Chromium and Tungsten Carbene Complexes of Thieno[3,2-*b*]thiophene

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Dinuclear carbene complexes with 3,6-dimethylthieno[3,2-*b*]thienylene (T′T′) and thieno[3,2-*b*]thienylene (TT) spacers were prepared using the classical Fischer method. Their reactivity in solution towards oxygen, as well as their structural features were investigated. Chromium and tungsten carbene complexes were synthesized via dilithiation of the thienothiophene, followed by the addition of the appropriate metal carbonyl complex and subsequent alkylation with triethyloxonium tetrafluoroborate. Monocarbene [M{C(OEt)T′T′H}(CO)$_5$], (M = Cr, **1**; W, **4**), biscarbene [(CO)$_5$M{C(OEt)T′T′C(OEt)}M(CO)$_5$], (M = Cr, **2**; W, **5**), and the products [M{C(OEt)T′T′C(O)OEt} (CO)$_5$], (M = Cr, **3**; W, **6**), where a metal moiety of **2** and **5** has been replaced by an ester functionality, were isolated. The reaction product afforded in the reaction of Cr(CO)$_6$ with lithiated thieno[3,2-*b*]thiophene, [Cr{C(OEt)TTC(O)Bu}(CO)$_5$], **7**, did not resemble any of the products isolated in the similar reaction of Cr(CO)$_6$ with lithiated 3,6-dimethylthieno[3,2-*b*]thiophene.

Introduction

The current interest in thiophenes as molecules with potential electro-optical properties for use as molecular devices[1] was recently extended to include thieno[3,2-*b*]thiophenes.[2] Research in this area has unfortunately been impeded by the lack of convenient synthetic methods. Since the discovery of the first stable transition metal carbene complex by Fischer and Maasböl in 1964,[3] research in this field has been extensive with wide application possibilities. Several mononuclear, as well as dinuclear[4] biscarbene complexes with various spacers have been prepared. The first biscarbene complex containing two different metal moieties, contains a 2,2′-bithienylene (T−T) spacer and was published in 1995,[5] however, the synthetic method was unsatisfactory. In this paper the syntheses of carbene complexes containing thieno[3,2-*b*]thiophene and 3,6-dimethylthieno[3,2-*b*]thiophene as bridging units in dinuclear biscarbene complexes are reported. This work represents an extension of previously published dinuclear biscarbene complexes with thienylene (T) spacers, [(CO)$_2$L$_3$M{C(OEt)TC(OEt)}ML$_3$(CO)$_2$], (M = Cr, L = CO; M = W, L = CO; M = Mn, L = Cp, MeCp).[6]

In an attempt to enhance the electron density and transmission properties of thieno[3,2-*b*]thiophene for potential application in non-linear optics, the synthesis of 2-arylthieno[3,2-*b*]thiophene was planned.[7] Various synthetic routes were proposed for this synthesis and intermediates containing metal fragments as substituents such as 2-tributylstannylthieno[3,2-*b*]thiophene, (thieno[3,2-*b*]thiophen-2-yl)boronic acid, and 2-thieno[3,2-*b*]thienylzinc chloride were prepared from lithio precursors. A number of α-substituted thienothiophene compounds have been synthesized in a similar manner via the monolithiated derivative e.g. selenium and tellurium compounds.[8] Several silyl compounds[9] were synthesized via the use of 2,5-disubstituted thieno[3,2-*b*]thiophenes, prepared by dilithiation of thieno[3,2-*b*]thiophene and followed by the subsequent reaction with electrophiles.

Results and Discussion

Examples of compounds containing thienothiophenes as bridging spacers are limited in the literature and mostly confined to main group metal compounds. The synthesis of thieno[3,2-*b*]thiophene was based on the work of Goldfarb and co-workers,[10] but several of the reaction steps were revised to obtain higher yields.[11,12,13] Since no practical short-step synthesis for thieno[3,2-*b*]thiophene, or substituted derivatives thereof, was available in the literature, the utilization of thienothiophenes in coordination chemistry with transition metals has been neglected. However, in 1994, Choi and co-workers[14] reported a one-pot synthesis of 3,6-dimethylthieno[3,2-*b*]thiophene, which promoted investigation of the properties of these molecules in coordination chemistry. This synthesis was based on the discovery made by Teste and Lozac'h[15] that the reaction of 2,5-dimethyl-3-hexyne-2,5-diol with elemental sulfur afforded 3,6-dimethylthieno[3,2-*b*]thiophene, although the yield was low. Choi re-examined this reaction and varied the reaction conditions until 3,6-dimethylthieno[3,2-*b*]thiophene was obtained in a reasonable yield.

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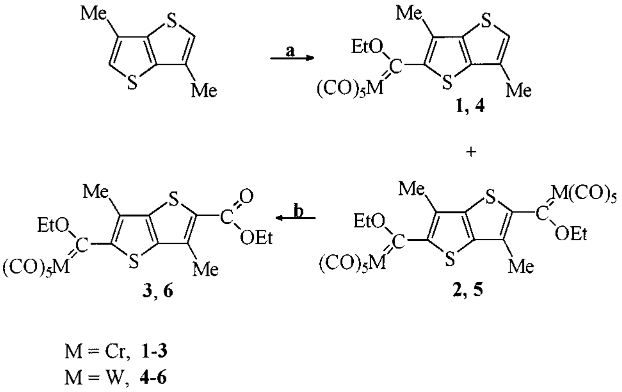
The novel carbene complexes **2** and **5** were synthesized using the classical Fischer method. The dimetallation of thieno[3,2-*b*]thiophene and 3,6-dimethylthieno[3,2-*b*]thiophene was based on the method described by Bugge.[13] The reactions were carried out in hexane and TMEDA was introduced together with butyllithium to form 2,7-dilithio species at elevated temperatures. Formation of biscarbene complexes followed after addition of the metal hexacarbonyl and subsequent quenching with the alkylating agent $Et_3O{\cdot}BF_4$. The synthetic procedure for the preparation of these complexes is outlined in Scheme 1.

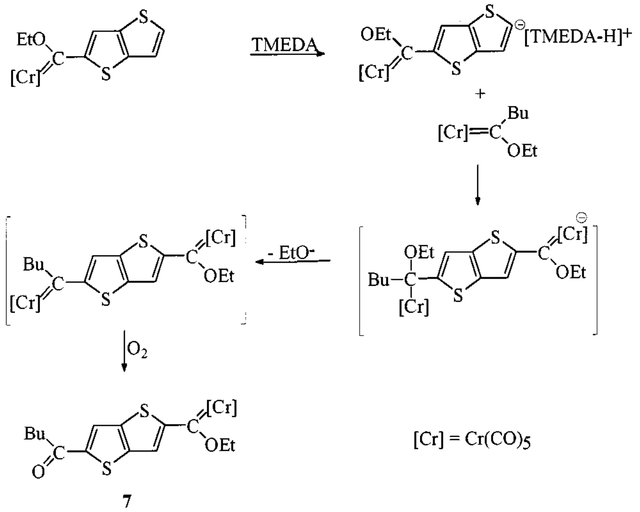


Scheme 1. Synthesis of the novel carbene complexes **1−6**; reagents: (a) 2 equiv. *n*BuLi, $M(CO)_6$, $Et_3O{\cdot}BF_4$; (b) O_2

Carbene complexes of chromium, complexes **1** and **2**, were crystallized from hexane/dichloromethane (1:1) solutions to affording red-orange needles for the monocarbene complex and purple-black crystals for the biscarbene complex. X-ray diffraction studies confirmed the structures of these compounds. Similar products, complexes **3** and **4**, were obtained for tungsten and characterized spectroscopically. Complexes **3** and **6** are suggested to have formed in solution by oxidation of the air-sensitive biscarbene complexes, involving trace amounts of oxygen.[6]

Complex **7** was isolated from the reaction between $Cr(CO)_6$ and thieno[3,2-*b*]thiophene and did not resemble any of the products obtained from the similar reaction with 3,6-dimethylthieno[3,2-*b*]thiophene. Although the synthetic procedure followed was identical, only complex **7** was isolated instead of the expected monocarbene and biscarbene complexes. The yield of **7** was low and implies the formation of other unstable compounds. The structural elucidation of this complex was based on the data collected with the use of NMR spectroscopy, infrared data, and mass spectrometry.

A possible reaction route to **7** is attributed to the enhanced acidity exhibited by the protons of the unsubstituted thienothiophene. Hence, the suggested formation of product **7**, as is illustrated in Scheme 2, can be explained by reaction of a deprotonated thienothiophene monocarbene complex and a metal butyl carbene to give a dinuclear ylide intermediate. Elimination of an ethoxy group follows and after subsequent oxidation of the more reactive metal butyl carbene end of the biscarbene, the final product, complex **7**, is afforded. TMEDA acts as a base and deprotonates the ring at the 7-position of the monocarbene complex, while its conjugated acid assists in the removal of the ethoxy group from the ylide.



Scheme 2. Suggested formation of complex **7**

The complexes were fully characterized and their NMR spectra recorded in deuterated chloroform. The monocarbene complexes, **1** and **4**, display a quadruplet signal for the H7 proton due to coupling with the methyl group on C6. This methyl signal is observed as a doublet and a coupling constant of ca. 1 Hz is determined for this four-bond coupling. It is interesting to note the significant difference in chemical shift values of the methylene resonance of the carbene ethoxy substituent on the spectra of the three tungsten complexes compared with the same signal on the spectra of the chromium complexes. The chemical shift is observed significantly more upfield for the tungsten complexes than for the chromium complexes, denoting that these resonance values are fairly characteristic for a specific metal and unaffected by the substituent on the 7-position of the 3,6-dimethylthieno[3,2-*b*]thiophene unit. Also characteristic is the position of the methylene resonances of the ester groups at $\delta \approx 4.35$ for both complexes **3** and **6**, which shows that the influence of the different metals is not transferred through the ligand to the other side of the thienothiophene rings. This was also observed for the corresponding thiophene complexes.[6] On the proton, as well as on the carbon NMR spectra of complexes **3** and **6** evidence for the further decomposition of these products to the 2,7-bis(ethyl ester) of 3,6-dimethylthieno[3,2-*b*]thiophene is observed and signifies the reactivity in solution towards oxygen of not only the biscarbene but also of the resulting monocarbene-ester complexes over prolonged periods of time.

Carbene carbon chemical shifts are found at characteristic values for the different metals on the ^{13}C NMR spectra. The values fall within the range of $\delta = 317-319$ for the chromium complexes, while these resonances are observed at $\delta = 292-297$ on the tungsten spectra. This same sequence is noted for the position of the $M(CO)_5$ peaks on the different spectra. The difference in chemical shift value ($\Delta\delta$) of the carbonyl resonances is approximately 10 ppm, with tungsten upfield from chromium. The methylene carbons of the carbene ethoxy group of the different metal spectra reveal the opposite trend, with the resonances of the chromium complexes observed upfield from those of the tungsten complexes.

The lower wavenumbers observed on the infrared spectra of the monocarbene complexes **1** and **4** compared with those of the biscarbene complexes, and the decomposition products, indicate stronger metal-carbonyl back bonding and thus a decrease in C−O bond order. This implies weaker metal to carbene carbon π-bonding. Alternatively, the substituents on the carbene carbon may play a greater role in stabilizing the electrophilic carbene carbon. The values reported for the monocarbene complexes of chromium and tungsten containing a phenyl substituent, $[Cr(CO)_5C(OEt)Ph]$[16] and $[W(CO)_5C(OMe)Ph]$,[17] are even higher than for the thiophene complexes, implying that the phenyl unit is a poorer donor of electron density relative to the thienyl or, consequently, the thienothienyl substituent.

From the structures of complexes **1** and **2**, as shown in Figure 1 and Figure 2, it is noted that the heteroaromatic spacer, the carbene carbon and the metal atom are all coplanar for both structures. The metal fragment is orientated towards the sulfur atom and away from the methyl substituent on the ring in complex **1**. For complex **2**, the two $Cr(CO)_5$ metal fragments are found on opposite sides of the spacer ligand, positioned towards the sulfur atom and away from the methyl substituent on the ring. This is in contrast with the structure of the biscarbene complex of chromium pentacarbonyl, constituting a thienylene.[6] In this complex, the metal fragments are found on the same side of the thiophene ring and on the side opposite to the sulfur atom in the ring. However, for the biscarbene complex of chromium pentacarbonyl with biphenylene as the bridging ligand, the metal moieties are again on opposite sides of the axis connecting the two carbene carbon atoms.[4b] The Cr metal is approximately octahedrally arranged, with two of the *cis*-carbonyl ligands bending away from the carbene carbon. This is indicated by the bond angles of 94.5(1)° for both the C(12)−Cr(1)−C(1) and C(12A)−Cr(1)−C(1) angles in **1** and 93.1(1)° for both the angles C(7)−Cr−C(1) and C(9)−Cr(1)−C(1) in **2**. On considering the positions of the ethyl group of the ethoxy substituent relative to the metal fragment in the solid state, the (*Z*)-isomer of this complex along the carbene−O bond is observed. This is in accordance with the observation in the literature that the (*Z*)-isomer is by far the most popular arrangement in the crystal structures of ethoxy- or methoxy-substituted carbene complexes of octahedrally coordinated metals.[18] Suggested delocalization in the ring system is promoted by the observed bond lengths, which are all very similar and correspond to distances between characteristic $C(sp^2)$ single bonds and $C(sp^2)$ double bonds.[19] In contrast to the observation made for complex **1** where only the one thiophene unit is affected, delocalization in complex **2** occurs throughout the whole heteroarene system, aided by the influence of the second metal fragment, which is absent in complex **1**.

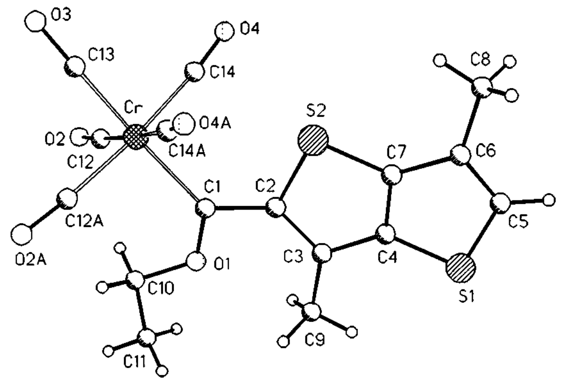


Figure 1. Molecular structure of complex **1**; selected bond lengths [Å] and angles [°]: Cr1−C1 2.081 (4), S1−C5 1.722(4), S1−C2 1.751(4), S2−C7 1.721(5), S2−C4 1.729(4), C1−C2 1.469(6), C2−C3 1.413(6), C3−C4 1.411(6), C4−C5 1.377(6), C5−C6 1.341(7), C6−C7 1.431(6), O1−C1−C2 104.9(3), O1−C1−Cr1 128.6(3), C2−C1−Cr1 126.5(3)

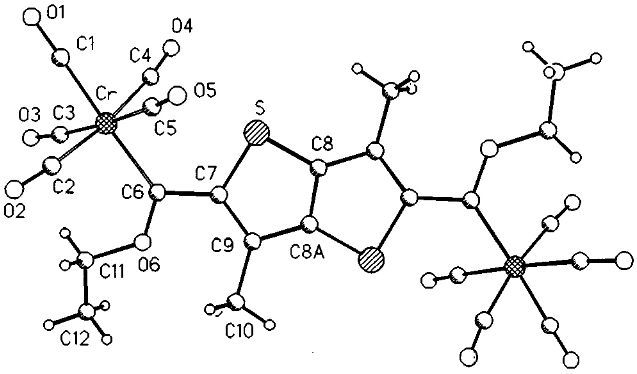


Figure 2. Molecular structure of complex **2**; selected bond lengths [Å] and angles [°]: Cr−C1 2.068(3), S−C4A 1.721(2), S−C2 1.745(3), C1−C2 1.473(4), C2−C3 1.393(4), C3−C4 1.415(4), C4A−C4 1.378(5), O6−C1−C2 105.0(2), O6−C1−Cr 129.2(2), C2−C1−Cr 125.7(2)

Conclusion

Transition metal biscarbene complexes with conjugated spacers are still limited in the literature. In this paper, we have reported the syntheses of biscarbene complexes with thienothiophene spacers, comprising two fused thiophene units. On comparing the relative stabilities in solution of these novel complexes with those of biscarbene complexes of thiophene, as described in the literature,[6] it was found that by increasing the number of thiophene units in the spacer, the stability of the complexes improves. However, formal stability studies were not conducted but the rate of decomposition of the individual complexes in solution was taken as a criterion. Biscarbene complexes convert into monocarbene-ester products within minutes after being dissolved in acetone or THF.

Experimental Section

General Remarks: All NMR spectra were recorded in deuterated chloroform, unless stated otherwise, using TMS as an internal standard on a Bruker ARX-300 spectrometer. − Infrared spectra were recorded on a BOMEM FT-IR spectrophotometer using dichloromethane as solvent unless otherwise specified. − Mass spectra were recorded at ca. 70 eV on a Finnigan Mat 8200 instrument, using the electron impact method.

All reactions were performed in an inert atmosphere of either nitrogen or argon by using standard Schlenk techniques and vacuum-line methods. Solvents were dried and distilled under nitrogen prior to use. − Column chromatography was carried out under nitrogen using either silica gel (particle size 0.063−0.200 nm) or neutral aluminium oxide as resin. − Most chemicals were used directly without prior purification. The following compounds were prepared using known literature methods: 3,6-dimethylthieno[3,2-*b*]thiophene,[14] 2,3,5-tribromothiophene,[11] 3-bromothiophene,[12] ethyl (3-thienylthio)acetate,[10] ethyl (2-formyl-3-thienylthio)acetate,[13] thieno[3,2-*b*]thiophene carboxylic acid, thieno[3,2-*b*]thiophene[12], and triethyloxonium tetrafluoroborate.[20]

Revised Synthesis of Thieno[3,2-*b*]thiophene: Synthesis of 2,3,5-tribromothiophene was effected according to the method described by Brandsma and Verkruijsse,[11] and involved the reaction of bromine (180.00 mL; 3.50 mol) and thiophene (80.00 mL, 1.00 mol) in a 48% aqueous HBr/diethyl ether solution (400 mL/100 mL) at elevated temperatures (75°C). The target product (97%) and HBr were formed. Reduction of 2,3,5-tribromothiophene (321.00 g, 1.00 mol) to obtain 3-bromothiophene (55%),[12] was performed using zinc dust (196.00 g, 3.00 mol) in 175 mL of acetic acid. Reaction of 3-bromothiophene (90.50 g, 0.55 mol) with elemental sulfur (17.60 g, 0.55 mol), followed by the addition of ethyl bromoacetate (61.4 mL, 0.55 mol), afforded ethyl (3-thienothio)acetate (73%). On reacting this acetate-substituted thiophene (26.60 g, 0.13 mol) with phosphorus oxychloride (30.00 g, 0.19 mol) in *N*,*N*-dimethylformamide (14.00 g, 0.19 mol) afforded ethyl(2-formyl-3-thienothio)acetate (85%) in a Vilsmeier formylation reaction.[13] Cyclization and the subsequent decarboxylation of this compound yielded thieno[3,2-*b*]thiophene.[10]

Chromium Carbene Complexes 1, 2, and 3: 3,6-Dimethylthieno[3,2-*b*]thiophene (0.67 g, 4.00 mmol) was dissolved in 50 mL of hexane. TMEDA (1.20 mL, 8.00 mmol) and *n*-butyl lithium (5.5 mL, 8.8 mmol) were added at room temperature. The mixture was refluxed for 45 minutes and then cooled to 0 °C. After the addition of 50 mL of THF, $Cr(CO)_6$ (1.76 g, 8.00 mmol) was added and the suspension stirred for an hour. The color of the reaction changed to dark brown. After completion of the reaction, the solvent was removed in vacuo. The residue was dissolved in 20 mL of dichloromethane. Triethyloxonium tetrafluoroborate (1.50 g, 8.10 mmol) was dissolved in 20 mL of dichloromethane and this was added to the cooled reaction mixture (−20 °C). An immediate color change to a purple solution was observed. Stirring was maintained for a further hour while the temperature was allowed to reach room temperature. The mixture was then filtered, the solvent removed, and the remainder purified on a silica gel column. Three products were isolated, starting with pure hexane as eluent and gradually increasing the polarity of the solvent by adding dichloromethane. The first was the orange monocarbene complex **1**. The second purple complex was the biscarbene complex **2**, while the third red-orange compound was characterized as **3**. This complex was isolated using a hexane/dichloromethane mixture (1:1) as eluent.

1: Yield 0.55 g (33%), m.p.173−177 °C. − $C_{16}H_{12}CrO_6S_2$ (416.4): calcd. C 46.15, H 2.91; found C 46.36, H 3.05. − IR (ν_{CO}; CH_2Cl_2) = 2055 (m), 1979 (w), 1938 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 7.18 (q, ^4J = 1.2 Hz, 1 H, H^7), 5.19 (q, ^3J = 7.0 Hz, 2 H, OCH_2CH_3), 2.47 (s, 3 H, Me^3), 2.41 (d, ^4J = 1.2, 3 H, Me^6), 1.71 (t, ^3J = 7.0, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 318.7 (carbene carbon), 222.8, 216.8 (CO), 150.1 (C^2), 144.7 (C^4), 142.6 (C^5), 130.8 (C^3), 129.5 (C^6), 128.2 (C^7), 76.4 (OCH_2CH_3), 18.6 (Me^3), 15.6 (OCH_2CH_3), 14.7 (Me^6). − MS (EI); *m*/*z*: 416 [M^+], 388 [M^+ − CO], 360 [M^+ − 2 CO], 332 [M^+ − 3 CO], 304 [M^+ − 4 CO], 276 [M^+ − 5 CO].

2: Yield 1.25 g (47%), $C_{24}H_{16}O_{12}S_2Cr_2$ (664.5): calcd. C 43.38, H 2.43; found C 43.61, H 2.62. − IR (ν_{CO}; CH_2Cl_2) = 2053 (m), 1986 (w), 1941 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 5.19 (q, ^3J = 7.1 Hz, 4 H, OCH_2CH_3), 2.47 (s, 6 H, Me^3), 1.74 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 223.6, 216.3 (CO), 167.7 (C^2), 149.8 (C^4), 131.9 (C^3), 76.6 (OCH_2CH_3), 17.6 (Me^3), 15.5 (OCH_2CH_3). − MS (EI); *m*/*z*: 636 [M^+ − CO], 552 [M^+ − 4 CO], 524 [M^+ − 5 CO].

3: Yield 0.23 g (12%), $C_{19}H_{16}O_8S_2Cr$ (488.5): calcd. C 46.72, H 3.31; found C 46.86, H 3.45. − IR (ν_{CO}; CH_2Cl_2) = 2057 (m), 1984 (w), 1940 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 5.20 (q, ^3J = 6.9 Hz, 2 H, $OCH_2CH_3{-}M$), 4.35 (q, ^3J = 7.2 Hz, 2 H, $OCH_2CH_3{-}O$), 2.70 (s, 3 H, Me^3), 2.43 (s, 3 H, Me^6), 1.72 (t, ^3J = 6.9 Hz, 3 H, $OCH_2CH_3{-}M$), 1.38 (t, ^3J = 7.2 Hz, 3 H, $OCH_2CH_3{-}O$). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 317.9 (carbene carbon), 223.3, 216.7 (CO), 163.6 (C^2), 163.1 (C^7), 142.7 (C^4), 142.0 (C^5), 130.6 (C^3), 129.7 (C^6), 76.4 ($OCH_2CH_3{-}M$), 61.4 ($OCH_2CH_3{-}O$), 17.7 (Me^3), 15.6 ($OCH_2CH_3{-}M$), 15.0 (Me^6), 14.4 ($OCH_2CH_3{-}O$). − MS (EI); *m*/*z*: 488 [M^+], 460 [M^+ − CO], 432 [M^+ − 2 CO], 404 [M^+ − 3 CO], 376 [M^+ − 4 CO], 348 [M^+ − 5 CO].

Tungsten Carbene Complexes 4, 5, and 6: 3,6-Dimethylthieno[3,2-*b*]thiophene (0.34 g, 2.00 mmol) was dissolved in 30 mL of hexane. TMEDA (0.60 mL, 4.00 mmol) and *n*-butyl lithium (2.80 mL, 4.40 mmol) were added to this solution at room temperature. The same procedure was followed as for the chromium analog with the addition of $W(CO)_6$ (1.40 g, 4.00 mmol). For alkylation triethyloxonium tetrafluoroborate (0.74 g, 4.00 mmol) was used. On purification using column chromatography, three bands separated. The eluent used involved hexane/dichloromethane mixtures of various compositions. While the first product was isolated using pure hexane as eluent, a 1:1 mixture was used to isolate the third product. The first monocarbene complex **4** was isolated as an orange solid. The second purple complex was characterized as the biscarbene complex **5**, while the third red-orange band was identified as **6**.

4: Yield 0.45 g (41%), m.p.187−189 °C. − $C_{16}H_{12}O_6S_2W$ (548.3): calcd. C 35.05, H 2.21; found C 35.23, H 2.40. − IR (ν_{CO}; CH_2Cl_2) = 2063 (m), 1989 (w), 1933 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 7.22 (q, ^4J = 1.1 Hz, 1 H, H^7), 5.02 (q, ^3J = 7.1 Hz, 2 H, OCH_2CH_3), 2.48 (s, 3 H, Me^3), 2.41 (d, ^4J = 1.1 Hz, 3 H, Me^6), 1.69 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 292.6 (carbene carbon), 201.9, 197.8 (CO), 150.2 (C^2), 144.1 (C^4), 144.1 (C^5), 132.1 (C^3), 131.0 (C^6), 128.8 (C^7), 79.0 (OCH_2CH_3), 18.9 (Me^3), 15.4 (OCH_2CH_3), 14.6 (Me^6). − MS (EI); *m*/*z*: 548 [M^+], 520 [M^+ − CO], 492 [M^+ − 2 CO], 464 [M^+ − 3 CO], 436 [M^+ − 4 CO], 408 [M^+ − 5 CO].

5: Yield 0.67 g (36%), $C_{24}H_{16}O_{12}S_2W_2$ (928.3): calcd. C 31.05, H 1.74; found C 31.14, H 1.82. − IR (ν_{CO}; CH_2Cl_2) = 2062 (m), 1983 (w), 1938 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 5.04 (q, ^3J = 7.1 Hz, 4 H, OCH_2CH_3), 2.48 (s, 6 H, Me^3), 1.72 (t, ^3J = 7.1 Hz, 6 H, OCH_2CH_3). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 202.2, 197.3 (CO), 164.9 (C^2), 149.3 (C^4), 123.5 (C^3), 79.6 (OCH_2CH_3), 18.4 (Me^3), 15.3 (OCH_2CH_3). − MS (EI); *m*/*z*: 932

[M^+], 903 [$M^+ - CO$], 874 [$M^+ - 2\,CO$], 818 [$M^+ - 4\,CO$], 788 [$M^+ - 5\,CO$].

6: Yield 0.11 g (9%), $C_{19}H_{16}O_8S_2W$ (620.3): calcd. C 36.79, H 2.61; found C 37.01, H 2.82. − IR (ν_{CO}; CH_2Cl_2) = 2065 (m), 1985 (w), 1936 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 5.03 (q, ^3J = 7.2 Hz, 2 H, $OCH_2CH_3{-}M$), 4.36 (q, ^3J = 7.2 Hz, 2 H, $OCH_2CH_3{-}O$), 2.70 (s, 3 H, Me^3), 2.44 (s, 3 H, Me^6), 1.70 (t, ^3J = 7.2 Hz, 3 H, $OCH_2CH_3{-}M$), 1.39 (t, ^3J = 7.2 Hz, 3 H, $OCH_2CH_3{-}O$). − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 296.3 (carbene carbon), 202.3, 197.8 (CO), 162.8 (C^2), 159.3 (C^7), 144.7 (C^4), 141.3 (C^5), 130.0 (C^3), 129.7 (C^6), 79.5 ($OCH_2CH_3{-}M$), 61.5 ($OCH_2CH_3{-}O$), 18.4 (Me^3), 15.2 ($OCH_2CH_3{-}M$), 14.8 (Me^6), 14.2 ($OCH_2CH_3{-}O$). − MS (EI); *m*/*z*: 620 [M^+], 592 [$M^+ - CO$], 564 [$M^+ - 2\,CO$], 536 [$M^+ - 3\,CO$], 508 [$M^+ - 4\,CO$], 480 [$M^+ - 5\,CO$].

Chromium Carbene Complex 7: Thieno[3,2-*b*]thiophene (0.56 g, 4.00 mmol) was dissolved in 30 mL of hexane. THF (100 mL) was added together with TMEDA (1.20 mL, 8.00 mmol) and *n*-butyllithium (5.50 mL, 8.80 mmol). The mixture was refluxed for 45 minutes and cooled to 0 °C, after which 100 mL of THF was added. $Cr(CO)_6$ (1.70 g, 8.00 mmol) was introduced and the mixture was stirred for an hour at room temperature. The solvent was evaporated and triethyloxonium tetrafluoroborate (1.50 g, 8.00 mmol), dissolved in 30 mL of dichloromethane, was added at −30 °C. The mixture was stirred for 15 minutes in the cold and for a further 45 minutes at room temperature, after which it was filtered and the solvent evaporated. The residue was column chromatographed with a hexane/dichloromethane (1:1) solution to yield the purple-pink product **7**.

7: Yield 0.79 g (42%), $C_{19}H_{16}O_7S_2Cr$ (472.5): calcd. C 48.30, H 3.42; found C 48.51, H 3.59. − IR (ν_{CO}; CH_2Cl_2) = 2058 (m), 1978 (w), 1943 (vs) cm^{-1}. − ^1H NMR ($CDCl_3$, 300.135 MHz): δ = 8.33 (s, 1 H, H^3), 7.82 (s, 1 H, H^6), 5.21 (q, ^3J = 7.0 Hz, 2 H, $OCH_2CH_3{-}M$), 2.93 [t, ^3J = 7.5 Hz, 2 H, $C(O)CH_2CH_2CH_2CH_3$], 1.74 [t, ^3J = 7.5 Hz, 2 H, $C(O)CH_2CH_2CH_2CH_3$], 1.69 (t, ^3J = 7.0 Hz, 3 H, $OCH_2CH_3{-}M$), 1.42 [t, ^3J = 7.5 Hz, 2 H, $C(O)CH_2CH_2CH_2CH_3$], 0.95 [t, J = 7.5 Hz, 3 H, $C(O)CH_2CH_2CH_2CH_3$]. − ^{13}C NMR ($CDCl_3$, 75.1 MHz): δ = 317.0 (carbene carbon), 223.5, 217.5 (CO), 194.5 (C=O), 164.0 (C^2), 155.1 (C^7), 146.8, 139.4, 134.4 (C^3, C^4, C^5, C^6, C^{10}, C^{11}), 75.7 ($OCH_2CH_3{-}M$), 43.0 [$C(O)CH_2CH_2CH_2CH_3$], 25.5 [$C(O)CH_2CH_2CH_2CH_3$], 22.8 [$C(O)CH_2CH_2CH_2CH_3$], 15.1 ($OCH_2CH_3{-}M$), 13.9 [$C(O)CH_2CH_2CH_2CH_3$]. − MS (EI); *m*/*z*: 472 [M^+], 444 [$M^+ - CO$], 416 [$M^+ - 2\,CO$], 388 [$M^+ - 3\,CO$], 360 [$M^+ - 4\,CO$], 332 [$M^+ - 5\,CO$].

X-ray Crystallographic Study: The intensity data for the compounds were collected at −90 °C on a Nonius−Kappa CCD diffractometer, using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects, but not for absorption.[21,22] The structures were solved by direct methods (SHELXS)[23] and refined by full-matrix least squares techniques against F_o^2 (SHELXL-97)[24]. The hydrogen atoms of the structures were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations. One molecule of chromium hexacarbonyl cocrystallized with two molecules of the monocarbene complex **1**. Other experimental details are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary material publication nos. CCDC-142023 (**1**) and CCDC-142024 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK [Fax: (internat.) +44 1223/336-033; E-mail: deposite@ccdc.cam.ac.uk].

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Table 1. Crystallographic data and data related to data acquisition and refinement for compounds **1** and **2**

	1		**2**	
Empirical formula	$CrC_{16}H_{12}O_6S_2 \cdot 0.5\,Cr(CO)_6$		$C_{24}H_{16}Cr_2O_{12}S_2$	
Formula mass	526.41		664.49	
Temperature	183(2) K		183(2) K	
Wavelength	0.71073 Å		0.71073 Å	
Crystal system	monoclinic		triclinic	
Space group	*C*2/m		*P*−1	
Unit cell dimensions	a = 30.4690(9) Å	α = 90°	a = 6.4052(5) Å	α = 71.172(5)°
	b = 7.5136(4) Å	β = 90.930(2)°	b = 8.8481(7) Å	β = 82.010(5)°
	c = 9.5477(4) Å	γ = 90°	c = 13.0304(6) Å	γ = 83.681(3)°
Volume	2185.5(2) Å^3		690.51(8) Å^3	
Z	4		1	
Density (calculated)	1.600 Mg/m^3		1.598 Mg/m^3	
Absorption coefficient	0.998 mm^{-1}		0.999 mm^{-1}	
F(000)	1064		336	
Crystal size	0.35 × 0.30 × 0.25 mm		0.30 × 0.30 × 0.10 mm	
Theta range for data collection	2.79 to 23.23°		3.22 to 23.31°	
Index ranges	$-33 \le h \le 33$, $-8 \le k \le 0$, $-10 \le l \le 10$		$0 \le h \le 7$, $-9 \le k \le 9$, $-13 \le l \le 14$	
Reflections collected	2961		3832	
Independent reflections	1620 [*R*(int) = 0.0233]		1857 [*R*(int) = 0.027]	
Refinement method	Full-matrix least-squares on F^2		Full-matrix least-squares on F^2	
Data/restraints/parameters	1587/0/175		1824/0/181	
Goodness-of-fit on F^2	0.947		1.047	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0356, $wR2$ = 0.1120		$R1$ = 0.0356, $wR2$ = 0.1039	
R indices (all data)	$R1$ = 0.0437, $wR2$ = 0.1377		$R1$ = 0.0386, $wR2$ = 0.1154	
Largest diff. peak and hole	0.350 and −0.356 e·Å^{-3}		0.247 and −0.379 e·Å^{-3}	

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