3 Bimetallic Titanoxycarbene Complexes

1. Introduction

The metallation of a transition metal acylate with a second transition metal complex containing an activated halide or even a cationic metal complex with a vacant coordination site, has been documented.[1-4] Beck and co-workers[5] showed that it was possible to synthesize heteronuclear bimetallic monocarbene complexes by reacting $[Re(CO)_5FBF_3]$ and $NEt_4[Cr(CO)_5\{C(O)R\}]$. More generally exploited is the use of titanocene dichloride as metallation reagent with chromium pentacarbonyl acylates as carbene complex precursors (Figure 3.1).

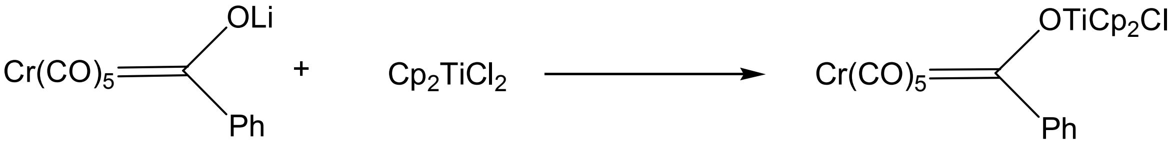


Figure 3.1 Reaction yielding a dimetallic titanoxy carbene complex

Interest in organotitanium(IV) compounds developed after the discovery that certain organotitanium(IV) compounds show higher carbanion selectivity than organolithium compounds. Classical organic C-C bond formation reactions e.g. Grignard-type or Wittig olefination reactions are very useful reactions but have certain limitations. These reagents are basic and extremely reactive, affording wide application but low chemoselectivity and limiting the number of additional functional groups that can be used. It was discovered that titanation of carbanions using $TiCl_2X_3$ leads to species with reduced basicity and reactivity.[6] In reactions with organic compounds such as aldehydes, ketones and alkyl halides, the stereoselectivity, regioselectivity as well as chemoselectivity are increased. Stereochemical predictions can therefore be made in many C-C bond-forming reactions, because the ligand X can be varied to control the electronic and steric nature of the reagents.

The arrival of Ziegler-Natta catalysts and the relevance of these compounds in organic syntheses, gave impetus to research in the field of organotitanium compounds. These heterogeneous catalysts are formed by mixing triethylaluminium and titanium tetrachloride and are used in the polymerization of ethylene, propylene and other α-olefins.[7,8]
The syntheses of various monomeric alkyl-titanium compounds was spurred on by the Ziegler-Natta polymerization process, one of them include $TiCH_3Cl_3$.[9]

A large number of η^5-cyclopentadienyltitanium compounds have been prepared, containing either one or two Cp ligands.[10] These Cp-groups are said to have a "stabilizing" effect on titanium-alkyl bonds due to their strong electron donating effect. This stabilizing effect can be very useful in adjusting carbanion-reactivity and selectivity . It was found that, when replacing a chlorine in compounds of the type $TiRCl_3$ by Cp-groups, the reactivity was reduced considerably.

The geometry of the titanocene dichloride complex is a distorted tetrahedron, with the two cyclopentadienyl rings tilted toward each other to form an open sandwich configuration and in complexes where titanocene dichloride (or probably other metallocenes of this type) is added, the halide moieties can easily be substituted for other groups such as alkyl or aryl groups (Figure 3.2). Also, when used with metal acylates by displacing one of the chloro ligands from titanocene dichloride the remaining chloro ligand becomes activated and can lead to the formation of two chromium carbene acylates being bridged by a titanocene fragment (Figure 3.2).[11]

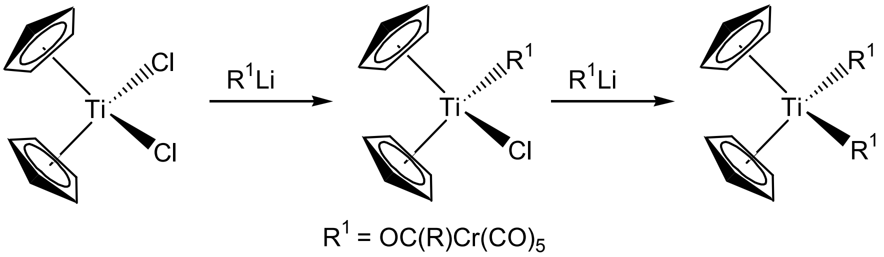


Figure 3.2 Substitution of a chlorine moiety in $TiCp_2Cl_2$

In this study, only titanocene dichloride was used for metallation and the products displayed two metal fragments, titanium(IV) and chromium(0) or tungsten(0). In order not to complicate matters and to control electronic and steric factors, the third substituent was again benzo[*b*]thiophene.

In the following compounds (**3** and **4**) two metal fragments are present, titanium(IV) (d^0), an early transition metal which can be classified as electron-deficient, as well as chromium(0) (d^6) or tungsten(0) (d^6), which are middle transition metals.

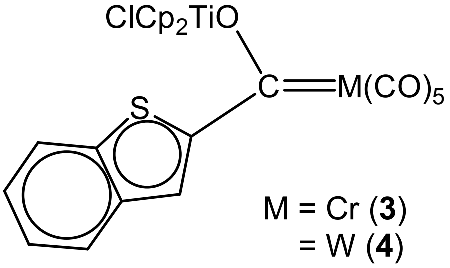
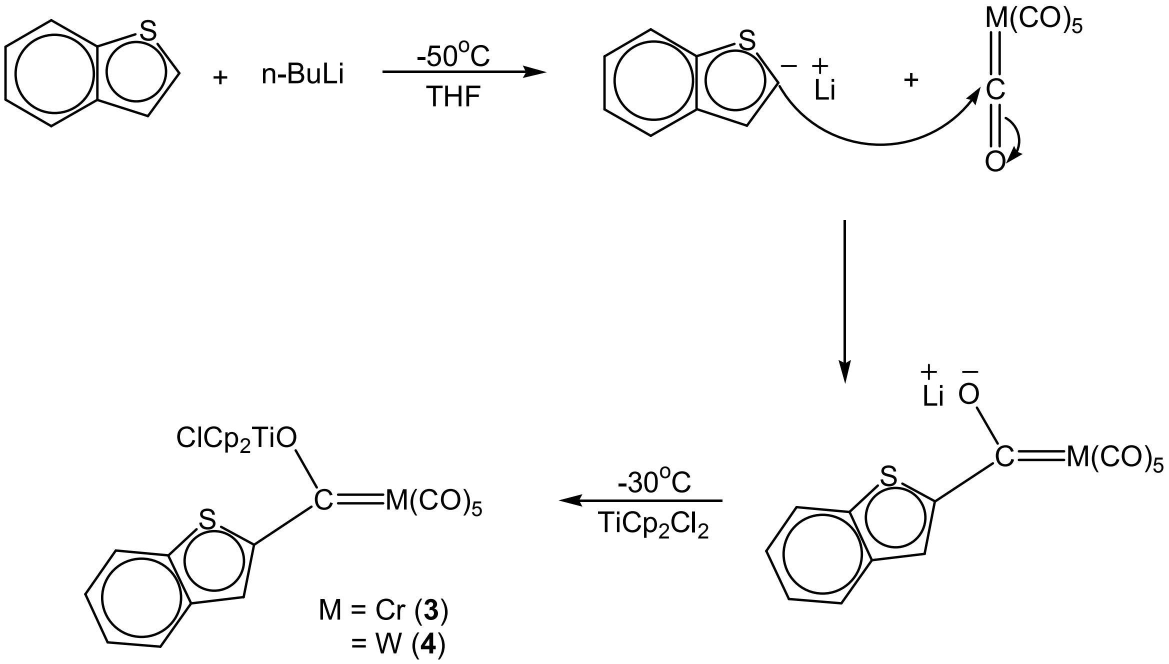


Figure 3.3 Bimetallic titanoxycarbene complexes synthesized in this chapter

By replacing an ethyl group with a titanocene group the oxygen of the carbene carbon should be affected electronically as well as sterically. The titanium(IV) centre is hard and will bind strongly to the hard oxygen atom.

2. Synthesis

Lithiation of the benzo[*b*]thiophene was achieved by the use of the strong base, n-butyllithium. The addition of the transition metal compounds $M(CO)_6$, with M = Cr or W afforded the metal acylates after which metallation with one equivalent titanocene dichloride took place. Metallation with titanocene dichloride is easily achieved due to the lability of a chloro ligand to afford the titanoxycarbene complexes **3** and **4** (Scheme3.1).



Scheme 3.1

The formation of the desired products, **3** (red-pink) and **4** (dark red), occurred with high yields and the complexes were purified and isolated using column chromatography with silica gel as stationary phase.

3. Spectroscopic characterization

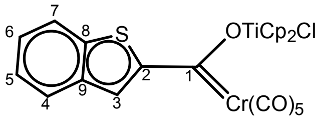
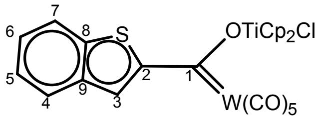
3.1 NMR Spectroscopy

^{1}H NMR spectra were recorded in $CDCl_3$ and C_6D_6. ^{13}C NMR spectra were only recorded in $CDCl_3$ due to poor solubility in C_6D_6. The same system of numbering of the carbon atoms and protons of benzo[b]thiophene used in Chapter 2 was applied to **3** and **4**.

^{1}H NMR Spectroscopy

The ^{1}H NMR data of the starting compound, benzo[*b*]thiophene, is summarized in chapter 2, while the ^{1}H NMR data of complexes **3** and **4** are reported in Table 3.1.

Table 3.1 ^{1}H NMR data of complexes **3** and **4**

Assignment	Complexes					
	Chemical shifts (δ, ppm) and coupling constants (J, Hz)					
	 **3**			 **4**		
Proton	δ	$^3J_{H-H}$	$^4J_{H-H}$	δ	$^3J_{H-H}$	$^4J_{H-H}$
H3[a]	8.43 (s)	-	-	8.35 (s)	-	-
H4	7.87 (dd)	8.1	-	7.85 (dd)	8.1	1.8
H5	7.50 (m)	8.1	1.2	7.52 (m)	8.1	-
H6	7.45 (m)	7.1	-	7.44 (m)	7.9	1.8
H7	8.04 (d)	7.1	1.2	8.03 (d)	7.9	-
Cp	6.55 (s)	-	-	6.55 (s)	-	-
H3[b]	8.64 (s)	-	-	8.56 (s)	-	-
H4	7.51	-	-	7.48 (d)	8.3	-
H5	7.09 (m)	-	-	7.00 (m)	8.3	-
H6	7.02 (m)	8.9	-	7.10 (m)	7.8	-
H7	7.53 (d)	8.9	-	7.52 (d)	7.8	-
Cp	5.88 (s)	-	-	5.87	-	-

[a] spectrum was recorded in $CDCl_3$

[b] spectrum was recorded in C_6D_6

When comparing chemical shift values of **3** and **4** with those of **1** and **2** in Chapter 2, a downfield shift (Δδ>0.1) can be recognised for the H3 protons. This can be ascribed to the

Ti-fragment that replaced the Et-fragment in the previous examples. The downfield signals of H3 indicate that the thiophene substituent in both **3** and **4** donates more electron density to the electron deficient carbene carbon (C1) in comparison with **1** and **2**. A possible reason for this is the competition between the electro positive Ti-fragment and the electron deficient carbene carbon atom to obtain electron density from the oxygen atom. Electron density shared between oxygen and C1 is polarized towards the oxygen. The ethyl groups on the other hand have an σ-inductive effect that increases the electron density of the oxygen assisting lone pair interaction of the oxygen with the carbene carbon atom.

When comparing all the other protons in the same manner, that is H4 - H7, a clear downfield shift for all the protons in benzothiophene can be recognised. This then indicates an electron withdrawing effect of the carbene carbon that influences the thiophene ring as well as the benzene ring (Figure 3.3). Thus, having a net electron withdrawing effect from the whole aromatic substituent (BT).

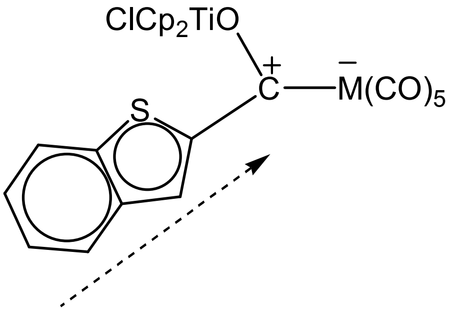


Figure 3.3 Net electron donation from benzo[*b*]thiophene

Free $TiCp_2Cl_2$ has a chemical shift of 6.57 ppm for the protons of the Cp-rings while the Cp's in **3** and **4**, resonate at 5.88 and 5.87 ppm. Once again a clear downfield shift is caused by the electron donation of the Cp rings to the electron deficient titanium supporting a resonance structure with a positive charge on the titanium ($TiCp_2Cl^+$).

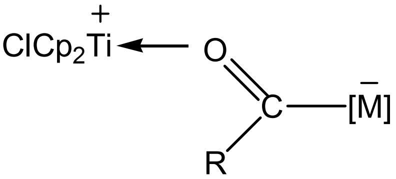


Figure 3.4 Electropositive character of Titanium[3]

^{13}C NMR spectroscopy

The ^{13}C NMR data of complexes **3** and **4** are reported in Table 3.2. The ^{13}C NMR data for complex **4** proved to be not as good as those of complex **3**, it was not possible to detect the signals for the carbene carbon (C1), that of C8 or C9, neither did the spectra indicate a resonance for the trans carbonyl of compound **4**.

Table 3.2 ^{13}C NMR data[a] of complexes **3** and **4**

Assignment	Complexes	
	Chemical shifts (δ, ppm)	
	3	**4**
C1	324.5	-
C2	140.8	141.1
C3	139.5	139.4
C4	122.9	123.1
C5	128.4	128.4
C6	125.4	125.5
C7	126.9	127.1
C8, C9	138.1	-
Cp's	118.7	118.7
CO	217.9 (cis) 224.9 (trans)	199.0 (cis)

[a] spectrum was recorded in $CDCl_3$

When looking at the ^{13}C NMR spectra of compound **3**, it is possible to distinguish between the individual carbons of the arene region, those are the carbons of the benzene ring and the thiophene ring individually (Figure 3.4) as well as those from the cyclopentadienyl ligands. The Cp-rings rotate freely in solution as is evident of single resonances for the protons as well as the carbons in the NMR spectra.

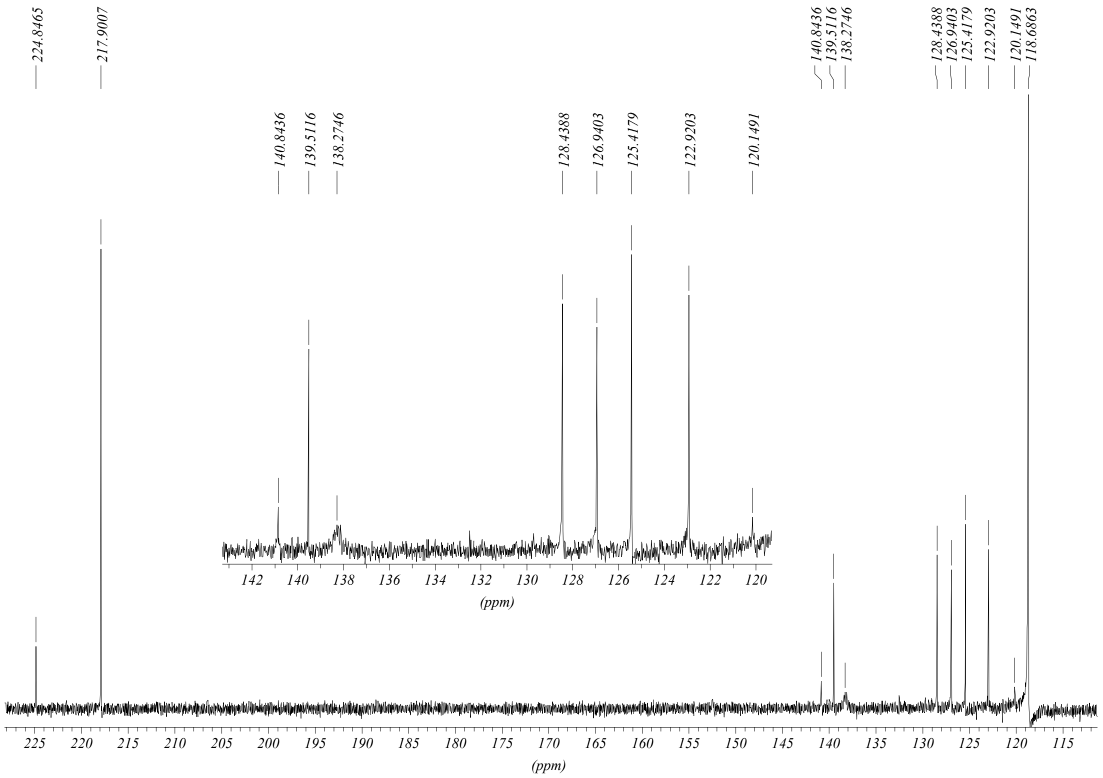


Figure 3.4 ^{13}C NMR spectrum of complex **3** in CDCl$_3$ showing the arene region

3.2 Infrared Spectroscopy

The data of the infrared spectra of compounds **3** and **4** are summarized in Table 3.3, the spectra of the compounds were recorded in hexane and dichloromethane, in order to see the difference of the vibrational spectra in the different solvents, complex **4** was used as example in Figure 3.4 to illustrate this.

The typical pattern for a M(CO)$_5$ (C$_{4v}$, square pyramidal geometry) is seen in the spectra recorded in dichloromethane in the CO region, but not in a non-polar hexane solution. Hexane is more inert towards the vibrational modes of the compounds and displays a greater resolution power in the spectra. In hexane the degeneracy associated with the E-band is lifted leading to the splitting of the E-band into two separate bands indicated as X and Y (Figure 3.5) of different vibrational frequencies. One of them will be of E-symmetry, while the other band can be either of general A or B symmetry.[12] This seems to indicate a deviation from C$_{4v}$ symmetry and a distortion of the equatorial plane of carbonyl ligands. Also significant is the relatively large difference between the wavenumbers of A$_1^2$

and the two bands of the E band. These observations are ascribed to a significant distortion of the equatorial plane by the bulky carbene ligand in solution.

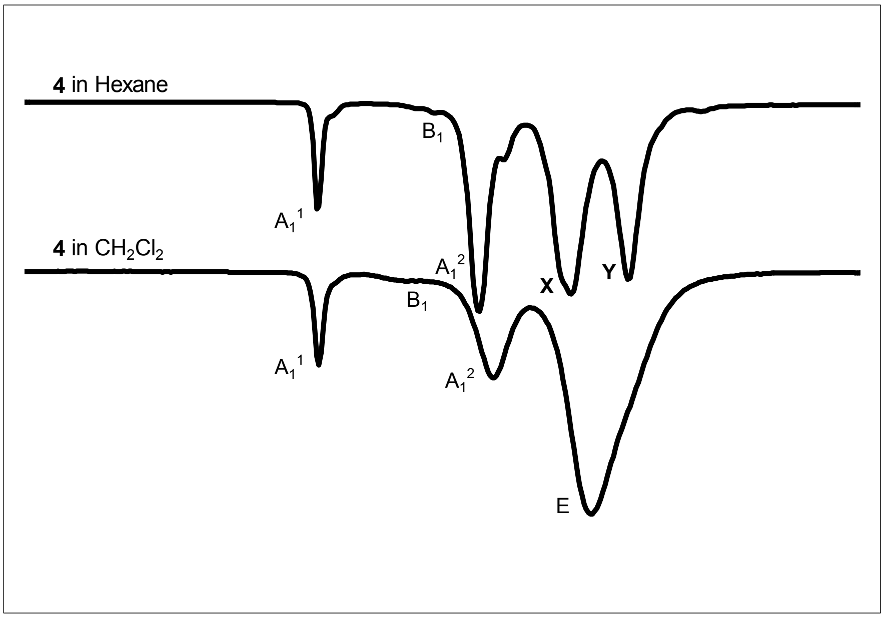


Figure 3.5 Stacked infrared spectrum of compound **4** in hexane and dichloromethane

Table 3.3 IR-data in the carbonyl region of complex **3** and **4**

Complex	Carbonyl vibrating frequencies (ν_{CO}, cm^{-1})			
	$A_1^{(1)}$	B_1	$A_1^{(2)}$	E
3[a]	2050m	1987w	1948s	1936vs, 1915s
3[b]	2050m	-	-	1931vs
4[a]	2050m	2000vw	1982vs	1938vs, 1911s
4[b]	2059m	2018vw	1975s	1929vs

[a] Hexane as solvent

[b] Dichloromethane as solvent

3.3 X-ray Crystallography

Final confirmation of the structure of **4** was obtained from a single crystal X-ray diffraction study. The complex were crystallised from a layered 1:1 dichloromethane:hexane solution. This method gave dark red-brown crystals of good quality for both complexes. Figure 3.6 represents the ORTEP[13] + POV-Ray[14] plot of the geometry of **4**, which also indicates the atom numbering scheme that was used for the structural data. Compound **4** crystallized in the space group P⌉ with a = 11.3533(6), b = 11.6696(6), c = 12.3627(7) Å, Z = 2. The most important bond lengths and angles are listed in Table 3.4 while the most important torsion angles are listed in Table 3.5. Other structural information is captured on the supplementary CD.

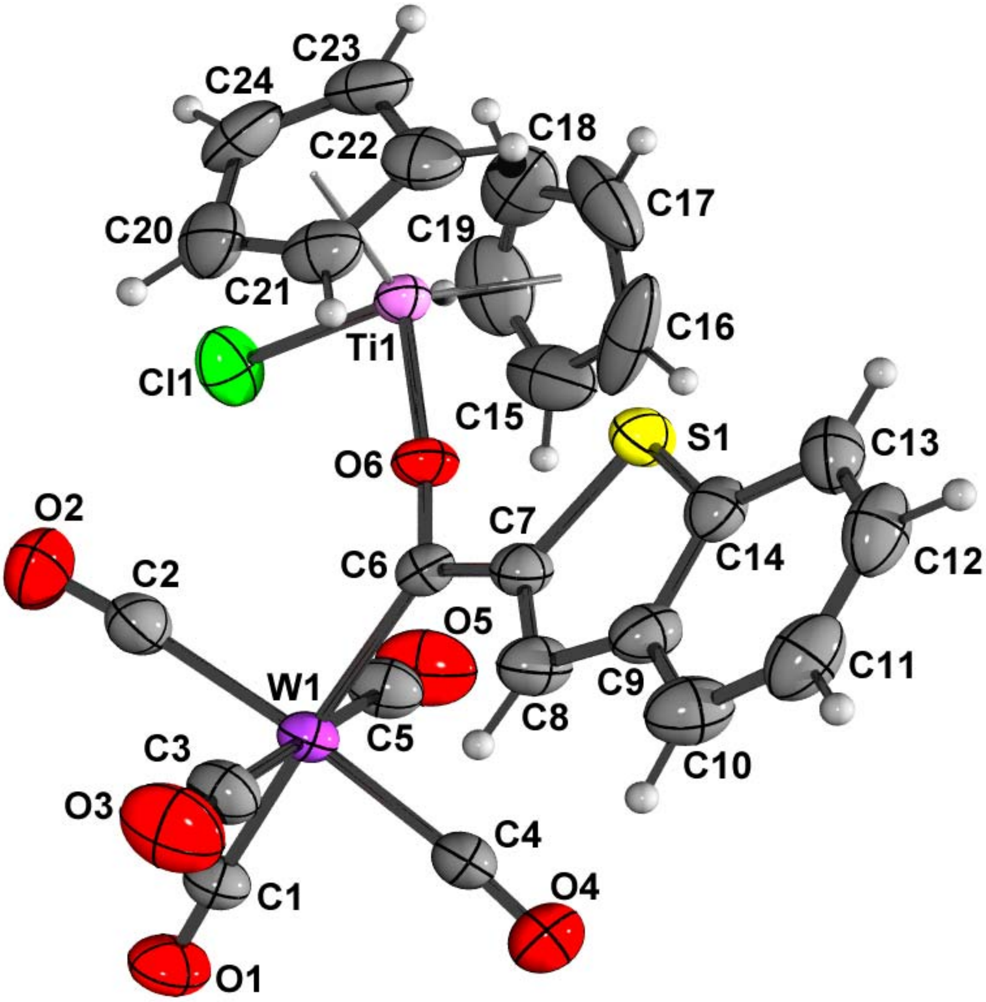


Figure 3.6 ORTEP + POV-Ray plot of the geometry of complex **4**

Table 3.4 Selected bond lengths and angles of **4**

Bond	Bond Lengths (Å)	Bond	Bond angles (°)
W(1)-C(6)	2.211(4)	C(1)-W(1)-C(6)	174.00(13)
C(6)-O(6)	1.279(4)	O(6)-C(6)-C(7)	112.7(3)
C(6)-C(7)	1.474(5)	O(6)-C(6)-W(1)	121.2(3)
O(6)-Ti(1)	1.931(2)	C(7)-C(6)-W(1)	125.9(2)
W(1)-C(1)	2.007(4)	C(6)-O(6)-Ti(1)	171.7(3)
W(1)-C(2,3,4,5)[a]	2.033(4)	C(6)-C(7)-S(1)	120.9(3)
C(7)-C(8)	1.368(5)		
C(8)-C(9)	1.436(5)		
C(9)-C(14)	1.394(6)		
C(14)-S(1)	1.730(4)		
C(7)-S(1)	1.755(4)		

[a] mean value

Table 2.5 Selected torsion angles of **4**

Bond	Torsion angle (°)
	1
C(2)-W(1)-C(6)-O(6)	-49.2(3)
O(6)-C(6)-C(7)-C(8)	169.7(4)
O(6)-C(6)-C(7)-S(1)	-9.8(4)
W(1)-C(6)-C(7)-S(1)	165.53(18)

Structural information shows that the carbene ligand in complex **4**, in the solid state, does not lie in a plane. This is seen by looking at the torsion angle O(6)-C(6)-C(7)-S(1) of 169.7(4)°. The BT substituent is planar with a torsion angle of only 0.8(5)° for S(1)-C(14)-C(9)-C(10). In this complex two of the carbonyl ligands bend away from the carbene carbon towards the trans carbonyl as seen by looking at C(3)-W(1)-C(6) (94.68(15)°) and C(4)-W(1)-C(6) (92.12(14)°).

The Ti(1)-O(6) bond in **4** is much longer than those of typical terminal titanium(IV) alkoxides (1.855 Å in $TiCp_2(OC_2H_5)Cl$)[15] and is in the same range as the bridging Ti-O-*i*-Pr interactions (1.918(2) Å in $\{(CO)_5CrC[OTi(O\text{-}i\text{-}Pr)_3][n\text{-}Bu]\}_2$.[3] This supports the notion that O(6)→C(6) π donation occurs at the expense of O(6)→Ti(1) π donation. It was suggested that π delocalization in the M-C-O-Ti unit is increased for titanoxycarbene complexes by virtue of the π acidity of the d^0 metal center, illustrated by the resonance structures in Figure 3.7.

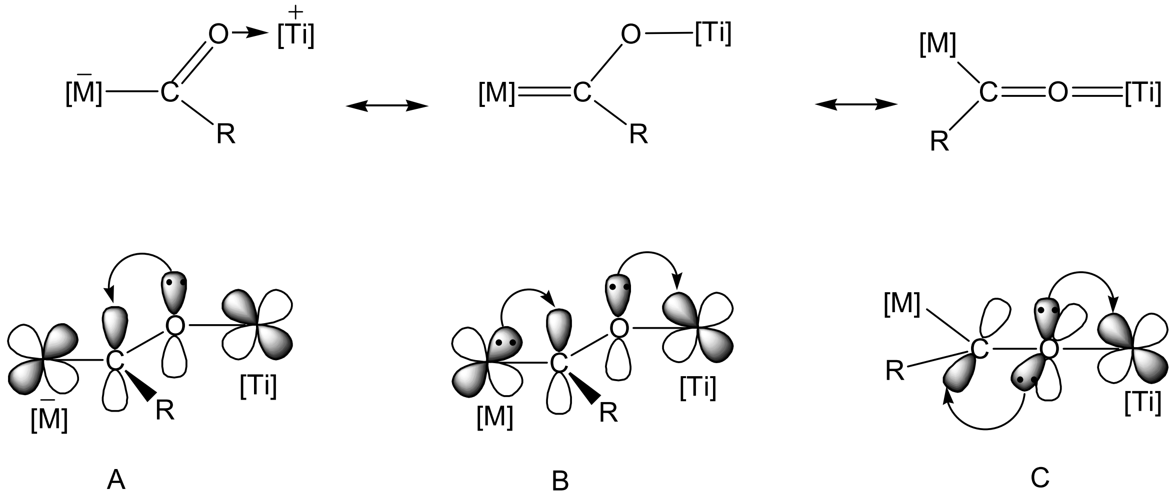


Figure 3.7 Orbital interactions in acyl (A) and carbene (B) resonance forms of titanoxycarbene complexes,[3] and the proposed interaction causing the near linear angles of titanoxycarbene complexes (C).

The combination of A and B suggests that π-electron density may be delocalized over the titanoxycarbene moiety to a greater extent than in alkoxycarbene systems. When looking at the near linear bond angle C(6)-O(6)-Ti(1) of 171.7(3)°, it is possible that electronic factors may play a role as also observed in previous work.[3] This angle suggests almost sp hybridization at O(6), allowing O(6)-Ti and O(6)-C(6) π overlap to occur using both p orbitals of O(6). This seems unlikely because of the long Ti-O bond distance. Steric considerations may well hold the key to the long Ti-O distance as the O(6)-C(6)-C(7) angle (112.7(3)°) is large compared to the corresponding angle in **2** (105.7(4)°).

When comparing bond C(6)-O(6) (1.279(4)) with that of an average alkoxycarbene system, being ±1.35 Å (1.315(6) Å for **2**), a stronger bond is identified for **4**, this stronger C-O interaction suggests that the "acyl" resonance structure A (Figure 3.7) is an important contributor to the bonding in these species, as has been noted by Erker for a series of zirconoxycarbene complexes.[16] The bond distances in the thiophene ring and the W-C(carbene) distance correspond well with those of **2** and the free thiophene molecule.

4. References

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