

# **The Synthesis of Fischer carbene complexes with metal-containing substituents**

by

**Elisia van der Watt**

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Supervisor: Professor S. Lotz

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## **Declaration**

I, the undersigned, hereby declare that the work contained in this dissertation is my own original work and that I have not previously in its entirety or in part submitted it at any university for a degree.

Signature:.....

Date:.....

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## Summary

Fischer carbene complexes with metal-containing substituents were synthesized, fully characterized and systematically investigated with respect to their steric and electronic properties. Chromium and tungsten carbene complexes with benzo[*b*]thiophene, ( $\eta^6$ -benzo[*b*]thiophene)tricarbonylchromium(0), ethyl and titanocene dichloride as substituents were prepared. The ( $\eta^6$ -benzo[*b*]thiophene)tricarbonylchromium(0) was prepared by the displacement of the ammine ligands in the complex  $[\text{Cr}(\text{NH}_3)_3(\text{CO})_3]$  by the heteroarene in the presence of boron trifluoride diethyl etherate in boiling dibutyl ether. The carbene complexes were prepared *via* the classical Fischer method, in which the precursor heteroaromatic derivative is lithiated, reacted with a metal hexacarbonyl and quenched with an alkylating or metallating reagent, triethyl oxonium tetrafluoroborate or titanocene dichloride. The yield of the carbene complexes was further improved by washing the metal acylate with hexane before alkylation or metallation.

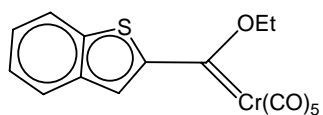
Carbene complexes with an ethoxy and a benzo[*b*]thienyl substituent of chromium- or tungsten pentacarbonyl were prepared and served as reference-complexes. Dimetallic Fischer carbene complexes were prepared by metallating the metal acylate with titanocene dichloride, thus yielding chromium and tungsten carbene complexes containing benzo[*b*]thiophene as heteroarene and a titanoxo-fragment as oxy substituent. Another type of dimetallic Fischer carbene complexes were obtained on reacting lithiated ( $\eta^6$ -benzo[*b*]thiophene)tricarbonylchromium(0) with chromium and tungsten hexacarbonyl and alkylating with triethyl oxonium tetrafluoroborate, thus yielding carbene complexes containing a metal-fragment  $\pi$ -bonded to the heteroarene

substituent. Trimetallic Fischer carbene complexes were synthesized for the first time by lithiation of ( $\eta^6$ -benzo[*b*]-thiophene)tricarbonylchromium(0) and metallation with titanocene dichloride. These unique complexes displayed a carbene carbon atom surrounded by three metal-fragments and were studied in solution and in the solid state. The titanoxo substituent showed large electronic and steric effects in the structures of the trimetallic carbene complexes. By contrast, the chromium tricarbonyl fragment as part of the benzo[*b*]thienyl substituent has important electronic consequences, but does not affect the trimetallic carbene complexes sterically in any way.

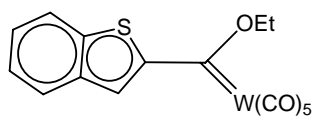


## List of Complexes

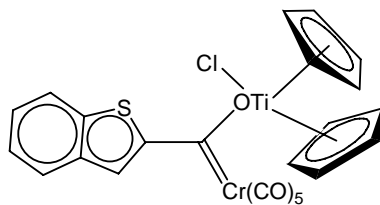
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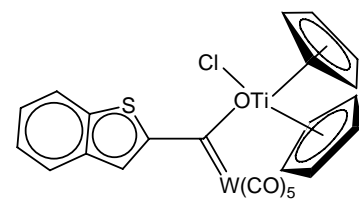
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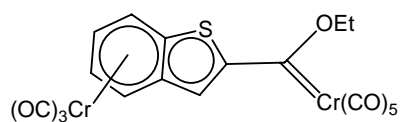
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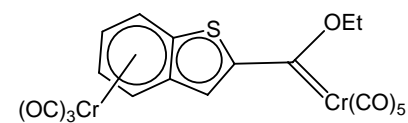
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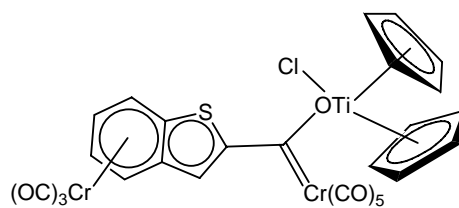
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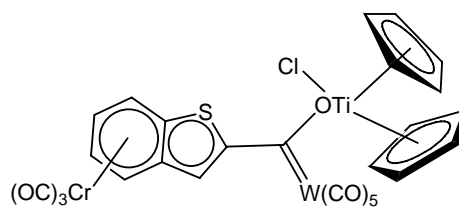
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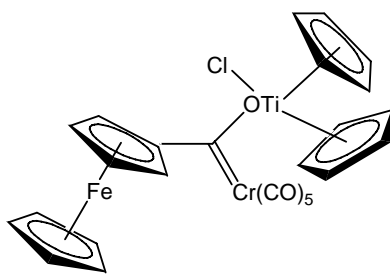
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9.





## List of Abbreviations

ar	:	aryl substituent
av	:	average
BT	:	benzo[ <i>b</i> ]thiophene
$\pi$ -BTCr(CO) <sub>3</sub>	:	( $\eta^6$ -benzo[ <i>b</i> ]thiophene)tricarbonylchromium(0)
Bu	:	butyl
Cp	:	$\eta^5$ -C <sub>5</sub> H <sub>5</sub>
d	:	doublet
dd	:	doublet of doublets
ddd	:	doublet of doublets of doublets
dddd	:	doublet of doublets of doublets of doublets
Et	:	ethyl
HETCOR	:	Heteronuclear Correlation Spectroscopy
IR	:	Infrared Spectroscopy
J	:	coupling constant
m	:	multiplet (NMR)
m	:	medium (IR)
m-s	:	medium to strong (IR)
Me	:	methyl
NMR	:	Nuclear Magnetic Resonance Spectroscopy
Ph	:	Phenyl
RT	:	room temperature
s	:	singlet (NMR)
s	:	strong (IR)

THF	:	tetrahydrofuran
TMEDA	:	N,N,N',N'-tetramethylethylenediamine
UV	:	ultraviolet
vs	:	very strong (IR)
vw	:	very weak (IR)
w	:	weak (IR)
Å	:	angstrom
$\delta$	:	chemical shift
$\eta^n$	:	number, n, of ring atoms bonded to the metal in a $\pi$ -ring fashion