7 Experimental

1. Standard Operational Procedure

All operations were carried out under an inert atmosphere of nitrogen or argon gas using standard Schlenk techniques. Solvents were dried and distilled in an inert atmosphere according to conventional laboratory methods. Most chemicals were used without prior purification, unless stated otherwise. Column chromatography, using Kieselgel 60 (particle size 0.0063-0.200 mm) or neutral aluminium oxide, as stationary phase, was used for all separations. The column was cooled with ice-water (0°C) in the column jacket or performed at room temperature.

2. Characterization Techniques

2.1 Nuclear Magnetic Resonance Spectroscopy

NMR spectra were recorded on a Bruker ARX-300 spectrometer and on a AVANCE 500 spectrometer. ^{1}H 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, e.g. ^{1}H $CDCl_3$ 7.24 ppm and ^{13}C $CDCl_3$ 77.00 ppm.

2.2 Infrared Spectroscopy

IR spectra were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer. All spectra were recorded using either dichloromethane or hexane as solvent. Only the vibrational bands in the carbonyl stretching region (ca. 1500-2200 cm^{-1}) were recorded.

2.3 X-ray Crystallography

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

2.4 UV spectroscopy

All the complexes were referenced to dichloromethane and spectra were measured in the range 200.0 to 800.0 nm in a quartz cell. A genesis spectronic 5 spectrophotometer was used.

3. Preparation of Starting Compounds

The following compounds were prepared according to known literature methods: Tisammine(tricarbonyl)chromium[1] and triethyl oxonium tetrafluoroborate.[2]

3.1 (η^6-benzo[*b*]thiophene)tricarbonylchromium[3-9]

Trisammine(tricarbonyl)chromium (2.00 g, 10.7 mmol) was dissolved in diethyl ether (~ 95 ml). Freshly distilled boron trifluoride diethyl etherate (3.95 ml, 33 mmol) was added to the solution, followed by 2.82g (21 mmol) of benzo[*b*]thiophene. The reaction mixture was stirred for 12h. Diethyl ether (100 ml) was added and the solution was cooled to 0°C after which 100 ml air-free water was added. The mixture was repeatedly extracted with diethyl ether until the extracts were virtually colourless. The ether extracts were combined and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The product was purified with column chromatography which afforded the starting compounds and the orange product. The crude product was recrystallized from dichloromethane and hexane. The orange crystals were washed with hexane and dried under reduced pressure. Yield: 0.97g (34%)

4. Preparation of Organometallic Compounds

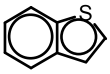
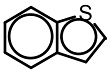
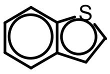
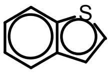
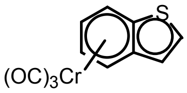
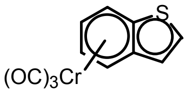
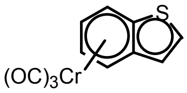
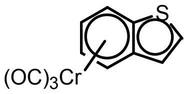
An excess of 10% of butyllithium was used in the syntheses. All complexes were synthesized according to the General Method.

4.1 General Method

The dropwise addition of a 1.6 mol dm^{-3} hexane solution of LiBu (0.7 ml, 1.1 mmol) to a cooled (-50°C) THF solution (12 cm^3) containing the heteroarene (1 mmol) afforded a lithiated thienyl species in high yields after 30 min. Addition of the metalhexacarbonyl (1 mmol) in small portions over 10 min resulted in a gradual change of colour. After stirring for 1 h in the cold, the reaction mixture was warmed to RT and stripped of solvent under reduced pressure. The residue was redissolved in dichloromethane, cooled to -30°C and carefully treated with triethyloxonium tetrafluroborate (**A**) or titanocene dichloride (**B**) (1 mmol), also dissolved in dichloromethane. After stirring for 1 h and allowing the reaction mixture to warm to RT, the dark coloured solution was filtered through kieselgel or neutral aluminium oxide and washed through with dichloromethane. The solution was dried in under reduced pressure. Details of the reaction are given in Table 7.1 and of the products in Table 7.2.

4.2 Synthesis of complexes 1-8

Table 7.1 Amount and substances used to synthesize complexes **1-8**

Complex	Heteroarene	Mass	Metal-carbonyl	Mass	**A/B**	Mass
1		0.14 g	$Cr(CO)_6$	0.22 g	**A**	0.30 g
2		0.14 g	$W(CO)_6$	0.35 g	**A**	0.30 g
3		0.14 g	$Cr(CO)_6$	0.22 g	**B**	0.25 g
4		0.14 g	$W(CO)_6$	0.35 g	**B**	0.25 g
5		0.27 g	$Cr(CO)_6$	0.22 g	**A**	0.30 g
6		0.27 g	$W(CO)_6$	0.35 g	**A**	0.30 g
7		0.27 g	$Cr(CO)_6$	0.22 g	**B**	0.25 g
8		0.27 g	$W(CO)_6$	0.35 g	**B**	0.25 g

A = Triethyl oxonium tetrafluoroborate

B = Titanocene dichloride

Table 7.2

4.3 Synthesis of complex 9

Ferrocene (0.76 g, 1 mmol) was dissolved in hexane. 1.6 mol dm^{-3} hexane solution of LiBu (0.7 ml, 1.1 mmol) and TMEDA (0.15 ml, 1 mmol) was mixed and added to the ferrocene and stirred while increasing the temperature, until the orange adduct precipitated from the hexane solution. The excess liquid was sucked from the precipitate *via* a pipette. The precipitate was cooled to -50°C. Chromium hexacarbonyl (0.22g, 1 mmol) was dissolved in freshly distilled THF and added to the cooled precipitate. After stirring for 1 h in the cold, the reaction mixture was warmed to RT and stripped of solvent under reduced pressure. The residue was washed several times with hexane, redissolved in dichloromethane, cooled to -30°C and carefully treated with titanocene dichloride (0.25g, 1 mmol), also dissolved in dichloromethane. After stirring for 1 h and allowing the reaction mixture to warm to RT, the red-brown coloured solution was filtered through kieselgel and washed through with dichloromethane. The solution was dried *in vacuo* and washed with hexane. The resulting dark brown product afforded two bands on purification with column chromatography (eluent: dichloromethane/hexane 1/1). The first orange band afforded the starting material, ferrocene, yield: 0.05 g (8%). The second red-brown product was identified as **9**, yield: 0.21 g (35%).

4.4 Analytical data of 1-8

Table 7.3 Analytical data of **1-8**

Complex	Molecular formula	Calculated (%)		Found (%)	
		C	H	C	H
1	$C_{16}H_{10}O_6CrS$	50.26	2.62	50.14	2.70
2	$C_{16}H_{10}O_6WS$	37.36	1.95	37.28	2.02
3	$C_{24}H_{15}O_6CrTiSCl$	50.85	2.65	50.73	2.91
4	$C_{24}H_{15}O_6WTiSCl$	41.25	2.15	41.01	2.37
5	$C_{19}H_{10}O_9Cr_2S$	44.02	1.93	43.64	2.07
6	$C_{19}H_{10}O_9CrWS$	35.10	1.54	34.82	1.83
7	$C_{27}H_{15}O_9Cr_2TiSCl$	48.58	2.25	48.35	2.49
8	$C_{27}H_{15}O_9CrWTiSCl$	40.56	1.88	40.14	2.01

5. References

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