

# Axial and equatorial carbene ligands of dimanganese and dirhenium monocarbene complexes: Synthesis, characterisation and structural studies

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## Abstract

The binuclear alkoxy carbene complexes  $[\text{M}_2(\text{CO})_9\{\text{C}(\text{OEt})\text{C}_4\text{H}_3\text{Y}\}]$  ( $\text{M} = \text{Mn}$ ,  $\text{Y} = \text{S}(\mathbf{1})$ ,  $\text{O}(\mathbf{2})$ ;  $\text{Re}$ ,  $\text{Y} = \text{S}(\mathbf{3})$ ,  $\text{O}(\mathbf{4})$ ) were synthesised and characterised, giving axial carbene ligands for the dimanganese complexes, and equatorial carbene ligands for the dirhenium complexes. Aminolysis of these complexes with ammonia and *n*-propylamine yielded complexes  $[\text{M}_2(\text{CO})_9\{\text{C}(\text{NHR})\text{C}_4\text{H}_3\text{Y}\}]$  ( $\text{R} = \text{H}$ ,  $\text{M} = \text{Mn}$ ,  $\text{Y} = \text{S}(\mathbf{5})$ ,  $\text{O}(\mathbf{6})$ ;  $\text{Re}$ ,  $\text{Y} = \text{S}(\mathbf{7})$ ,  $\text{O}(\mathbf{8})$ ;  $\text{R} = \text{propyl}$ ,  $\text{M} = \text{Mn}$ ,  $\text{Y} = \text{S}(\mathbf{9})$ ,  $\text{O}(\mathbf{10})$ ;  $\text{Re}$ ,  $\text{Y} = \text{S}(\mathbf{11})$ ,  $\text{O}(\mathbf{12})$ ). For the smaller  $\text{NH}_2$ -substituted carbene ligands, the X-ray structures determined showed equatorial carbene ligands for both dimanganese and dirhenium complexes, while the  $\text{NHPr}$ -substituted carbene complexes retained the original configurations of the precursor alkoxy carbene complex, indicating that the steric effects of both the  $\text{M}(\text{CO})_5$ -fragment and the carbene ligand substituent can affect the coordination site of the carbene ligands of Group VII transition metal complexes in the solid state.

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**Keywords:** Carbene complexes; Manganese; Rhenium; Metal carbonyls; Axial; Equatorial

## 1. Introduction

The classical Fischer method of carbene synthesis was used to synthesise binuclear complexes of the type  $[(\text{CO})_9\text{M}_2\{\text{C}(\text{OR}')\text{R}\}]$  ( $\text{M} = \text{Mn}$ ,  $\text{Tc}$ ,  $\text{Re}$ ;  $\text{R} = \text{alkyl}$  or  $\text{aryl}$ ;  $\text{R}' = \text{alkyl}$ ) [1]. Following the first paper reporting the synthesis of the alkoxy carbene complexes  $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OEt})\text{Ph}]$  and  $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OEt})\text{Me}]$ , there was some uncertainty as to whether the carbene ligand was in an equatorial or an axial position. From the IR spectrum, eight bands were observed for  $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OEt})\text{Me}]$ , corresponding to the  $C_s$ -symmetry (nine bands expected) of an *eq*- $[\text{Mn}_2(\text{CO})_9\text{L}]$  complex. However, for  $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OEt})\text{Ph}]$  only five  $\nu_{\text{CO}}$ -bands, possibly indicating *ax*- $[\text{Mn}_2(\text{CO})_9\text{L}]$ , were seen in the IR spectrum. Shortly after this, Huttner and Regler [2] reported the crystal structure

of  $[\text{Mn}_2(\text{CO})_9\text{C}(\text{OEt})\text{Ph}]$ , and found the carbene ligand to be in the equatorial position. It was clear that bulky ligands could cause steric complications in the crowded equatorial positions. As a result the ethyl group was found in the *cis* configuration with respect to the C–O bond, in contrast to the *trans* configuration of the methyl group found in the X-ray crystal structure of  $[\text{Cr}(\text{CO})_5\{\text{C}(\text{OMe})(\text{Ph})\}]$  [3]. This also demonstrated that assignments of structures based on the number of infrared bands must be done with care as spectra may display fewer peaks due to overlap.

After the serendipitous discovery of binuclear monocarbene complexes of manganese,  $[\text{Mn}_2(\text{CO})_9(\text{carbene})]$ , with cyclic alkoxy carbene ligands from  $\text{Na}[\text{Mn}(\text{CO})_5]$  and 1,3-dihaloalkanes [4], a detailed mechanistic study of the reactions of  $\text{Na}[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Mn}$ ,  $\text{Re}$ ) with 1,3-dihaloalkanes followed [5]. These complexes displayed equatorially substituted carbene ligands for both manganese and rhenium [6]. We ascribe the presence of these carbene ligands in the preferred, electronically favoured equatorial position

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for manganese to sterically less demanding cyclic carbene ligands. Since the synthesis of the first aminocarbene complexes of transition metals, it was recognised that these complexes are more stable than their alkoxy analogues [7], and they are increasingly being seen as versatile starting materials for the synthesis of nitrogen-containing heterocyclic compounds [8]. Post and Watters were the first to report the preparation of binuclear metal carbonyl complexes and characterisation with methylaminocarbene ligands [9]. From the infrared and Raman data, they concluded that both complexes  $[M_2(CO)_9\{C(NHCH_3)Me\}]$  ( $M = Mn, Re$ ) were equatorially substituted. While the dirhenium aminocarbene complex could be isomerised into a *cis-trans* mixture about the C–N bond, no *trans* dimanganese aminocarbene complex could be isolated.

In order to investigate the possibility of manipulating the position of carbene ligands of the Group VII binuclear complexes, alkoxy- and amino-substituted carbene complexes, illustrated in Scheme 1, were synthesised and characterised for comparison of the steric and electronic

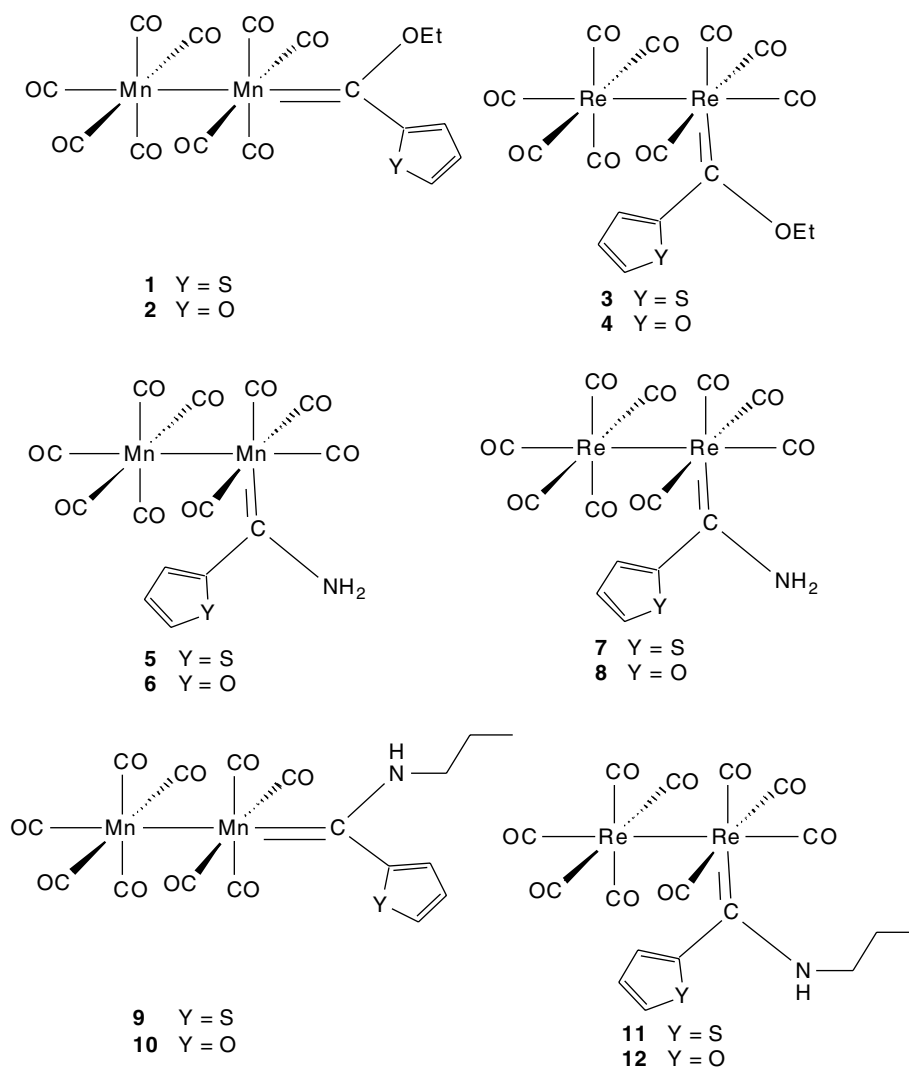
properties. The complexes **1**, **3** and **5** have already been synthesised in our laboratories, and their crystal structures are reported [10].

## 2. Results and discussion

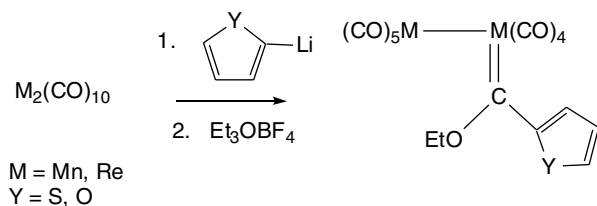
### 2.1. Synthesis

In a typical experiment (Scheme 2), the bimetallic carbene complexes were prepared by reacting the bimetallic decacarbonyl precursors with lithiated thiophene or furan in THF at low temperature [11]. After removing the THF under reduced pressure, the residue was dissolved in dichloromethane and alkylated by  $Et_3OBF_4$ . Purification of the product to remove unreacted bimetal decacarbonyl was achieved by column chromatography. The binuclear monocarbene complexes **1–4** were isolated in yields ranging from 64% to 72%.

Synthesis of the aminocarbene complexes was carried out as described by Klabunde and Fischer [12] (Scheme



Scheme 1.



Scheme 2.

3). A slow stream of ammonia was bubbled through a solution of the binuclear ethoxycarbene complex dissolved in diethyl ether at room temperature. The colour of the solution changed rapidly from red to orange. After thin layer chromatography confirmed that all of the ethoxycarbene complex had been converted, the solvent was removed and the aminocarbene complex were purified by column chromatography on aluminium oxide. Complexes **5–8** were obtained in yields greater than 85%.

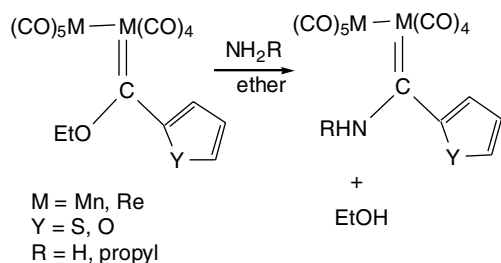
The procedure was repeated, but instead of bubbling ammonia gas through the solution, excess *n*-propylamine was added to the reaction mixture in ether, to obtain the *n*-propylamine-substituted carbene complexes **9–12** in yields ranging from 75% to 87%. When repeating the aminolysis with the more bulky secondary amines, diethylamine and diisopropylamine, no aminocarbene products were obtained [13].

## 2.2. Characterisation of the complexes

The new compounds were characterised in solution by NMR and IR spectroscopy and mass spectrometry, with data values tabulated in Table 1.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the dirhenium complexes were recorded in deuterated chloroform, but spectra of high resolution could only be obtained in acetone- $d_6$  for the dimanganese complexes. Fig. 1 shows the atom numbering used in the assignment of chemical shifts.

Slow decomposition of the products with time was observed during the recording of the spectra, and broadening of the signals in the case of the N-containing complexes occurred. In the  $^1\text{H}$  NMR spectra of the manganese complexes **5**, **6**, **9** and **10**, the heteroarene and amine protons are duplicated in a major and minor isomer. The N–H proton signals in the spectrum of **9** and **10** overlapped, so that these protons of both isomers could not be assigned



Scheme 3.

unambiguously. The same duplication of carbon resonances was observed in the  $^{13}\text{C}$  NMR spectra for the complexes. We suspect that in solution, a mixture of equatorial and axial aminocarbene manganese complexes exist. No  $^{13}\text{C}$  NMR spectra could be obtained for **9** and **12** due to excessive decomposition of the complexes during spectrum recording. A significant upfield shift of the signals of the C1 carbene carbon atom of  $\Delta\delta = 20\text{--}50$  ppm is observed in all recorded spectra of the aminocarbene complexes, when compared to the ethoxycarbene analogues, although a smaller upfield shift for the arene carbon atoms is seen. This is ascribed to the greater ability of the nitrogen lone pair to donate electron density to the electrophilic carbene carbon atom.

The infrared spectra of the carbonyl stretching frequencies of **1–4** were recorded in hexane, while that of **5–12** were recorded in dichloromethane due to the insolubility of these complexes. The carbonyl stretching modes of equatorially and axially substituted bimetal nonacarbonyl complexes were summarised by Ziegler et al. [14]. All the dirhenium complexes synthesised displayed the expected typical nine-band pattern in their infrared spectra indicating an equatorially substituted bimetal nonacarbonyl complex ( $C_s$ -symmetry). These bands include six  $A'$  bands and three  $A''$  bands. On the other hand, the IR spectrum of *ax*- $[\text{M}_2(\text{CO})_9\text{L}]$  is observed to have only five bands: the three  $A^1$  bands and two E bands ( $C_{4v}$ -symmetry). The IR spectra of the dimanganese ethoxycarbene complexes **1**, **2** displayed only five carbonyl stretching bands in the carbonyl region indicating *ax*- $[\text{Mn}_2(\text{CO})_9\text{L}]$ . A search of the Cambridge Structural Database revealed that only one other axially substituted carbene complex of dimanganese nonacarbonyl has been structurally characterised [15]. This complex has the unusual carbene ligand,  $[\text{M}] = \text{C}(\text{NMe}_2)\text{-OAl}_2(\text{NMe}_2)_5$  [16]. The five-band pattern was also observed for both **9** and **10**, the *n*-propylamine-substituted carbene complexes of dimanganese, indicating that the complexes retained their axial configuration during the aminolysis reaction.

## 2.3. Crystal and molecular structures of the complexes **2**, **4**, **6** and **10**

The molecular arrangements around the metal are essentially similar for the thienyl and furyl-substituted carbene complexes, and complexes **2**, **4**, **6** and **10** are shown as representative examples. Single crystal X-ray diffraction studies confirmed the molecular structure of complexes, supporting the information obtained from the infrared data. The complexes crystallised from a dichloromethane:hexane (1:1) solution by layering of the solvents, yielding orange-red crystals for **2** and **4** and light orange crystals for **6** and **10** of good quality. Figs. 2–5 represent the ORTEP [17] + POV-Ray [18] drawings of the molecular structures of **2**, **4**, **6** and **10**, and the atom numbering schemes. Anisotropic displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are shown

Table 1  
Spectral data of complexes

Complex	IR ( $\nu_{\max}/\text{cm}^{-1}$ ) in the carbonyl region	$^1\text{H}$ NMR ( $\delta/\text{ppm}$ and $J/\text{Hz}$ )	$^{13}\text{C}$ NMR ( $\delta/\text{ppm}$ and $J/\text{Hz}$ )
2	2087m (A <sub>1</sub> (1)), 2006m (A <sub>1</sub> (2)), 1992vs (E(1)), 1971m (A <sub>1</sub> (3)), 1936m (E(2))	7.19 (dd, 3.9, 1.9, H3), 6.85 (dd, 3.9, 0.7, H4), 7.46 (dd, 3.9, 0.7, H5), MnCOEt: 5.28 (q, 7.0), 1.76 (t, 7.0)	301.0 (C1), 163.9 (C2), 112.8 (C3), 110.1 (C4), 149.5 (C5), 223.9 (Mn(CO) <sub>4</sub> ), 221.4, 219.5 (Mn(CO) <sub>5</sub> ), 74.2, 15.1 (MnCOEt)
4	2102w (A'(1)), 2045m (A'(2)), 2016s (A'(3)), 2002vs (A''(1)), 1992s (A'(4)), 1974m (A''(2)), 1955m (A'(5)), 1945m (A'(6)), 1923w (A''(3))	7.09 (dd, 3.6, 0.8, H3), 6.58 (dd, 3.6, 1.8, H4), 7.77 (dd, 1.6, 0.8, H5), ReCOEt: 4.58 (q, 7.0), 1.69 (t, 7.0)	283.2 (C1), 165.5 (C2), 114.7 (C3), 113.9 (C4), 151.6 (C5), 193.9 (Re(CO) <sub>4</sub> ), 190.4, 188.5 (Re(CO) <sub>5</sub> ), 77.6, 14.7 (ReCOEt)
6	2082m (A'(1)), 2012s (A'(2) and A'(3)), 1984vs (A''(1) and A'(4)), 1977s (A''(2)), 1956m (A'(5)), 1935s (A'(6) and A''(3))	7.50 (H3), 6.78 (H4), 7.96 (H5), 10.49, 9.90 (s, s, NH <sub>2</sub> ). Isomer: 6.79 (H3), n.o. (H4), 7.54 (H5), 9.48, n.o. (s, NH <sub>2</sub> )	275.4 (C1), 150.8 (C2), 121.0 (C3), 117.1 (C4), 123.5 (C5), 233.6 (Mn(CO) <sub>4</sub> ), 228.4, 226.2 (Mn(CO) <sub>5</sub> ). Isomer: 267.6 (C1), 150.2 (C2), 117.3 (C3), 116.9 (C4), 120.9 (C5), 229.1 (Mn(CO) <sub>4</sub> ), 224.2, n.o. (Mn(CO) <sub>5</sub> )
7	2099w (A'(1)), 2035m (A'(2) and A'(3)), 1992vs (A''(1) and A'(4)), 1984s (A''(2)), 1961m (A'(5)), 1932s (A'(6) and A''(3))	7.60 (dd, 5.2, 0.9, H3), 7.19 (dd, 5.0, 3.9, H4), 7.58 (dd, 4.0, 1.0, H5), 8.32, 8.14 (s, s, NH <sub>2</sub> )	268.8 (C1), 166.7 (C2), 131.6 (C3), 128.9 (C4), 130.8 (C5), 198.8 (Re(CO) <sub>4</sub> ), 196.2, 184.0 (Re(CO) <sub>5</sub> )
8	2098w (A'(1)), 2034m (A'(2) and A'(3)), 1990vs (A''(1) and A'(4)), 1983s (A''(2)), 1958m (A'(5)), 1931s (A'(6) and A''(3))	7.53 (dd, 5.0, 1.6, H3), 6.62 (dd, 5.0, 3.9, H4), 7.62 (dd, 3.8, 1.8, H5), 8.87, 8.03 (s, s, NH <sub>2</sub> )	238.0 (C1), n.o. (C2), 126.0 (C3), 114.3 (C4), 145.8 (C5), 200.5 (Re(CO) <sub>4</sub> ), 197.9, 184.8 (Re(CO) <sub>5</sub> )
9	2083w (A <sub>1</sub> (1)), 2029m (A <sub>1</sub> (2)), 1985vs (E(1)), 1975s (A <sub>1</sub> (3)), 1926m (E(2))	7.47 (H3), 6.82 (H4), 7.05 (H5), 3.42 (NH), 1.67, 1.24, 0.96 (NPr)	n.o.
10	2082m (A <sub>1</sub> (1)), 2012s (A <sub>1</sub> (2)), 1984vs (E(1)), 1957s (A <sub>1</sub> (3)), 1928m (E(2))	7.41 (H3), 6.75 (H4), 7.64 (H5), 3.52 (NH), 1.74, 1.00, 0.84 (NPr)	255.1 (C1), 157.4 (C2), 122.7 (C3), 113.6 (C4), 145.4 (C5), 225.3 (Mn(CO) <sub>4</sub> ), 221.7, n.o. (Mn(CO) <sub>5</sub> ), 55.0, 23.0, 11.1 (NPr). Isomer: 241.8 (C1), 155.5 (C2), 115.7 (C3), 112.3 (C4), 143.5 (C5), 223.8 (Mn(CO) <sub>4</sub> ), 220.9, n.o. (Mn(CO) <sub>5</sub> ), 53.3, 22.7, 10.8 (NPr)
11	2098w (A'(1)), 2034m (A'(2) and A'(3)), 1992vs (A''(1) and A'(4)), 1982s (A''(2)), 1959m (A'(5)), 1928m (A'(6) and A''(3))	7.64 (dd, 5.0, 1.0, H3), 6.90 (dd, 5.0, 3.7, H4), 7.07 (dd, 3.6, 1.1, H5), 8.52 (s, NH), 1.18 (t, 7.0, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ) 1.66 (tt, 7.2, 7.5, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ), 0.94 (t, 7.4, NCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> )	239.3 (C1), 150.4 (C2), 127.0 (C3), 124.2 (C4), 128.2 (C5), 199.9 (Re(CO) <sub>4</sub> ), 193.9, 190.2 (Re(CO) <sub>5</sub> ), 56.5, 29.7, 10.9 (NPr)
12	2098w (A'(1)), 2033m (A'(2) and A'(3)), 1990s (A''(1) and A'(4)), 1982s (A''(2)), 1958m (A'(5)), 1930s (A'(6) and A''(3))	7.65 (H3), 6.89 (H4), 7.65 (H5), 8.60 (NH), 1.24, 1.08, 0.99 (NPr)	n.o.

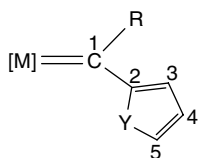
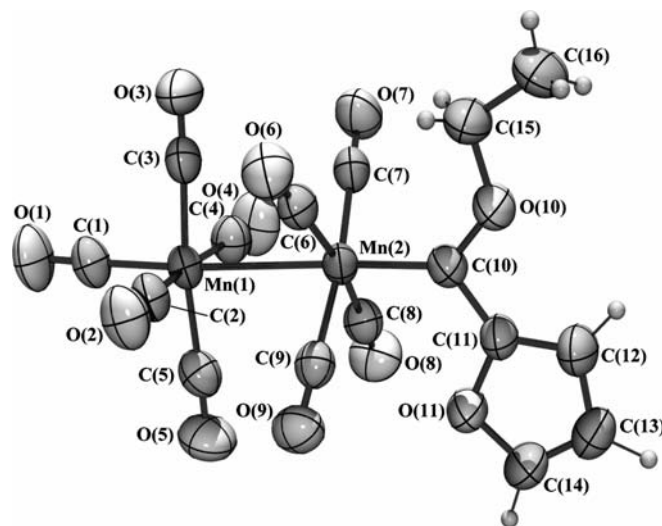


Fig. 1. Atom numbering scheme used in NMR chemical shift assignments.

as arbitrary sized spheres. Crystal data and experimental details are given in Section 3. Selected bond lengths and angles for the complexes are tabulated in Table 2 and dihedral angles between selected planes are tabulated in Table 3.

The coordination of all the metal atoms is approximately octahedral with the two sets of the equatorial carbonyl ligands being staggered. For complexes **2** and **10**, the carbene ligand is in the axial position and is therefore *trans* to the metal–metal bond. The *n*-propylamino-substituent in **10** is disordered and two orientations of the group were observed and refined to give site occupancies of 0.57(2) and 0.43(2) respectively.

The plane incorporating the carbene carbon and heteroarene ring is approximately perpendicular to the equatorial

Fig. 2. The molecular structure of complex **2** showing the atom numbering scheme.

plane of the carbonyl ligands (Table 3) and is in an intermediate position between the carbonyl ligands around Mn(2) for **2** and **10**. The carbene ligand is in the *trans*-configuration about the C–X bond (X = O, N) for **2**, **4** and **10**.

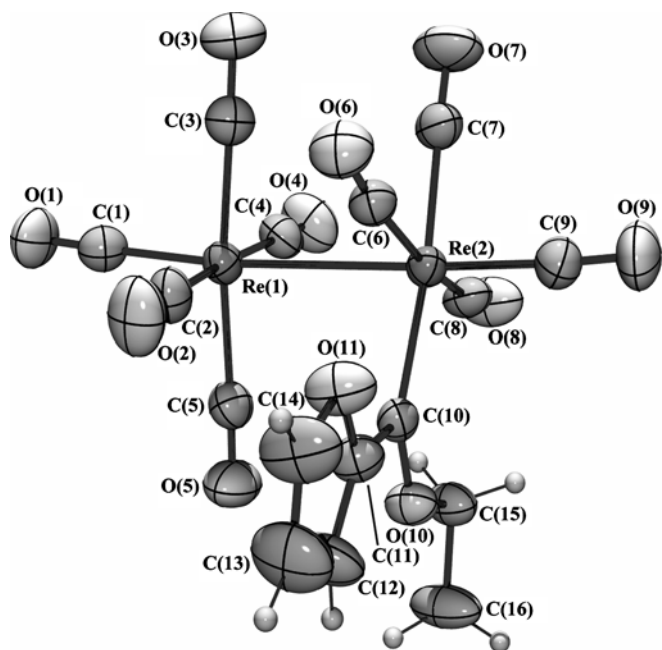


Fig. 3. The molecular structure of complex **4** showing the atom numbering scheme.

The metal–carbon(carbonyl) bond distance *trans* to the Mn–Mn bond is significantly shorter than the mean distance of the Mn–C(carbonyl) bond lengths in the equatorial planes (Table 2).

In complexes **2** and **10**, where the carbene ligand is in an axial position, the equatorial carbonyls on the two metal

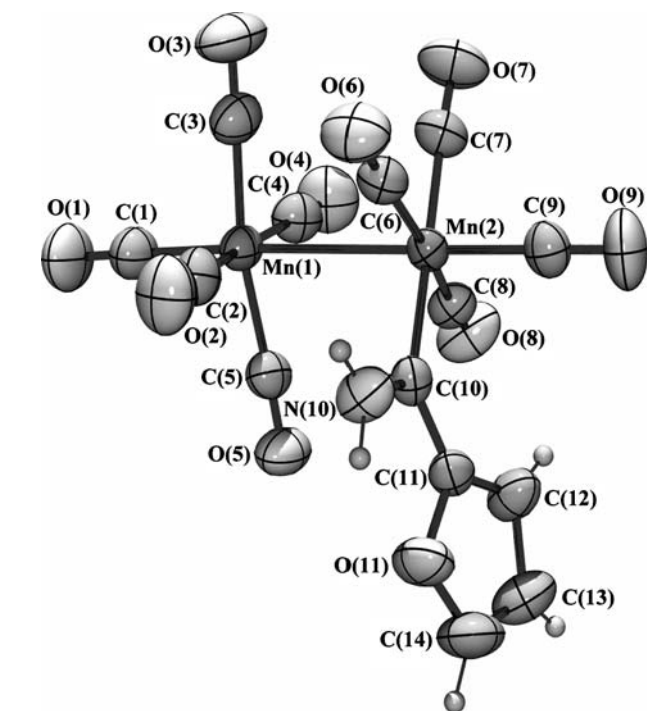


Fig. 4. The molecular structure of complex **6**, showing the atom numbering scheme.

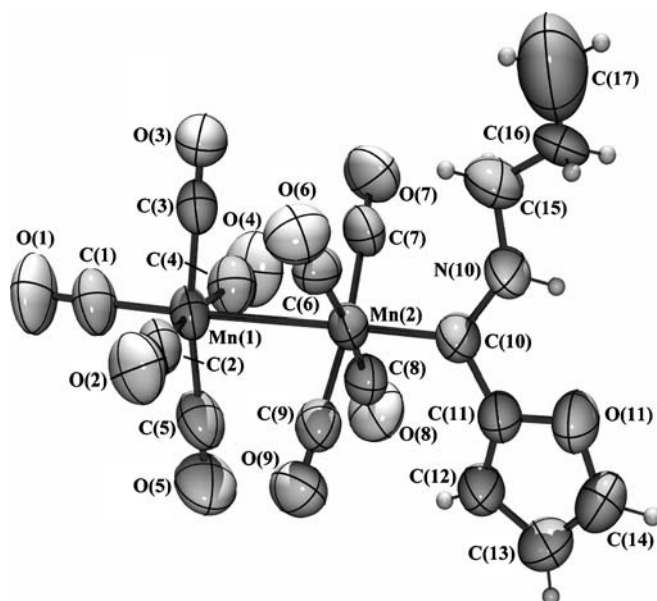


Fig. 5. The molecular structure of complex **10** showing the atom numbering scheme and illustrating the major (57%) orientation of the disordered *n*-propylamino-substituent.

atoms adopt a staggered conformation: for example, the torsion angles C(3)–Mn(1)–Mn(2)–C(7) is  $-45.90(11)^\circ$  for **2** and C(5)–Mn(1)–Mn(2)–C(9) is  $-45.8(2)^\circ$  for **10**. For **6** the analogous torsion angle, C(5)–Mn(1)–Mn(2)–C(8) is  $-40.64(9)^\circ$  however the dirhenium complex, **4**, has a less staggered conformation: the analogous torsion angle C(3)–Re(1)–Re(2)–C(8) is only  $-30.93(19)^\circ$ . This less staggered conformation is necessary to accommodate the OEt group of the carbene ligand with respect to the neighbouring carbonyl ligand, C(6), O(6), on Re(2). The longer Re(1)–Re(2) bond length ( $3.0809(3) \text{ \AA}$ ) can accommodate the carbene ligand in the equatorial site but in a less staggered conformation. For **6** the less bulky NH<sub>2</sub> group of the carbene ligand can be accommodated equatorially without a significant reduction of the staggered conformation. However, in complexes **2** and **10** the bulkier OEt and NHPr groups of the carbene ligands would require substantially less staggered conformations if the carbene ligands were to occupy equatorial sites and the shorter Mn–Mn bond lengths (ca.  $0.15 \text{ \AA}$  less than that of Re–Re) could not accommodate such conformations. Therefore the carbene ligands are forced to occupy the electronically less favourable axial sites. Most of the *eq*-[Mn<sub>2</sub>(CO)<sub>9</sub>(carbene)] complexes studied crystallographically have cyclic carbene ligands that causes less steric hindrance compared to carbene complexes with two separate substituents [6].

The average Mn–CO and Mn–Mn bond lengths of the aminocarbene complexes **6** and **10** are very similar to that of the ethoxycarbene precursors, although the Mn–C(carbene) bond lengths for **6** ( $2.028(2) \text{ \AA}$ ) and **10** ( $1.994(5) \text{ \AA}$ ) are significantly longer than the corresponding distance in **2** ( $1.932(2) \text{ \AA}$ ), indicating a weaker Mn–C(carbene) bond.

Table 2  
Selected bond lengths and angles for **2**, **4**, **6** and **10**

	<b>2</b> (M = Mn, X = O)	<b>4</b> (M = Re, X = O)	<b>6</b> (M = Mn, X = N)	<b>10</b> (M = Mn, X = N)
<i>Bond lengths (Å)</i>				
M(1)–M(2)	2.9316(5)	3.0809(3)	2.9331(4)	2.9190(9)
M(1)–C(1)	1.813(2)	1.934(4)	1.8106(9)	1.798(5)
M(2)–C(9)		1.923(5)	1.793(2)	
Mean M(1)–C(x) (x = 2, 3, 4, 5)	1.846(3)	1.989(5)	1.847(2)	1.844(6)
Mean M(2)–C(x) (x = 6, 7, 8, 9 for <b>2</b> , <b>10</b> , (x = 6, 8 for <b>4</b> , <b>6</b> ))	1.858(2)	1.990(4)	1.844(2)	1.834(6)
M(2)–C(7)		1.992(5)	1.836(2)	
M(2)–C(10)	1.932(2)	2.129(4)	2.028(2)	1.994(5)
C(10)–X(10)	1.332(3)	1.323(5)	1.310(2)	1.351(1)
C(10)–X(10a)				1.39(2)
C(10)–C(11)	1.446(3)	1.457(5)	1.452(2)	1.454(6)
C(11)–O(11)	1.379(3)	1.367(5)	1.376(2)	1.376(6)
<i>Bond angles (°)</i>				
M(2)–C(10)–X(10)	131.79(16)	130.2(3)	124.6(1)	124.1(7)
M(2)–C(10)–X(10a)				128.0(7)
X(10)–C(10)–C(11)	103.25(18)	103.1(3)	111.2(2)	111.9(6)
X(10a)–C(10)–C(11)				106.3(7)
C(11)–C(10)–M(2)	124.96(15)	126.6(3)	124.1(1)	122.2(3)

Table 3  
Dihedral angles (°) between selected least-squares planes for **2**, **4**, **6** and **10**

Planes	<b>2</b> (M = Mn, X = O)	<b>4</b> (M = Re, X = O)	<b>6</b> (M = Mn, X = N)	<b>10</b> (M = Mn)	
				X(10) = N(10)	X(10) = N(10a)
Coordination plane perpendicular to the M–carbene C bond				1 M(2), C(6), C(7), C(8), C(9) ( <b>2</b> and <b>10</b> ) 2 M(2), C(6),(8), C(9), M(1) ( <b>4</b> and <b>6</b> )	
Plane of the bonding geometry about the carbene C, C(10)				3 M(2), X(10), C(11)	
Plane of the furan ring				4 O(11), C(11), C(12), C(13), C(14)	
1 and 3	89.29(7)			87.6(4)	83.8(4)
2 and 3		85.23(8)	85.67(5)		
3 and 4	6.2(2)	5.99(20)	12.11(8)	13.0(5)	9.6(6)

A very short C(carbene)–N bond length [**6** (1.310(2) Å); **10** (1.351(12) Å)] indicates more double bond character and implies a high degree of electron donation from the nitrogen lone pair to the electrophilic carbene carbon [19]. This is also evident from the chemical shift of the carbene carbon atom at 269 ppm for **5**, 275 ppm for **6** and 255 ppm for **10** compared to 307 ppm for **1** and 301 ppm for **2**.

The Mn–C(carbene) bond is also slightly shorter for the axial carbene ligand in **10** compared to the equatorial carbene ligand of **6**. This means that the carbene carbon in the axial position must participate more in  $\pi$ -backbonding, due to the metal–metal bond *trans* to it, compared to when carbonyl ligands are *trans* to the carbene ligand in the equatorial position. As a result of this, the nitrogen atom in the axial carbene ligand shows less participation in the stabilisation of the carbene carbon, as indicated by the slightly longer C(carbene)–N bond length of **10** compared with those for **5** [10] or **6**.

The furyl ring in the two ethoxycarbene complexes, **2** and **4**, are closer to being coplanar with the plane of the bonding geometry about the carbene carbon than for the two aminocarbene complexes, **6** and **10**: the dihedral angles between the planes are ca. 6° for **2** and **4** and ca. 12° for **6**

and **10** (Table 3). Moreover, the furyl rings are orientated so that the furyl oxygen, O(11), is approximately *trans* to O(10) in **2** and **4**, but is approximately *cis* to N(10) in **6** and **10**. This can be ascribed to hydrogen bonding of the NH-proton to the furyl oxygen, with non-bonding distances of 2.137 Å for **6** and 2.172 Å for **10**.

The small NH<sub>2</sub>-group of **6** can be accommodated adjacent to the carbonyl ligands C(2)–O(2), C(5)–O(5) and C(6)–O(6) in the equatorial plane. The steric hindrance caused by the bulkier *n*-propylamine group in **10** forces the carbene ligand in the axial position, as it cannot be accommodated between the carbonyl ligands of the neighbouring metal centre. This is illustrated by the space-filling model of **6** in Fig. 6 and **10** in Fig. 7.

Fig. 6 shows the NH<sub>2</sub> group (N(1), H(1a), H(1b)) in relation to the adjacent carbonyl (C(6), O(6)) on Mn(2) and the adjacent carbonyl (C(2), O(2)) on Mn(1). As can be seen from Fig. 5, in **10** the nitrogen atom is orientated away from the adjacent carbonyl ligands. Steric hindrance is caused by the CH<sub>2</sub>-group bonded to the nitrogen. Fig. 6 illustrates the major component (C(15), H(15a), H(15b)) of the CH<sub>2</sub> of the disordered propylamine group in relation to the adjacent carbonyls (C(6), O(6) and C(7), O(7)) on Mn(2). The carbonyl (C(3), O(3)) is also shown space filled.

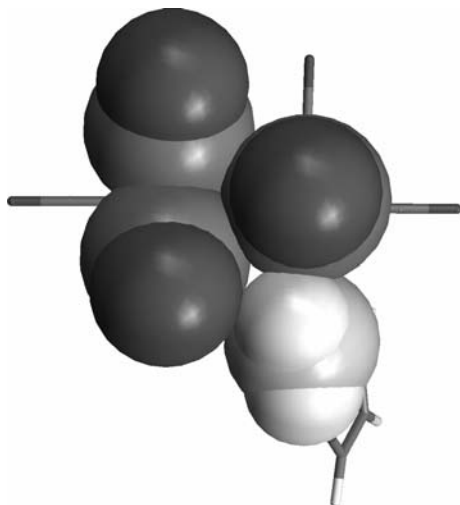


Fig. 6. Partial space-filling model of **6** illustrating the position of the substituent  $\text{NH}_2$ -group on the *eg*-carbene ligand.

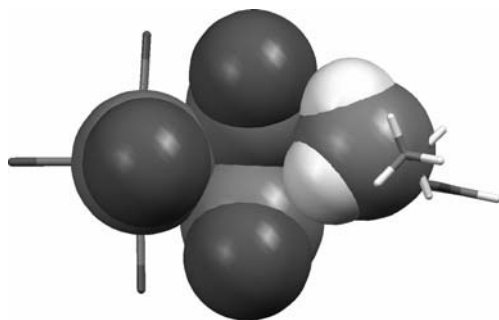


Fig. 7. Partial space-filling model of **10** illustrating the position of the substituent *n*-propylamine on the *ax*-carbene ligand.

This study indicated that the bulkiness of a  $\text{M}(\text{CO})_5$ -fragment, as well as that of the carbene ligand substituent, can affect the coordination site of a carbene ligand. It is clear that although the equatorial position is the electronically favoured position for the carbene ligands, steric effects can force the carbene ligand to occupy an axial position. It was assumed that the carbene ligand would have taken up an equatorial position based on the many reported studies of cyclic carbene ligands which are not very bulky [6,20]. The steric constraints are much more pronounced for the manganese complexes compared to the rhenium complexes, because of the much shorter Mn–Mn bond length compared to the Re–Re bond length. The aminocarbene ligand is a weaker  $\pi$ -acceptor from the rhenium with the electrophilic carbene carbon atom stabilised predominantly by electron donation from the nitrogen lone pair. The aminocarbene ligand would therefore preferentially be found at an equatorial site *trans* to a carbonyl ligand compared to being in an axial position opposite the Re–Re bond, unless forced by steric reasons to occupy the axial position. On the other hand, the ethoxycarbene ligand is a better  $\pi$ -acceptor ligand in  $[\text{Mn}_2(\text{CO})_9(\text{carbene})]$  complexes, and can be better stabilised in an axial position.

It is therefore possible to manipulate the position of the carbene ligand merely by varying the steric effects of the substituent on the carbene ligand.

### 3. Experimental

#### 3.1. General remarks

Unless otherwise stated, all manipulations were carried out using standard Schlenk and vacuum-line techniques. Column chromatography was carried out under a nitrogen atmosphere using silica gel (particle size 0.063–0.200 nm) and aluminium oxide as stationary phase, the column cooled to  $-30^\circ\text{C}$  with isopropanol. All solvents used were purified by standard procedures and distilled under nitrogen immediately prior to use. The triethyloxonium tetrafluoroborate used as alkylating agent was prepared according to the literature procedure [21]. All other reagents were purchased from commercial suppliers and used without further purification. Melting points were recorded on a hot stage Gallenkamp melting apparatus and are uncorrected. Mass spectra were recorded on a VG 70SEQ Mass Spectrometer, with the resolution for FAB = 1000 in a field of 8 kV. 3-Nitrobenzyl alcohol was used as matrix and Xe as bombardment gas. IR spectra were recorded on a Perkin–Elmer Spectrum RXI FT-IR spectrophotometer with a NaCl cell. All spectra were recorded using either dichloromethane or hexane as solvent. The vibrational stretching bands in the carbonyl region (ca.  $1500\text{--}2200\text{ cm}^{-1}$ ) were recorded for all complexes. NMR spectra were recorded on a Bruker ARX-300 and on an AVANCE 500 spectrometer.  $^1\text{H}$  NMR spectra were recorded at 300.135 and 500.139 MHz and  $^{13}\text{C}$  NMR spectra at 75.469 and 125.75 MHz respectively. The signal of the deuterated solvent was used as reference:  $^1\text{H}$   $\text{CDCl}_3$  7.24 ppm, acetone- $d_6$  2.09 ppm and  $^{13}\text{C}$   $\text{CDCl}_3$  77.00 ppm, acetone- $d_6$  205.87 ppm. For resolution enhancement of the manganese complexes, longer acquisition times were achieved by manual shimming and manipulation of the sweep width during data recording.

#### 3.2. Crystallography for complexes **2**, **4**, **6** and **10**

The crystal data collection and refinement details for complexes **2**, **4**, **6** and **10** are summarised in Table 4. All data sets were collected on a Siemens P4 diffractometer with a Bruker SMART 1K CCD detector using graphite-monochromated, Mo  $\text{K}\alpha$  radiation at  $20^\circ\text{C}$  by means of phi and omega scans. Data were corrected for Lorenz polarisation effects and structures were solved by direct methods using SHELXS [22] and refined by full-matrix least squares techniques. In the structure refinements all hydrogen atoms for **2**, **6** and the hydrogen atoms attached to the furan ring for **10** were freely refined with isotropic displacement parameters. All hydrogen atoms for **4** and the hydrogen atoms of the disordered propylamino substituent for **10** were added in calculated positions and treated as riding on

Table 4  
Crystallographic data for complexes **2**, **4**, **6** and **10**

Complex	<b>2</b>	<b>4</b>	<b>6</b>	<b>10</b>
Chemical formula	Mn <sub>2</sub> C <sub>16</sub> H <sub>8</sub> O <sub>11</sub>	Re <sub>2</sub> C <sub>16</sub> H <sub>8</sub> O <sub>11</sub>	Mn <sub>2</sub> C <sub>14</sub> H <sub>5</sub> O <sub>10</sub> N	Mn <sub>2</sub> C <sub>17</sub> H <sub>11</sub> O <sub>10</sub> N
MW (g mol <sup>-1</sup> )	486.10	748.6	457.07	499.15
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	12.4868(14)	12.9646(8)	12.0713(9)	12.7412(13)
<i>b</i> (Å)	12.3976(14)	15.6580(9)	9.0817(7)	12.9836(13)
<i>c</i> (Å)	12.5593(14)	19.3844(11)	15.8406(12)	12.6967(12)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	92.723(2)	90	92.5930(10)	90.0000(10)
$\gamma$ (°)	90	90	90	90
Volume (Å <sup>3</sup> )	1942.1(4)	3935.0(4)	1734.8(2)	2100.4(4)
<i>Z</i>	4	8	4	4
<i>d</i> <sub>calcd</sub> (mg m <sup>-3</sup> )	1.663	2.527	1.750	1.578
$\mu$ (mm <sup>-1</sup> )	1.357	12.350	1.510	1.254
$\theta$ (°)	2.31 ≤ $\theta$ ≤ 26.47	2.60 ≤ $\theta$ ≤ 26.58	2.57 ≤ $\theta$ ≤ 26.49	2.76 ≤ $\theta$ ≤ 26.44
Crystal size (mm <sup>3</sup> )	0.36 × 0.23 × 0.18	0.34 × 0.22 × 0.20	0.36 × 0.34 × 0.24	0.46 × 0.24 × 0.16
Index range	-15 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 14 -4 ≤ <i>l</i> ≤ 15	-16 ≤ <i>h</i> ≤ 16 -14 ≤ <i>k</i> ≤ 18 -24 ≤ <i>l</i> ≤ 12	-14 ≤ <i>h</i> ≤ 11 -11 ≤ <i>k</i> ≤ 5 -19 ≤ <i>l</i> ≤ 19	-15 ≤ <i>h</i> ≤ 15 -15 ≤ <i>k</i> ≤ 16 -15 ≤ <i>l</i> ≤ 5
Number of reflections collected	10,177	2012	9176	10,635
Number of independent reflections	3652	3784	3301	3943
Parameters	294	263	265	311
<i>R</i> <sub>1</sub> ( <i>F</i> <sub>0</sub> <sup>2</sup> > 2σ <i>F</i> <sub>0</sub> <sup>2</sup> )	0.0303	0.0205	0.0274	0.0522
<i>wR</i> <sub>2</sub> (all data)	0.0846	0.0520	0.0760	0.1592

the atom to which they are attached with isotropic displacement parameters calculated as  $X \times U_{eq}$  of the atom to which they are attached,  $X = 1.5$  for the methyl hydrogens and 1.2 for all other hydrogens. All non-hydrogen atoms were refined with anisotropic displacement parameters. In structure **10** two orientations of the disordered propylamino substituent were observed. The conformations of the two components were such that the positions of the methyl carbon C(17) and C(17a) approximately coincided. Attempts to refine separate positional and/or displacement parameters for C(17) and C(17a) were unstable and so C(17) and C(17a) were refined with common positional and displacement parameters. Site occupation factors for the two orientations were refined but were constrained to sum to 1.0. Crystal data and other experimental procedures and refinement parameters are given in Table 4.

### 3.3. Synthesis

#### 3.3.1. *ax*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(OEt)2-thienyl}] **1** [10]

Thiophene (0.185 g, 2.2 mmol, 0.175 mL) was stirred while adding *n*-BuLi (2.2 mmol, 1.6 M, 1.4 mL) in 40 mL THF at -20 °C under an inert N<sub>2</sub> atmosphere. Stirring was continued for 30 min. Yellow [Mn<sub>2</sub>(CO)<sub>10</sub>] (0.78 g, 2 mmol) was added to the reaction mixture at -70 °C, resulting in a colour change of the reaction mixture to orange-red while stirring for 1 h. Stirring was then continued for an additional 30 min at room temperature. THF solvent was evaporated under reduced pressure. Et<sub>3</sub>OBF<sub>4</sub> (0.42 g, 2.2 mmol) in dichloromethane was added to the

reaction mixture at -30 °C and stirred until reaction completion. LiBF<sub>4</sub> salts were removed by filtering and reaction products were purified via column chromatography using hexane/dichloromethane (4:1) as eluent. Recrystallisation of the orange product (0.723 g) was done by solvent layering of hexane/dichloromethane (3:1). Yield: 72% for Mn<sub>2</sub>C<sub>16</sub>H<sub>8</sub>O<sub>10</sub>S (502.18). Mp 85–87 °C. MS (FAB): *m/z* 502 (M<sup>+</sup>, 2%), 390 (15, M-4CO), 279 (2, M-Mn-6CO). Complexes **2–4** were prepared similarly to **1** by reacting the corresponding bimetal decacarbonyls with 10% excess of the lithiated heteroarenes.

#### 3.3.2. *ax*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(OEt)2-furyl}] **2**

Furan (0.150 g, 2.2 mmol, 0.160 mL) was lithiated and when reacted with [Mn<sub>2</sub>(CO)<sub>10</sub>] (0.78 g, 2 mmol), afforded 0.661 g of the orange product. Yield: 68% for Mn<sub>2</sub>C<sub>16</sub>H<sub>8</sub>O<sub>11</sub> (486.11). Mp 123–125 °C. MS (FAB): *m/z* 486 (M<sup>+</sup>, 9%), 413 (8, M-CO-OEt), 374 (7, M-4CO), 263 (35, M-Mn-6CO), 235 (45, M-Mn-7CO), 207 (30, M-Mn-8CO).

#### 3.3.3. *eq*-[Re<sub>2</sub>(CO)<sub>9</sub>{C(OEt)2-furyl}] **4**

Furan (0.150 g, 2.2 mmol) and [Re<sub>2</sub>(CO)<sub>10</sub>] (1.31 g, 2 mmol) afforded the product. Yield: 74% for Re<sub>2</sub>C<sub>16</sub>H<sub>8</sub>O<sub>11</sub> (748.66). Mp 57–60 °C. (FAB): *m/z* 749 (M<sup>+</sup>, 28%), 721 (5, M-CO), 423 (19, M-Re-5CO).

#### 3.3.4. *eq*-[Mn<sub>2</sub>(CO)<sub>9</sub>{C(NH<sub>2</sub>)2-furyl}] **6**

The dimanganese ethoxycarbene precursor complex **2** (0.97 g, 2 mmol) was dissolved in diethyl ether at room



temperature, and a slow stream of  $\text{NH}_3(\text{g})$  was bubbled through the reaction solution until the colour of the reaction mixture changed from red to orange. After evaporation of the solvent under reduced pressure and purification on aluminium oxide, the light yellow product (0.87 g) was obtained and recrystallised by solvent layering of hexane/dichloromethane (1:1). Yield: 95% for  $\text{Mn}_2\text{C}_{14}\text{H}_5\text{O}_{10}\text{N}$  (457.07). Mp 116–117 °C. MS (FAB):  $m/z$  457 ( $\text{M}^+$ , 22%), 401 (14, M–2CO), 345 (10, M–4CO), 306 (15, M–2CO–carbene), 278 (27, M–3CO–carbene), 250 (37, M–4CO–carbene), 222 (26, M–5CO–carbene), 194 (26, M–6CO–carbene).

Complexes **7–8** were prepared similarly to **6** by bubbling ammonia gas through solutions of the corresponding binuclear ethoxycarbene complexes.

### 3.3.5. *eq*-[ $\text{Re}_2(\text{CO})_9\{\text{C}(\text{NH}_2)2\text{-thienyl}\}$ ] **7**

Dirhenium nonacarbonyl 2-thienyl ethoxycarbene (**3**) (1.53 g, 2 mmol) afforded 1.25 g of orange solid. Yield: 85% for  $\text{Re}_2\text{C}_{14}\text{H}_5\text{O}_9\text{SN}$  (735.68). Product decomposed during the Mp analysis. MS (FAB):  $m/z$  736 ( $\text{M}^+$ , 7%), 409 (52, M–Re(CO)<sub>5</sub>), 381 (13, M–Re–6CO).

### 3.3.6. *eq*-[ $\text{Re}_2(\text{CO})_9\{\text{C}(\text{NH}_2)2\text{-furyl}\}$ ] **8**

Dirhenium nonacarbonyl 2-furyl ethoxycarbene (**4**) (1.50 g, 2 mmol) afforded 1.24 g of orange solid. Yield: 86% for  $\text{Re}_2\text{C}_{14}\text{H}_5\text{O}_{10}\text{N}$  (719.62). Product decomposed during the Mp analysis. MS (FAB):  $m/z$  719 ( $\text{M}^+$ , 19%), 664 (7, M–2CO), 636 (6, M–3CO), 393 (94, M–Re(CO)<sub>5</sub>), 365 (24, M–Re–6CO), 337 (6, M–Re–7CO).

The same procedure was followed for the synthesis of complexes **9–12**, but instead of bubbling ammonia gas through the solution, excess *n*-propylamine was added to the reaction mixture in each case with the corresponding precursor complex **1–4**.

### 3.3.7. *ax*-[ $\text{Mn}_2(\text{CO})_9\{\text{C}(\text{propylamino})2\text{-thienyl}\}$ ] **9**

Reaction of complex **1** (1.00 g, 2 mmol) and *n*-propylamine (0.30 g, 5 mmol, 0.41 mL) yielded yellow product (0.77 g). Yield: 75% for  $\text{Mn}_2\text{C}_{17}\text{H}_{11}\text{O}_9\text{SN}$  (515.22). Product decomposed during the Mp analysis. MS (FAB):  $m/z$  459 (38, M–2CO), 306 (19, M–2CO–carbene).

### 3.3.8. *ax*-[ $\text{Mn}_2(\text{CO})_9\{\text{C}(\text{propylamino})2\text{-furyl}\}$ ] **10**

Complex **2** (0.97 g, 2 mmol) and *n*-propylamine (0.30 g, 5 mmol, 0.41 mL) afforded 0.78 g product. Yield: 78% for  $\text{Mn}_2\text{C}_{17}\text{H}_{11}\text{O}_{10}\text{N}$  (499.15). Product decomposed during the Mp analysis. MS (FAB):  $m/z$  499 ( $\text{M}^+$ , 12%), 304 (100, M–2CO–carbene), 278 (32, M–3CO–carbene), 250 (42, M–4CO–carbene), 222 (29, M–5CO–carbene), 194 (31, M–6CO–carbene).

### 3.3.9. *eq*-[ $\text{Re}_2(\text{CO})_9\{\text{C}(\text{propylamino})2\text{-thienyl}\}$ ] **11**

Again, excess *n*-propylamine and complex **3** (1.53 g, 2 mmol) yielded 1.26 g of light orange product. Yield: 81%. Product decomposed during Mp analysis. No  $\text{M}^+$  observed in MS (FAB) analysis.

### 3.3.10. *eq*-[ $\text{Re}_2(\text{CO})_9\{\text{C}(\text{propylamino})2\text{-furyl}\}$ ] **12**

Complex **4** (1.50 g, 2 mmol) and excess *n*-propylamine yielded 1.33 g orange solid. Yield: 87% for  $\text{Re}_2\text{C}_{17}\text{H}_{11}\text{O}_{10}\text{N}$  (761.70). Product decomposed during the Mp analysis. No  $\text{M}^+$  observed in MS (FAB) analysis.

## 4. Supplementary material

CCDC 613008, 613009, 613010 and 613011 contain the supplementary crystallographic data for **2**, **4**, **6** and **10**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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