃(CO)₁₀(μ-H)₂] and [Os₅(CO)₁₀(MeCN)₄] react with 2-vinylpyridine with C–H bond cleavage at the vinyl carbon atom to give the triosmium cluster [Os₅(CO)₁₀(η¹:η²:η¹-NC₅H₄CH═CH)(μ-H)] with an open structure. A similar bonding mode of NC₅H₄CH═CH has been reported in [Os₅(CO)₂₀(μ-η¹:η²:η¹-NC₅H₄CH═CH)(μ-H)] [19], [Os₄Rh(CO)₁₃(μ-η¹:η²:η¹-NC₅H₄CH═CH)(μ-H)] [20] and in the mononuclear carbonyl complex [Re(NC₅H₄CH═CH)(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 [Os₃(CO)₁₀(MeCN)₄] to afford the C–H oxidative-addition product [Os₃(CO)₁₀(μ-η²-NC₅H₆O)(μ-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 [Re₂(CO)₈(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. Me₃NO · 2H₂O was purchased from Lancaster and water from it was removed and a Dean-Stark apparatus using benzene as a solvent. The starting compound [Re₂(CO)₈(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 \([\text{Re}_2(\text{CO})_8(\mu-\eta^1:\eta^2-\text{NC}_5\text{H}_4\text{CH}≡\text{CH}_2)]\) (1) (61 mg, 39%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calc. for C_{15}H_7N_1O_8Re_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, 1Hₐ), 2.08 (dd, J = 1.6, 9.2 Hz, 1Hₐ), 1.87 (dd, J = 1.6, 11.4 Hz, 1Hₐ). 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 C_{13}H_9N_1O_10Re_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 C_{16}H_{18}N_2O_{10}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 \([\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_3\text{H}_3\text{N(CH}_3)\text{)}_2]\) (4) (30 mg, 18%) as yellow crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calc. for C_{16}H_{12}N_4O_8Re_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-\([\text{ReCl}(\text{CO})_3(\eta^1-\text{NC}_3\text{H}_3\text{N(CH}_3)\text{)}_2]\) (5) (22 mg, 26%) as colorless crystals after recrystallization from hexane/CH_2Cl_2 at −4 °C. Anal. Calc. for C_{11}H_{10}ClN_4O_3Re: 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
(CDCl$_3$): 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 Kα 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) = 1.2$B$(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.

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<th>3</th>
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<td>12.7458(12)</td>
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<td>$c$ (Å)</td>
<td>16.0788(17)</td>
<td>13.2940(14)</td>
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<td>Crystal size (mm&lt;sup&gt;3&lt;/sup&gt;)</td>
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<td>0.811 and −0.618</td>
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3. Results and discussion

Reaction of [Re<sub>2</sub>(CO)<sub>8</sub>(MeCN)<sub>2</sub>] with 5 equiv. of 2-vinylpyridine in refluxing benzene afforded the new compound [Re<sub>2</sub>(CO)<sub>8</sub>(μ-η<sup>1</sup>·η<sup>2</sup>-NC<sub>5</sub>H<sub>4</sub>CH=CH<sub>2</sub>)<sub>] (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, [RuCl<sub>2</sub>(2-CH<sub>2</sub>CHC<sub>5</sub>H<sub>3</sub>N)] [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-η<sup>1</sup>·η<sup>2</sup>-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 accord 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 [Re<sub>2</sub>(CO)<sub>10</sub>] [28], 3.036(1) Å in [Re<sub>2</sub>(CO)<sub>8</sub>(μ-η<sup>1</sup>·C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>)<sub>] [4] and 3.084(1) Å in [Re<sub>2</sub>(CO)<sub>8</sub>(μ-η<sup>3</sup>·C<sub>12</sub>H<sub>10</sub>N<sub>2</sub>)<sub>] [2b]. The three
equatorial CO ligands bonded to Re(1) have torsion angles of the order 81(1)° to 155(4)° with respect to Re(2)–C(8) which is typical of [M₂(CO)₁₀–Lₓ] 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{η²-H₂B(timMe)}₂(4-NMe₂py)] (timMe = 2-mercaptot-1-methylimidazolyl) [30] and 2.211(6) Å in [Re₂(CO)₆(μ-η³-C₁₂H₁₀N₂)] [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 η²-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 [Re₂(CO)₆(μ-η³-C₁₂H₁₀N₂)] and is longer than an uncoordinated C–C double bond lengths [4]. The formation of 1 from [Re₂(CO)₆(MeCN)₂] and 2-vinylpyridine simply requires displacement of the two acetonitrile ligands.

Scheme 1.
Fig. 1. Molecular structure of complex $[\text{Re}_2(\text{CO})_8(\mu-\eta^1:\eta^2-\text{NC}_4\text{H}_9\text{O})]$ (1). Selected bond distances (Å) and angles (°): Re(1)–C(1) = 1.911(4), Re(1)–C(3) = 1.921(5), Re(1)–C(2) = 1.997(5), Re(1)–C(4) = 1.998(5), Re(1)–N(1) = 2.208(4), Re(1)–Re(2) = 3.0331(3), Re(2)–C(6) = 1.949(5), Re(2)–C(8) = 1.949(5), Re(2)–C(5) = 1.992(5), Re(2)–C(7) = 1.990(5), Re(2)–C(10) = 2.287(4), Re(2)–C(9) = 2.325(5), N(1)–Re(1)–Re(2) = 83.1(1), C(6)–Re(2)–Re(1) = 79.8(1), C(8)–Re(2)–Re(1) = 170.5(2), C(5)–Re(2)–Re(1) = 87.6(1), C(7)–Re(2)–Re(1) = 82.5(1), C(10)–Re(2)–Re(1) = 72.4(1), C(9)–Re(2)–Re(1) = 107.9(1).

The solid-state structure of 1 is supported by the solution spectroscopic data. The $\nu$(CO) absorption spectrum indicates that all the carbonyl groups are terminal. In particular, the $^1$H NMR spectrum of 1 in the aromatic region contains two doublets at $\delta$ 8.59 ($J = 5.2$ Hz), 7.06 ($J = 7.8$ Hz) and two triplets at $\delta$ 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 $\delta$4.77 ($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 $^1$H 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 $\eta^1$-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 $[\text{Re}_2(\text{CO})_8(\mu-\eta^2-\text{NC}_4\text{H}_9\text{O})(\mu-H)]$. 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 $[\text{Re}_2(\text{CO})_8(\eta^1-\text{NC}_4\text{H}_9\text{O})]$ (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 [Re₂(CO)₆(MeCN)] impurity in [Re₂(CO)₈(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 [Re₂(CO)₉L] (L = t-BuNC, P(CH₂C₆H₅)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 carbonyls 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 [Re₂(CO)₁₀] [28], in which two square-pyramidal Re(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 η¹-coordinated aromatic nitrogen heterocycles [4], [30]. This is due to the fact that the “amino” nitrogen atoms possess sp³ hybridization rather than sp² 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 sp³ 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)°.
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 [Re₄(CO)₈(η¹-NC₅H₄)] 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 [Re₂(CO)₈(MeCN)₂] with 5 equiv. of 1-methylimidazole in refluxing benzene gave the dinuclear compound [Re₂(CO)₈(η¹-NC₃H₃N(CH₃))₂] (4) and the mononuclear compound fac-[ReCl(CO)₅(η¹-NC₃H₃N(CH₃))] (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'-methylimidazole ligands and a terminally coordinated Cl ligand which was contributed by the solvent (CH$_2$Cl$_2$) [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)° in 5. The basic structure of 5 is very similar to that of the recently reported thiazole analog *fac*[Re(CO)$_3$(Cl){η'-NC$_3$H$_3$S}$_2$] [8]. The *trans* angles about rhenium range from 175.4(1) to 179.0(1)° which are comparable to the corresponding angles in *fac*[Re(CO)$_3$(Cl){η'-NC$_3$H$_3$S}$_2$] {range from 175.4(1) to 179.3(2) Å} [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*[Re(CO)$_3$(Cl){η'-NC$_3$H$_3$S}$_2$] {2.185(6)–2.210(6) Å} [21] and [Re(CO)$_3$(η'-dpp)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*[Re(CO)$_3$(Cl){η'-NC$_3$H$_3$S}$_2$] {1.914(7) Å} [29] and [Re(CO)$_3$(η'-dpp)Cl] {1.915(7) Å} [32].

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*[Re(CO)$_3$(Cl){η'-NC$_3$H$_3$S}$_2$] [21], [Re(CO)$_3$(tpy)Cl] [33], [Re(CO)$_3$(ph-tpy)Br] [34] and [Re(CO)$_3$(diimine)Cl] [35]. The $^1$H 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 [Re₂(CO)₈(MeCN)₂] with heterocyclic ligands are remarkably sensitive to the structure of the heterocycles used. For example, the reaction of [Re₂(CO)₈(MeCN)₂] with 2-vinylpyridine leads not to the expected product [Re₂(CO)₈(η¹⁻NC₅H₅CH=CH₂)] or [Re₂(CO)₈(μ,η²⁻NC₅H₄CH=CH₂)(μ-H)] but instead to [Re₂(CO)₈(μ⁻η¹⁻NC₅H₄CH=CH₂)], a unique example of a dirhenium compound containing μ⁻η¹⁻NC₅H₄CH=CH₂ ligand whereas morpholine affords simple substitution products [Re₂(CO)₈(η¹⁻NC₅H₄O₂)] (3) and [Re₂(CO)₈(η¹⁻NC₅H₃N(CH₃)] (4). In sharp contrast, 1-methylimidazole furnishes the mononuclear compound fac-[ReCl(CO)₈{η¹⁻NC₅H₃N(CH₃)}₂] (5) as the major product together with [Re₂(CO)₈{η¹⁻NC₅H₃N(CH₃)}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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