

6 Experimental

6.1 Standard Operating Procedure

All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried and distilled under an atmosphere of nitrogen. Ether and THF were distilled from sodium metal, with benzophenone as indicator. Dichloromethane and hexane were distilled from phosphorous pentoxide. Most chemicals were used without prior purification, unless stated otherwise. Column chromatography, using Kieselgel 60 (particle size 0.0063 - 0.200mm) or neutral aluminium oxide 90 was used as resin for all separations. The column was cooled with isopropanol (-30 °C) in the column jacket.

6.2 Characterization Techniques

6.2.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker ARX-300 spectrometer and on an AVANCE 500 spectrometer. ^1H NMR spectra were recorded at 300.135 and 500.139 MHz and ^{13}C NMR spectra at 75.469 and 125.75 MHz respectively. The signal of the deuterated solvent was used as reference: ^1H CDCl_3 7.24

ppm, acetone-d₆ 2.09 ppm and ¹³C CDCl₃ 77.00 ppm, acetone-d₆ 205.87 ppm. For resolution enhancement of the manganese complexes, longer acquisition times were achieved by manual shimming and manipulation of the sweep width.

6.2.2 Infrared Spectroscopy

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 - 2200 cm⁻¹) were recorded for all complexes, as well as the N-H vibrational frequencies in the range of 3300 - 3500 cm⁻¹ for the aminocarbene complexes in Chapter 4.

6.2.3 Fast Atom Bombardment Mass Spectrometry

FAB-MS spectra were recorded on a VG 70SEQ Mass Spectrometer, with the resolution for FAB = 1000 in a field of 8 kV. Nitrobenzyl alcohol was used as solvent and internal standard. The spectra were recorded by Mr T. van der Merwe at the University of the Witwatersrand.

6.2.4 X-Ray Crystallography

Data collection and structure determinations were done by Mr Dave Liles, University of Pretoria. X-ray crystal structure analysis was done from data collected at 20°C on a Siemens P4 Bruker 1K CCK diffractometer using graphite-monochromated, Mo-K α radiation. Data were corrected for Lorenz polarization effects and structures were solved by direct methods (SHELXS) and refined by full-matrix least squares techniques. In the structure

refinements all hydrogen atoms were added in calculated positions and treated as riding on the atom to which they are attached. All non-hydrogen atoms (except those refined as rigid groups) were refined with anisotropic displacement parameters, all isotropic displacement parameters for hydrogen atoms were 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. In structures **2**, **7** and **11** some disorder was observed. The parameters for the major orientations were refined freely. The minor orientations were refined as rigid bodies with geometries derived from those of the major orientations. Site occupation factors for the major and minor orientations were refined but constrained to sum to 1.0.

6.2.5 UV-Visible Spectroscopy

All the complexes were referenced to diethyl ether and spectra measured in a range of 200.0 - 800.0 nm in a quartz sample cell. A Hewlett-Packard 8452A Diode Array spectrophotometer and a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer were used.

6.2.6 Kinetic Measurements

The kinetics of the aminolysis reactions were followed at ambient pressure in the thermostated cell compartment (quartz sample cell) of a Shimadzu UV-2101 PC UV-Vis scanning spectrophotometer. Reported rate constants are the average of at least four kinetic runs. OLIS KINFIT^[1] software was employed to calculate k_{obs} values from absorbance vs time traces by fitting single- or double exponential functions through the data points.

6.3 Preparation of Compounds

6.3.1 Preparation of Starting Compounds

6.3.1.1 Triethyl oxonium tetrafluoroborate^[2]

Epichlorohydrin (140.0 g, 119 mL, 1.51 mol) was added dropwise to a solution of sodium-dried ether (500 mL) and freshly distilled boron fluoride etherate (284.0 g, 252 mL, 2.00 mol) at a rate sufficient to maintain vigorous boiling (about 1 hour is needed). The mixture was refluxed and allowed to stand at RT overnight. Supernatant ether was withdrawn from the crystalline mass of triethyloxonium tetrafluoroborate under an inert N₂ atmosphere. Crystals were washed with ether; yield 244 - 272 g (85 - 95%).

6.3.2 Preparation of Organometallic Complexes

6.3.2.1 General Method of Carbene Formation^[3-5]

An excess of 10% butyllithium was used in the syntheses. Complexes **1** - **5** were synthesized according to the general method given below:

Method:

The heteroarene (2.2 mmol) 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 N₂ atmosphere. Stirring was continued for 30 minutes. Yellow Mn₂(CO)₁₀ (2 mmol, 0.78 g) [white Re₂(CO)₁₀ (2 mmol, 1.31 g) in the case of the synthesis of **5**] 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 RT. THF solvent was evaporated under reduced pressure. Et₃OBF₄ (2.2 mmol, 0.42 g) in dichloromethane was added to the reaction mixture at -30 °C and stirred until reaction completion. LiBF₄ salts were removed by filtering and reaction products were purified via column

chromatography using hexane/dichloromethane (4:1) as eluent. Recrystallization of products was done by solvent layering of hexane/dichloromethane (1:1). Products **1** - **5** were obtained.

Table 6.1 Information of individual complexes synthesized

Complex	Heteroarene (2.2 mmol)	Product obtained				
		Colour	Molar mass (g/mol)	Mass (g)	mmol	Yield (%)
1	2,2'- bithiophene (0.366 g)	orange solid	584.30	0.760	1.30	65
2	thiophene (0.185 g, 0.175 mL)	orange solid	502.18	0.723	1.44	72
3	furan (0.150 g, 0.160 mL)	orange solid	486.11	0.661	1.36	68
4	N-methyl pyrrole (0.178 g, 0.196 mL)	orange solid	499.16	0.629	1.26	63
5	furan (0.150 g, 0.160 mL)	orange- red solid	748.66	1.108	1.48	74

6.3.2.2 Cleaving of Metal-Metal Bonds^[6;7]

Method:

To a minimum volume of hexane solvent was added the binuclear monocarbene precursor complex **1** (1 mmol, 0.58 g) and Br₂ (1.1 mmol, 0.176

g, 0.056 mL) while stirring at RT under an inert N₂ atmosphere until reaction was complete. The unreacted Br₂ was removed under reduced pressure. Products **6** and [Mn(CO)₅Br] were obtained. Complex **7** was prepared in a similar fashion from precursor **2** (1 mmol, 0.50 g) and I₂ (1 mmol, 0.26 g). Unreacted I₂ was separated on an aluminium oxide 90 column with a hexane eluent, and products **7** and [Mn(CO)₅I] were purified using silica gel column chromatography. The complexes were crystallized from a hexane/dichloromethane (3:1) solution by layering of the solvents.

Table 6.2 Information of cleavage products

Complex	Product obtained					Product [Mn(CO) ₅ X]		
	Colour	Molar mass (g/mol)	Mass (g)	mmol	Yield (%)	Mass (g)	mmol	Yield (%)
6 (X = Br)	dark red	516.21	0.108	0.21	21	0.113	0.41	41
7 (X = I)	red	434.09	0.187	0.43	43	0.154	0.48	48

6.3.2.3 Aminolysis of Ethoxycarbene Complexes^[8-10]

Method:

The binuclear ethoxycarbene precursor complex (2 mmol) (**2** (1.00 g), **3** (0.97 g), **5** (1.50 g) as well as [Re₂(CO)₉{C(OEt)(2-thienyl)}]^[11] (1.53 g), respectively) was dissolved in diethyl ether at RT, and a slow stream of NH₃(g) was bubbled through the reaction solutions 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 (for the dimanganese complexes) or silica gel (for the dirhenium complexes), products **8**, **9**, **12** and **13** respectively, were obtained.

The reaction procedure was repeated using the same precursors, in the same amounts, but instead of bubbling ammonia through the solution, excess propylamine (5 mmol, 0.30 g, 0.41 mL) was added to the reaction mixture and products **10**, **11**, **14** and **15** were obtained from the individual reactions.

Recrystallization of products was done by solvent layering of hexane/dichloromethane (1:1).

Table 6.3 Information of aminolysis reaction products

Complex	Colour	Molar mass (g/mol)	Mass (g)	mmol	Yield (%)
8	orange	473.14	0.84	1.78	89
9	light orange	457.07	0.87	1.90	95
10	orange-yellow	515.22	0.77	1.50	75
11	orange-yellow	499.15	0.78	1.56	78
12	orange	735.68	1.25	1.70	85
13	orange	719.62	1.24	1.72	86
14	orange-yellow	777.76	1.26	1.62	81
15	orange-yellow	761.70	1.33	1.74	87

6.4 Analytical Data of Complexes 1 - 15

Melting points were recorded on a hot stage Gallenkamp melting apparatus and are uncorrected. Most complexes decomposed during heating, and only melting points for complexes **1 - 3**, **5 - 9** could be determined, as listed in Table 6.4, as well as the elemental analyses done for the carbon and hydrogen atoms of the complexes. The C and H elemental analyses were

performed by the analytical laboratories of ARC-LNR Institute for Soil, Climate and Water.

Table 6.4 Analytical data of **1 - 15**

Complex	Molecular formula	Mp (°C)	Calculated (%)		Found (%)	
			C	H	C	H
1	Mn ₂ C ₂₀ H ₁₀ O ₁₀ S ₂	103-106	41.11	1.73	41.56	1.81
2	Mn ₂ C ₁₆ H ₈ O ₁₀ S	85-87	38.27	1.61	38.51	1.74
3	Mn ₂ C ₁₆ H ₈ O ₁₁	123-125	39.53	1.66	40.23	1.65
4	Mn ₂ C ₁₇ H ₁₁ O ₁₀ N	-	40.91	2.22	40.90	2.32
5	Re ₂ C ₁₆ H ₈ O ₁₁	57-60	25.67	1.08	26.12	1.12
6	MnC ₁₅ H ₁₀ O ₅ S ₂ Br	103-106	34.90	1.96	35.08	2.08
7	MnC ₁₁ H ₈ O ₅ SI	103-106	30.43	1.86	30.81	1.98
8	Mn ₂ C ₁₄ H ₅ O ₉ SN	116-117	35.54	1.07	35.46	1.11
9	Mn ₂ C ₁₄ H ₅ O ₁₀ N	116-117	36.79	1.10	35.98	1.06
10	Mn ₂ C ₁₇ H ₁₁ O ₉ SN	-	39.63	2.15	40.24	2.20
11	Mn ₂ C ₁₇ H ₁₁ O ₁₀ N	-	40.91	2.22	41.35	2.43
12	Re ₂ C ₁₄ H ₅ O ₉ SN	-	22.86	0.69	23.12	1.01
13	Re ₂ C ₁₄ H ₅ O ₁₀ N	-	23.37	0.70	23.42	0.98
14	Re ₂ C ₁₇ H ₁₁ O ₉ SN	-	26.25	1.43	26.24	1.48
15	Re ₂ C ₁₇ H ₁₁ O ₁₀ N	-	26.81	1.46	27.07	1.48

6.5 References

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