Fischer Dinuclear and Mononuclear Bis-Carbene Complexes of Thiophene and Thiophene Derivatives
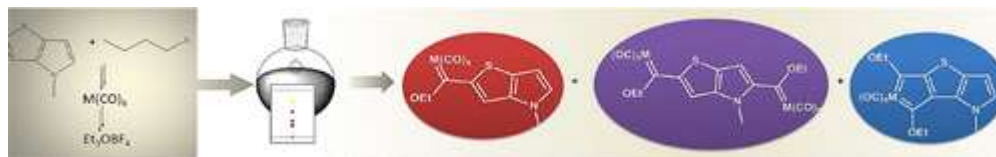
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Abstract

The reaction of dilithiated thiophene and thiophene derivatives with group 6 transition metal carbonyl precursors and subsequent alkylation afforded linearly arranged Fischer 2,5-bis-carbene and the rare unsymmetrical 2,3-bis-carbene chelated complexes. The latter requires a second lithiation to occur at an adjacent, less reactive site on the thiophene ring. The control of reactivity sites was investigated and achieved by either blocking more reactive positions with substituents or activating less reactive positions by lithium–halogen exchange reactions. A series of Fischer bis-carbene chelates were synthesized by manipulating the above variables. Structural features of Fischer mono-carbene, mononuclear bis-carbene, and bis-carbene chelated complexes were studied by IR, NMR, and single-crystal X-ray diffraction.

Introduction

In five-membered heteroaromatic systems the most reactive carbons are those in the positions adjacent to the heteroatom. It is well-known that the sulfur atom in thiophene will stabilize both carbanions and carbocations in these positions.[1-3] Comparison of the different acidities of the thiophene protons, by H/D exchange experiments, showed the α-positions to be 500 times more acidic than the β-positions.[4] This is also reflected by the chemical shifts for the α- and β-protons in the ^{1}H NMR spectrum of thiophene (CDCl$_3$), which were found at 7.20 (H2/H5) and 6.96 ppm (H3/H4), respectively.[5, 6] Therefore, dilithiation occurs preferentially at the 2- and 5-positions, leaving the 3- and 4-positions unreacted. The classical Fischer method of carbene synthesis requires an organolithium reagent, metal carbonyl, and an appropriate strong alkylating agent.[7] The syntheses of dinuclear bis-carbene complexes with arene spacers have for many years depended on the most reactive sites for lithiation reactions.[8] Dilithiated thiophene and thiophene chains can be used to give linearly assembled bis-carbene complexes containing a π-conjugated spacer between the two carbene ligands at the termini of the spacer.[9, 10] Hence, by incorporating the carbene ligands, communication is possible from one metal to the second metal fragment at the other end of the molecule via the π-frame of the molecule. In addition, it was found that these bimetallic bis-carbene complexes are reasonably stable in the solid state but displayed enhanced reactivity in solution at the carbene centers.[10, 11] In mixed-metal bis-carbene complexes of this type regioselective template reactions at the carbene centers could be accomplished.[10] A bis-carbene complex with a bithienyl spacer ligand is shown in Figure 1.[11, 12]
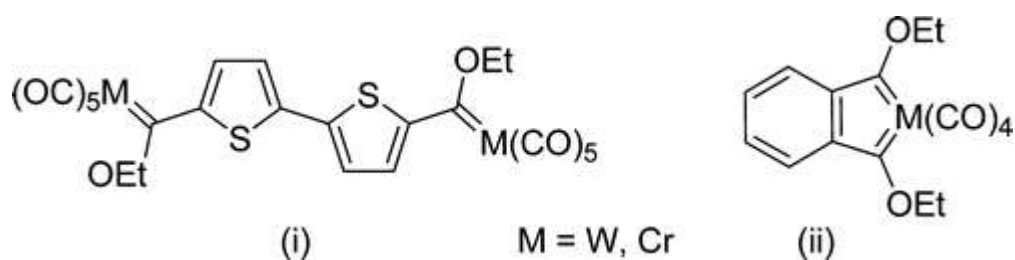
Figure 1. Bis-carbene complexes (i) with a bithienylene spacer forming a rod[11] and (ii) with benzene to give a five-membered chelated ring.[13]

In contrast, for a five-membered ring to form the backbone of a mononuclear bis-carbene chelate, it is necessary to generate two adjacent carbanions. This can be synthetically very challenging. A successful example is a dianion of benzene, which was prepared by an indirect method using a mercury polymer.[14, 15] The polymer was cleaved and finally afforded a chelated bis-carbene complex (Figure 1).[13, 16] Nitrogen-containing heterocyclic carbene and bis-carbene complexes (NHC's) display high stabilities, and there are many examples in the literature.[17-19] Mononuclear bis-carbene complexes with alkoxy substituents are scarce and much more reactive.[20] The few bis-alkoxycarbene chelates known and reported many years ago are symmetrically substituted compounds. The identical carbene ligands displayed nonselective reactivity patterns at both carbene carbon centers.[21-23] Recently we reported the first examples of a chelated ring with two alkoxycarbene ligands attached to a thiophene backbone and coordinated to transition metals.[24]

In this study we chose thiophene as a template to study carbene complex formation. Less reactive sites may be activated and become potential sites for the attachment of alkoxycarbene moieties, or inversely, typically reactive sites can be blocked and hence the activity diverted to other ring positions. It is well-known in lithium–halogen exchange reactions that the halogens may change sites in a so-called base-catalyzed halogen dance (BCHD) reaction.[25] The reactivities of thiophene substrates with bromo substituents are reliant on the nature of the organolithium agent. *n*-Butyllithium reacts first at the site containing the halogen substituent, whereas LDA preferably reacts at the remaining α-proton in the ring, avoiding the brominated site.[26] Lithium–halogen exchange reactions are reversible when using *n*-BuLi; thus, the change in the reaction conditions might affect the outcome of the intermediates that form. These include the BCHD products mentioned above, the decomposition of the lithium reagent, or the formation of products resulting from unreacted *n*-BuLi.

Results and Discussion

Synthesis

Unlike the case for bithienyl (Figure 1), treatment of thiophene with 2 equiv of *n*-butyllithium (*n*-BuLi) in THF did not afford the desired metal acylate in satisfactory yield.[12] The yield can be improved by reacting *n*-BuLi-TMEDA in hexane at elevated temperatures with thiophene or 2,5-dibromothiophene.[27] Scheme 1 shows the dilithiation of thiophene at the 2- and 5-positions for the synthesis of the complex $[(CO)_5W\{C(OEt)C_4H_2SC(OEt)\}W(CO)_5]$ (**1**).
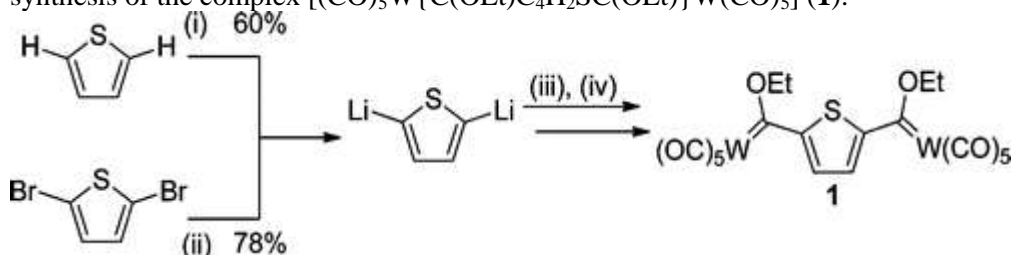
Scheme 1. [a]

[a]Legend: (i) *n*-BuLi-TMEDA; (ii) *n*-BuLi; (iii) W(CO)$_6$; (iv) [Et$_3$O][BF$_4$].

Lithium–halogen exchange occurs relatively quickly, at low temperatures, with high yields and therefore opens an opportunity for lithiation at less reactive positions.(30, 31) A typical problem after lithiation at such low temperatures is the poor solubility of the metal carbonyl in the reaction mixture in carbene synthesis. During this stage of the reaction, conditions can be changed to dissolve the metal carbonyl. The duration and/or the temperature at this step of the reaction may be increased. The bis-carbene complex **1** displayed two alkoxycarbene ligands in typically activated thiophene positions. Complex **1** was characterized by using infrared and NMR spectroscopy as well as mass spectrometry. Crystals of **1** suitable for X-ray diffraction studies were obtained from dichloromethane/hexane solutions (Figure 2). The ^{1}H NMR spectrum of **1** displayed a proton signal at 7.97 ppm in CDCl$_3$ (H3/H4), emphasizing the strong electron-withdrawing effect of the carbene carbon atoms on the thiophene ring in comparison to thiophene.(32, 33) This signal is upfield for H3 and downfield for H4 in comparison to that observed for the corresponding monocarbene complex, [W(CO)$_5${C(OEt)C$_4$H$_3$S}],(34, 35) indicating the combined effect of two vs one electron-withdrawing carbene ligands attached to the thiophene spacer. The ^{13}C NMR spectrum of **1** exhibited a chemical shift of 312.5 ppm for the carbene carbon, which is similar to that for other analogous mono-carbene complexes.(36)
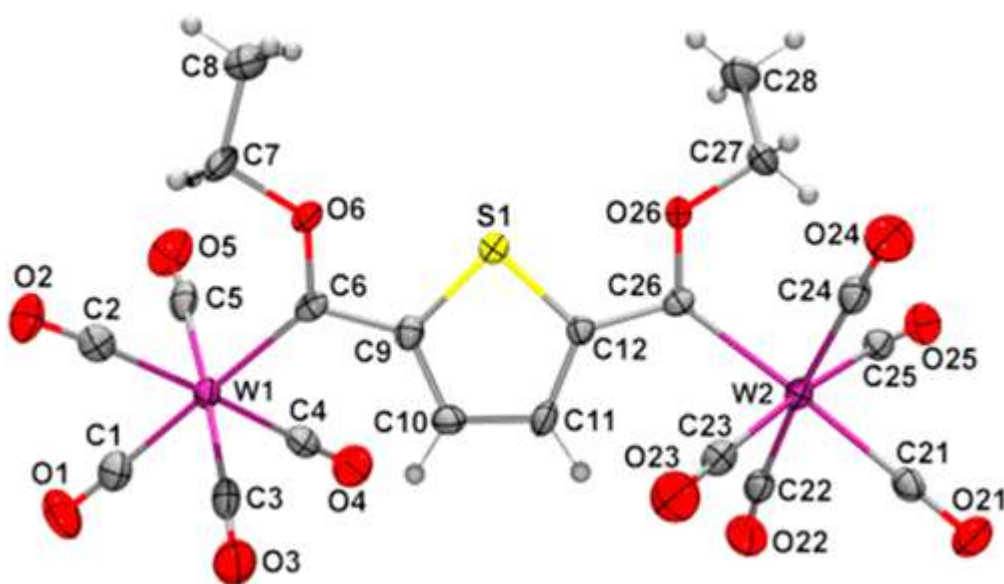

Figure 2. ORTEP(28)/POV-Ray(29) representation of [CO)$_5$W{C(OEt)C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**1**), showing the orientation of the ethoxy groups and atom-numbering scheme. Atomic displacement ellipsoids are shown at the 50% probability level.

It was anticipated that blocking of an activated α-position could direct the metalation to the neighboring carbon atom at the β-position. Synthesis of mono-metal complexes that have a bis-carbene chelate ring requires access to both the 2- and 3-positions. Two strategies seemed feasible: the first was to block one or both sites on one side of the thiophene ring, and the second was to activate one or both of the less reactive sites (positions 3 and 4) by introducing bromine substituents. An electron-withdrawing substituent in an α position should enhance the acidity of the adjacent thiophene proton, while electron-donating substituents should require an even stronger base or other means to deprotonate a β-carbon.(37) Also, the blocking group needed to be sufficiently unreactive to disallow any side reactions that may compete with the desired lithiations.

2-Methylthiophene (**A**) was chosen as a possible contender (Figure 3). Because of the inductive effect of the blocking methyl substituent, it was anticipated that the 4-position would be less reactive compared to the 3-position for the second lithiation of 2-lithio-5-methylthiophene. However, side reactions such as deprotonation on the methyl substituent presented a drawback to this strategy. This work was extended to investigate the role of the thienyl moiety on the ring site and methyl activations. Bis(thiophen-2-yl)methane (DTM, **B**) was chosen as an alternative substrate. 2,2′-Bithiophene was

excluded from the study, because it yielded only the known bis-carbene rods.(11, 12) The complete blocking of one side by using [3,2-*b*]-fused thiophene substrates was seen as ideal for the forced formation of bis-carbene chelated complexes. Benzo[3,2-*b*]thiophene (**C**) and 4-methyl-4*H*-thieno[3,2-*b*]pyrrole (**D**) were selected for this purpose. It was assumed that the benzene fragment would have little effect on the acidity of the thienyl ring, whereas it was expected that the less reactive pyrrole ring could have a marked effect on activating the remaining thiophene protons. The relative acid strengthening effect of the heteroatom in a five-membered ring for the elements is S > O > N.(38) For proton acidities in THF, the reactivity of 2-methylthiophene is slightly less(39) than those of thiophene (pK_a 33.0), benzo[3,2-*b*]thiophene (33.5), and 1-methyl-1*H*-pyrrole (39.5). The acidity of the methylpyrrole protons in THF is inadequate to react with a lithiated amine (LDA), in comparison to thiophene in 4-methyl-4*H*-thieno[3,2-*b*]pyrrole, and therefore also afforded very low yields using *n*-BuLi-TMEDA (4%) or *n*-BuLi (3%).(40) For consistency in the following discussion the numbering scheme shown in Figure 3 is used for NMR data of complexes. Atom numbering pertaining to crystal structures is indicated in the appropriate figures.
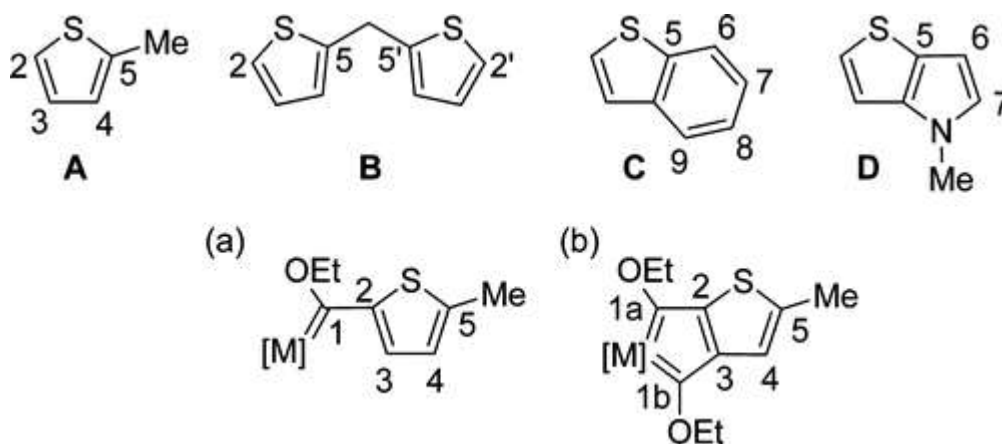

Figure 3. Thiophene derivatives selected for lithiation reactions.

In the case of 2-methylthiophene, mono-lithiation occurred at the 2-position of the thiophene ring. The resulting stable Fischer mono-carbene complexes [M(CO)$_5${C(OEt)C$_4$H$_2$(Me)S}] (M = Cr (**2a**), W (**2b**)) could be isolated after treatment of 2-lithio-5-methylthiophene with the metal carbonyls and alkylating agent. These complexes were prepared in high yields (ca 70%), with some butylcarbene complex [M(CO)$_5${C(OEt)Bu}](41) being obtained as a byproduct. Reacting 2-methylthiophene with 2 equiv of *n*-BuLi or LDA did not afford the desired 2,3-dilithiated species. The second deprotonation was at the methyl substituent.(39, 42) After treatment with the metal carbonyl and subsequent alkylation, the resulting methylene bis-carbene complexes [M(CO)$_5${C(OEt)C$_4$H$_2$SCH$_2$C(OEt)}M(CO)$_5$] (M = Cr (**3a**), W (**3b**)) were formed but were too reactive to isolate(43) (Scheme 2). The purple fractions **3a,b** were studied by NMR spectroscopy after being separated by flash chromatography. The spectra revealed chemical shifts for which assignments could be made that supported the structures of **3**.(41, 43-45) During the recording of the spectra decomposition of **3a,b** was observed.


2a M = Cr (29%)
2b M = W (36%)

3a M = Cr (37%)
3b M = W (31%)
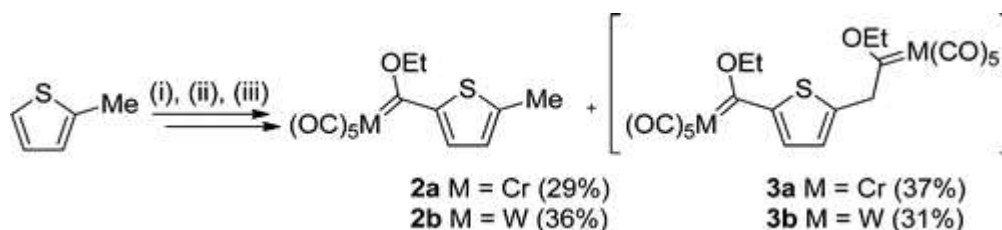
Scheme 2. [a]

[a]Legend: (i) *n*-BuLi; (ii) M(CO)$_6$; (iii) [Et$_3$O][BF$_4$].

Two different sets of chemical shifts were observed in the ^{1}H and ^{13}C NMR spectra of **3a,b** resulting from the two different carbene ligands. The ^{13}C NMR spectra displayed carbene resonances for the methylene and thienylene carbene carbons at 378.0 and 314.2 ppm for **3a** and 334.1 and 287.5 ppm for **3b**, respectively. Also, the two metal pentacarbonyl fragments gave duplicate sets of signals for the trans carbonyls (Cr 223.2, 221.9 ppm and W 204.3, 202.1 ppm) and for the cis carbonyls (Cr 217.2, 216.0 ppm and W 197.5, 197.1 ppm). During the isolation and recording of the NMR spectra for **3a,b** additional methylene signals appeared on the spectra in the range typical for the ethoxycarbene substituents of carbene ligands. Methylene protons in the carbene complexes $[Cr(CO)_5(C(OEt)Me]$ have been shown to be acidic and display enhanced reactivity.(46-48) The additional chemical shift values of the ethoxy groups corresponded with those observed before, for mono-carbene complexes resulting from carbene–carbene coupled olefinic products (3.7–3.9 ppm)(49) and metal oxidized ester products (4.3–4.1 ppm).(9, 10)

A sequential lithiation procedure was then employed, and 2-methylthiophene was reacted with 1 equiv of *n*-BuLi, followed by the addition of the appropriate metal carbonyl. Only thereafter was the reaction mixture treated with another 1 equiv of *n*-BuLi and alkylated. Anionic protection of metal acylates in sequential lithiation procedures of this kind have been used successfully before in metal carbene synthesis.(10, 33) Subsequent alkylation of the lithiated intermediates again afforded **2a,b** as major products, in spite of the electron-withdrawing properties of the 2-monoacyl metalate moiety. This route also did not yield the desired bis-carbene chelated complexes. It was hoped that the deprotonation at the methyl substituent could be prevented by employing a lithium–halogen exchange reaction at the 3-position. Fröhlich and co-workers(50) studied the reaction of 2-bromo-5-methylthiophene with LDA. In our case, to synthesize the desired 2,3-bis-carbene chelated complex, it was decided to use 3-bromo-5-methylthiophene. To secure lithiation at the 2- and 3-positions, the lithiation was done sequentially and both the order of lithiation and nature of the lithium base were carefully chosen. If the first lithiation was at the bromine site (3-position), the lithiated molecule quickly reacted with another 3-bromothiophene substrate and gave 3-bromo-2-lithio-5-methylthiophene. However, if the first lithiation occurred at the 2-position, which is the most active site using LDA, the rearrangement step would be bypassed and the second lithiation could occur at the 3-bromine position. During the reaction an excess of base was avoided, thus allowing the reaction to continue without deprotonating the methyl group. While the lithium–halogen exchange process was incomplete, the mono-carbene complexes $[M(CO)_5\{C(OEt)C_4HBr(Me)S\}]$ (M = Cr (**4a**), W (**4b**)) and **2a** or **2b** were obtained as minor products. The major products from this reaction were the targeted bis-carbene chelated complexes $[M(CO)_4\{C(OEt)_2C_4H(Me)S\}]$ (M = Cr (**5a**), W (**5b**)). Both reaction sequences afforded the bis-carbene chelates, but yields were increased when the sequence was such that base-catalyzed halogen dancing (BCHD) was avoided (Scheme 3).
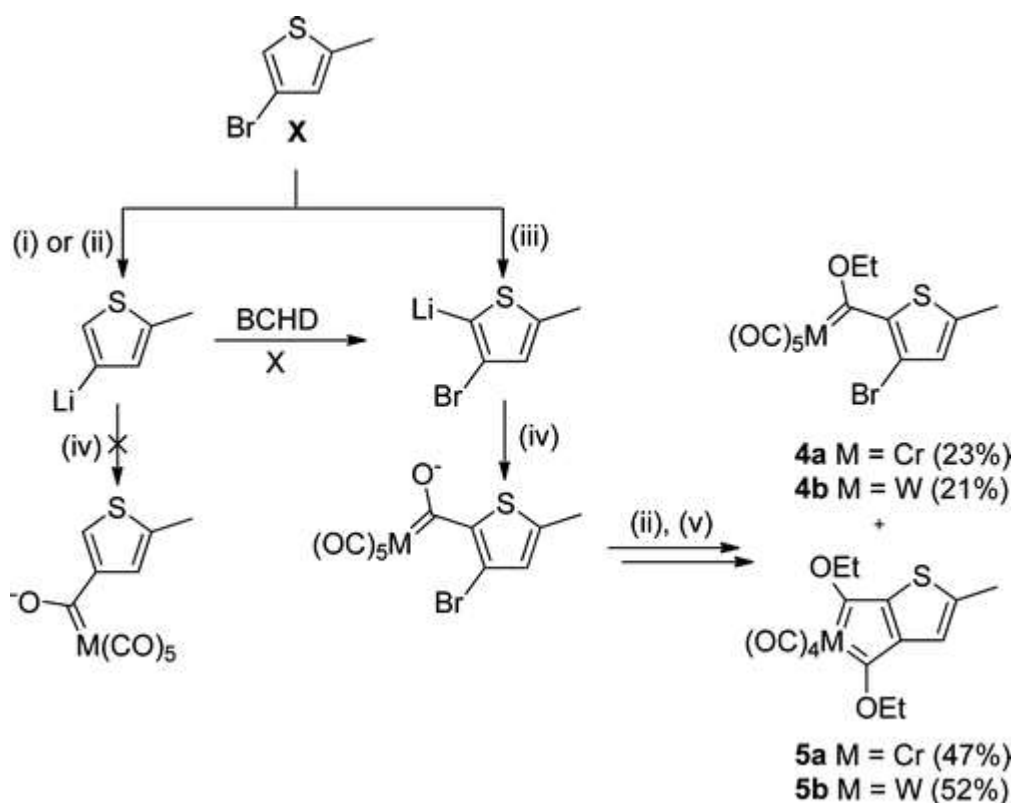
Scheme 3. [a]

[a]Legend: (i) *t*-BuLi; (ii) *n*-BuLi; (iii) LDA; (iv) M(CO)$_6$; (v) [Et$_3$O][BF$_4$].

In the ^{1}H NMR spectra of **4a,b**, which have bromo substituents between the carbene and H4 proton, the H4 resonances are found upfield (Cr 6.77, W 6.90 ppm) compared to the resonances for **2a,b** and the monocarbene complexes [M(CO)$_5${C(OEt)C$_4$H$_3$S}] (M = Cr, W).(33) The ^{1}H and ^{13}C NMR spectra of **5a,b** confirmed the formation of bis-carbene chelate rings. The H4 chemical shift of both the chromium and tungsten analogues of the methyl-bis-carbene chelated complexes are upfield (Cr 6.60, W 6.71 ppm) compared to those of **2a,b** and **4a,b**. These upfield shifts indicated a smaller involvement of the thienyl moiety with the chelate rings. The presence of two different carbene ligands was evidenced by two sets of signals for the ethoxy substituents in the ^{1}H NMR spectra for the carbene ligands, two carbene carbon signals in the ^{13}C NMR spectrum, and a pattern of four infrared bands in the carbonyl region corresponding to the M(CO)$_4$ fragment. The two carbene ligands of the chelate ring in **5a,b** are in different electronic environments and hence gave distinguishable chemical shifts for all protons in the NMR spectra. In addition to J_3 coupling constants for both **5a** and **5b**, J_4 coupling constants for H4 (q, 1.2 Hz) and the Me substituent (d, 1.2 Hz) were observed for **5b.** The ^{13}C NMR spectra displayed unique features such as two carbene carbon resonances for the different carbene ligands and two carbonyl resonances, one for the carbonyl ligands trans to each other and a second for the carbonyl ligands trans to the carbene ligands. The latter feature was also observed in the symmetrically orientated bis-carbene chelated complexes with a benzene substituent.(16) The region of chemical shift values in the ^{13}C NMR spectra correlated more closely with that of two dicarbonyl systems (M(CO)$_2$ with cis and trans carbonyls) rather than those found for tetracarbonyl complexes (M(CO)$_4$, M = Cr, W).(36, 51) This was not evident from the infrared spectra of **5a,b**, where typical M(CO)$_4$ patterns associated with C_{2v} symmetry(52) were observed. A crystal structure determination of **5a** confirmed the molecular structure of the bis-carbene chelated complex and is shown in Figure 4.
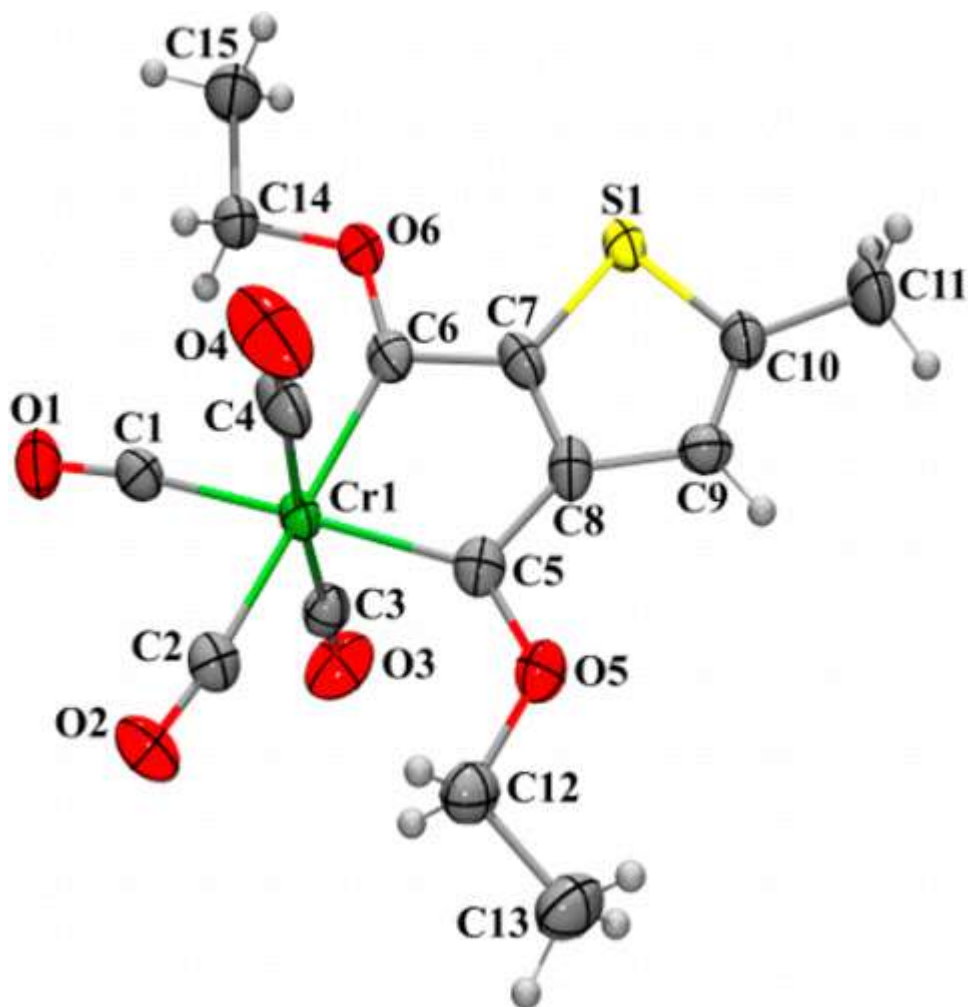
Figure 4. ORTEP(28)/POV-Ray(29) drawing of [Cr(CO)$_4${C(OEt)}$_2$C$_4$H(Me)S] (**5a**) showing the atom-numbering scheme. Atomic displacement ellipsoids are shown at the 50% probability level.

The instability observed for the bis-carbene complexes that contained a methylene carbene substituent (**3a,b**) was further investigated. It was previously reported that bis(thiophen-2-yl)methane (DTM, **B** in Figure 1) can be selectively lithiated at either the 2-position of the thienyl group or at the central methylene carbon (5-position, pK_a ca. 36) depending on the base, solvent, and temperature.(53) Monolithiation in THF with LDA resulted only in deprotonation at the methylene carbon atom, while the same reaction at low temperature with *n*-BuLi afforded predominantly lithiation at the 2-position of a thienyl ring. Dilithiation of DTM with 2 equiv of *n*-BuLi in THF at low temperature did not proceed quantitatively, and it was clear that some competitive methylene lithiation occurred. Products quickly converted in solution during purification procedures. ^{1}H NMR studies on the crude reaction mixture revealed signals indicating that the methylene acylate intermediate, under the prevailing basic reaction conditions, readily converted into unstable dithienyl vinylidene and hydroxyvinyl complexes. The separation of these products from the major compound, the bis-carbene complexes [(CO)$_5$M{C(OEt)C$_4$H$_2$SCH$_2$C$_4$H$_2$SC}(OEt)M(CO)$_5$] (M = Cr (**6a**), W (**6b**)), required the repeated use of column chromatography with hexane as eluting agent (Scheme 4).
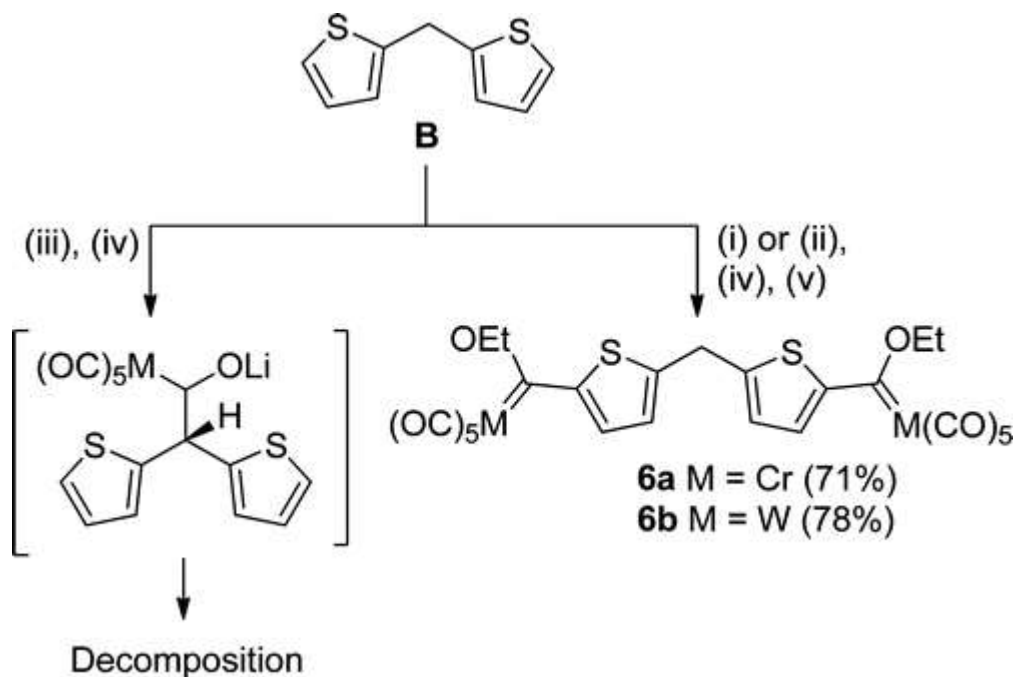
Scheme 4. [a]

[a]Legend: (i) *n*-BuLi-TMEDA; (ii) LDA or *n*-BuLi (THF/TMEDA); (iii) *n*-BuLi; (iv) M(CO)$_6$; (v) [Et$_3$O][BF$_4$].

Unlike thiophene, DTM does not have a conjugated π-system, and it is anticipated that the bent bis-carbene complex will behave more like two separate monocarbene units. The bis-carbene complexes **6a,b** are dark red, in comparison to the violet color of **1** or the bis-carbene rods with bithienyl spacers.(12) A chemical shift of 8.02 ppm for H3 in **6b** places it between those of the tungsten bis-carbene complex **1** (7.95 ppm) and the mono-carbene complex [W(CO)$_5${C(OEt)C$_4$H$_3$S}].(33)

The conjugated condensed ring system of benzo[3,2-*b*]thiophene (**C**) allows for 2,3-deprotonation of the thienyl group, since the 4,5-positions have been blocked. Treatment of benzo[3,2-*b*]thiophene with 2 equiv or more of *n*-BuLi only produced the known benzo[3,2-*b*]thienyl monocarbene complexes,(54) the butylcarbene complex, and decomposition products. The last products resulted from additional lithiations at the benzene ring. It was evident that dilithiation of **C** was not nearly quantitative by this route. When using a stepwise lithiation procedure, it was expected that the formation of the metal acylate at the 2-position of benzo[3,2-*b*]thiophene would sufficiently delocalize the negative charge and potentially activate the 3-position for a second lithiation. Enhanced activation was achieved by starting with 2,3-dibromobenzothiophene (Scheme 5) as the precursor, and the blue chelated bis-carbene complexes [M(CO)$_4${C(OEt)}$_2$C$_8$H$_4$S] (M = Cr (**7a**), W (**7b**)) were synthesized in very high yields.
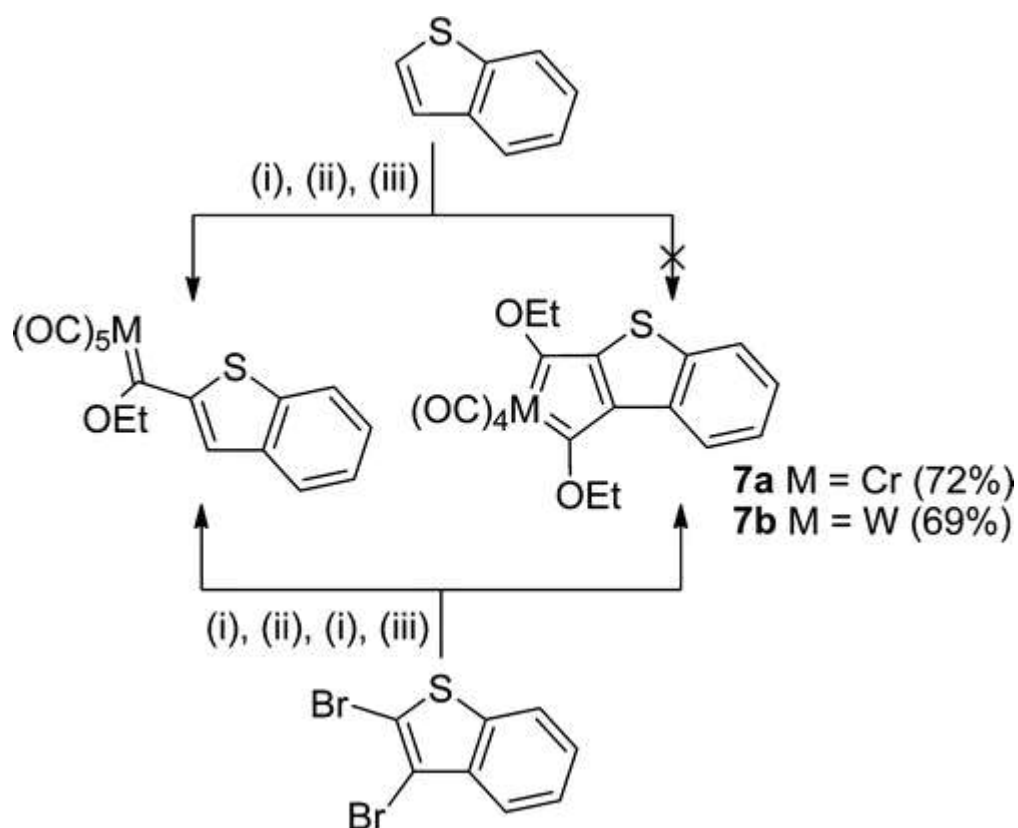
Scheme 5. [a]

[a]Legend: (i) *n*-BuLi; (ii) M(CO)$_6$; (iii) 2 equiv of [Et$_3$O][BF$_4$].

In the ^{1}H NMR spectra of **7a,b**, the signals for H7 and H6 of the benzene ring overlapped. The signals farthest downfield at 8.18 ppm for **7a** and 8.20 ppm for **7b** were assigned to H9, and coupling constants were used to discriminate between the chemical shifts of the H7 and H6 signals. As was the case for **5a,b**, two carbene ligands in different chemical environments are evident from the two different sets of chemical shifts for the protons of the ethoxy substituents. The solid-state structures of the bis-carbene chelated complexes **7a,b** are shown in Figure 5.
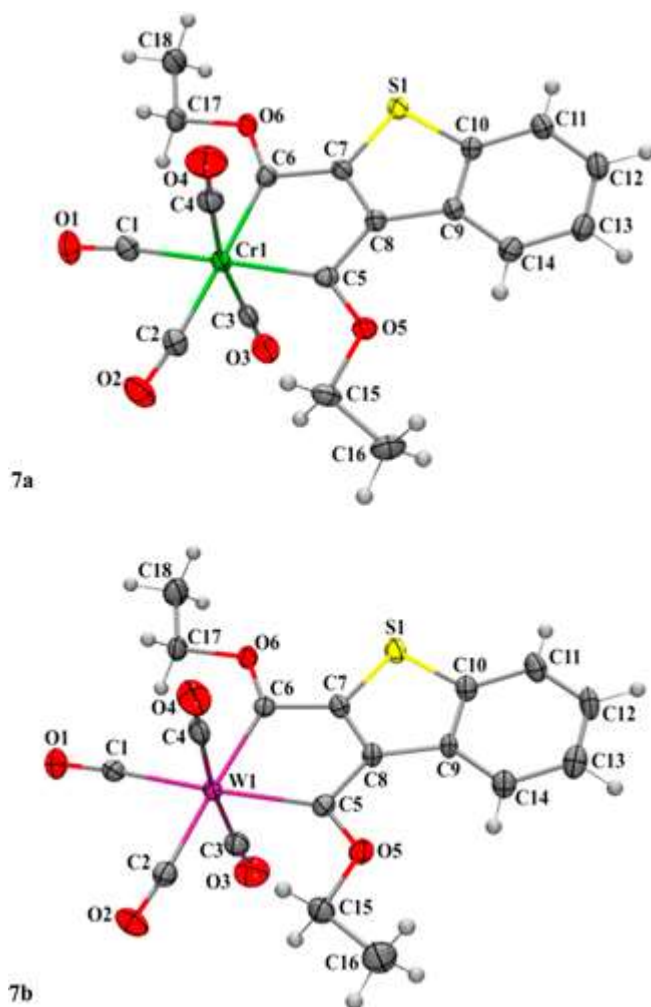
Figure 5. ORTEP(28)/POV-Ray(29) drawings of $[Cr(CO)_4\{C(OEt)\}_2C_8H_4S]$ (**7a**) and $[W(CO)_4\{C(OEt)\}_2C_8H_4S]$ (**7b**) showing the atom-numbering scheme. Atomic displacement ellipsoids are shown at the 50% probability level.

The synthesis of **D** was based on a modified procedure by Hemetsberger and Knittel.(55) The synthesis of pyrrole-condensed heterocycles mostly involves an alkyl azido-acrylate as a key intermediate. This compound undergoes facile thermal cyclization, to yield the condensed thieno[3,2-*b*]pyrrole. The modified synthesis used for **D** used represents an alternative reaction route, and the procedure is included in the Supporting Information with new and improved ^{1}H and ^{13}C NMR data.(55-59)

The ease of mono- and dilithiation of heteroaryl rings revealed that the lithiation of the thiophene rings in bithienyl(11, 12) or 3,3′-dimethylthieno[3,2-*b*]thiophene(60) was achieved more readily in comparison to the same lithiations in 1,1′-dimethylbipyrrole(12) or 1,4-dimethylpyrrolo[3,2-*b*]pyrole.(61) The lithiation of **D** was performed in hexane with 2 equiv of a TMEDA-BuLi mixture at elevated temperature or in THF with 2 equiv of *n*-BuLi below 0 °C (Scheme 6).
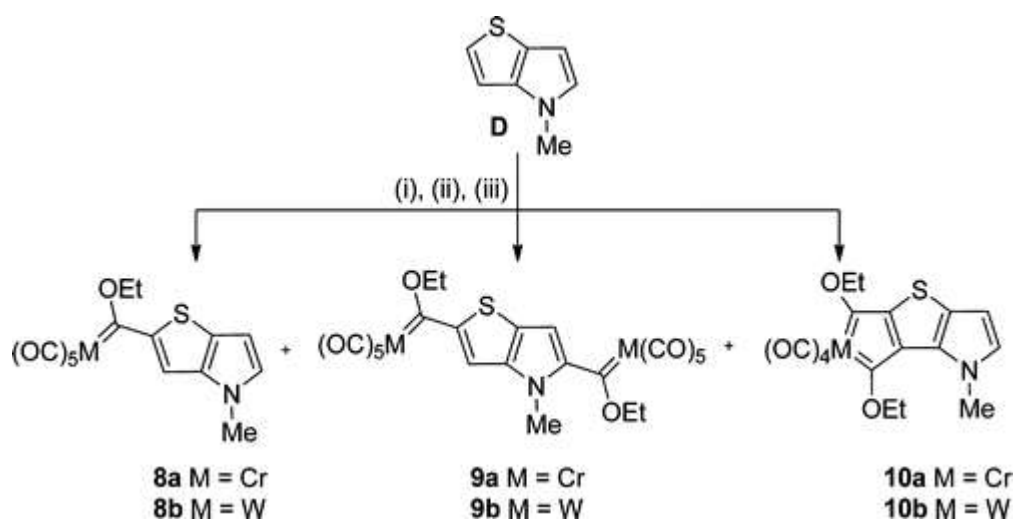
Scheme 6. [a]

In addition to monolithiation at the 2-position of thiophene, a mixture of dilithiated species confirmed deprotonation at either the 7-position on the pyrrole ring or the 3-position of the thiophene ring. The lithiated reaction mixture reacted with $M(CO)_6$ when added in small portions and, after alkylation of the metal acylates, afforded the mono-carbene complexes $[M(CO)_5\{C(OEt)C_6H_3N(Me)S\}]$ (M = Cr (**8a**), W (**8b**)), the dinuclear bis-carbene complexes $[2,5-\{M(CO)_5C(OEt)\}_2C_6H_2N(Me)S]$ (M = Cr (**9a**),(52) W (**9b**)), and the mononuclear bis-carbene chelated complexes $[M(CO)_4\{C(OEt)\}_2C_6H_2N(Me)S]$ (M = Cr (**10a**), W (**10b**)). To maximize the formation of the bis-carbene chelates **10a,b**, deprotonation was done consecutively. This method reduced the amounts of **8a,b** formed. The yields of **9a,b** could be increased to 15–20% by adding another 1 equiv of $M(CO)_6$ after the second lithiation. It was clear that the second lithiation on the thiophene ring competed favorably with that on the pyrrole ring, even though the mono-lithiation remained the dominant reaction even with 2 equiv of n-BuLi. Unlike the case for **C**, the thiophene protons are more acidic because of the pyrrole ring, allowing for the lithiation of both positions without having to make use of a lithium–halogen exchange reaction.

The electron-withdrawing effect of the carbene carbons on the thiophene rings is again evident when comparing the chemical shift values of the ring protons. In **8a,b** H3 is most affected (Cr 8.07, W 7.99 ppm) while H7 was also affected (Cr 7.07, W 7.11 ppm) in comparison to the same protons in **D** (H3 7.00 and H7 6.89 ppm). Introduction of a second carbene ligand on the pyrrole ring in **9b** shifted the H6 resonance downfield (7.59 ppm) in comparison to **D** (6.49 ppm), while H3 was slightly upfield (7.89 ppm) in comparison to **8a,b**. In the bis-carbene chelated complexes **10a,b** the effect on the pyrrole ring was a downfield shift for H7 and an upfield shift for H6. As the number of carbene ligands increases on going from **8a,b** to **9a,b** and **10a,b** the chemical shifts of the N-Me protons are shifted downfield (**D** 3.80, **8a** 3.84, **8b** 3.83, **9a** 3.86,(52)**9b** 3.88, **10a** 3.91, and **10b** 3.94 ppm), indicating greater involvement of the nitrogen lone pair in charge delocalization toward the carbene ligands. Figure 6 shows the contributing structures for electron delocalization in the heteroarene rings caused by the electrophilic Fischer carbene carbon atoms, which correlate with the chemical shifts in the ^{1}H NMR spectra.
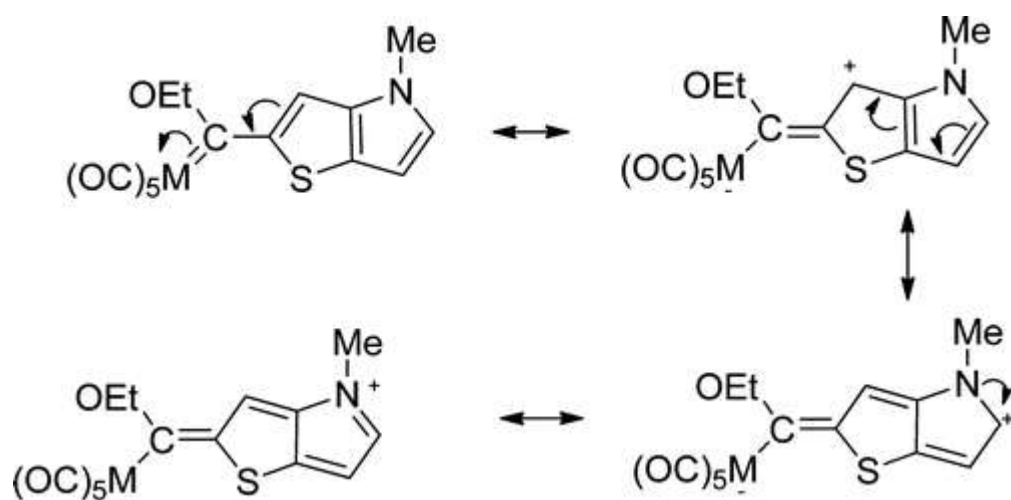
Figure 6. Contributing structures and charge delocalization over the thiophene and pyrrole rings as a result of carbene substituents.

The difference in properties of the two carbene ligands in the chelated rings of **10a,b** and the bis-carbene complex **9b** were clearly demonstrated by two separate sets of resonances in the ^1H and ^{13}C NMR spectra. Suitable crystals for single-crystal X-ray diffraction studies of **8a,b** (Figure 7) and **10a,b** (Figure 8) were obtained after some days by cooling concentrated hexane solutions of the pure compounds.
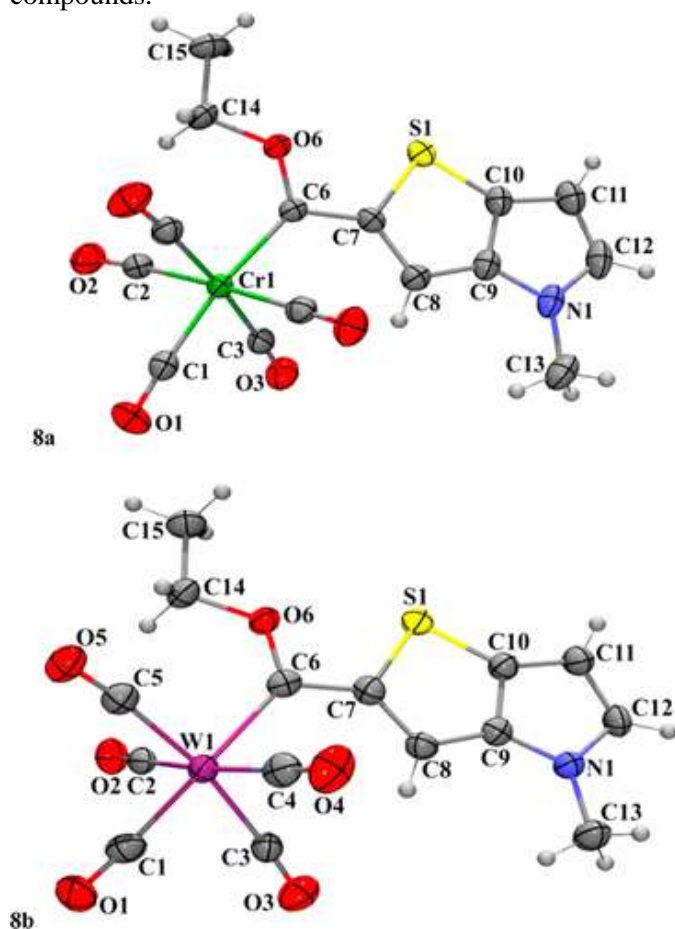

Figure 7. ORTEP(28)/POV-Ray(29) drawings of [Cr(CO)$_5$\{C(OEt)C$_6$H$_2$N(Me)S\}] (**8a**) and [W(CO)$_5$\{C(OEt)C$_6$H$_2$N(Me)S\}] (**8b**) showing the atom-numbering schemes. Atomic displacement ellipsoids are shown at the 50% probability level.

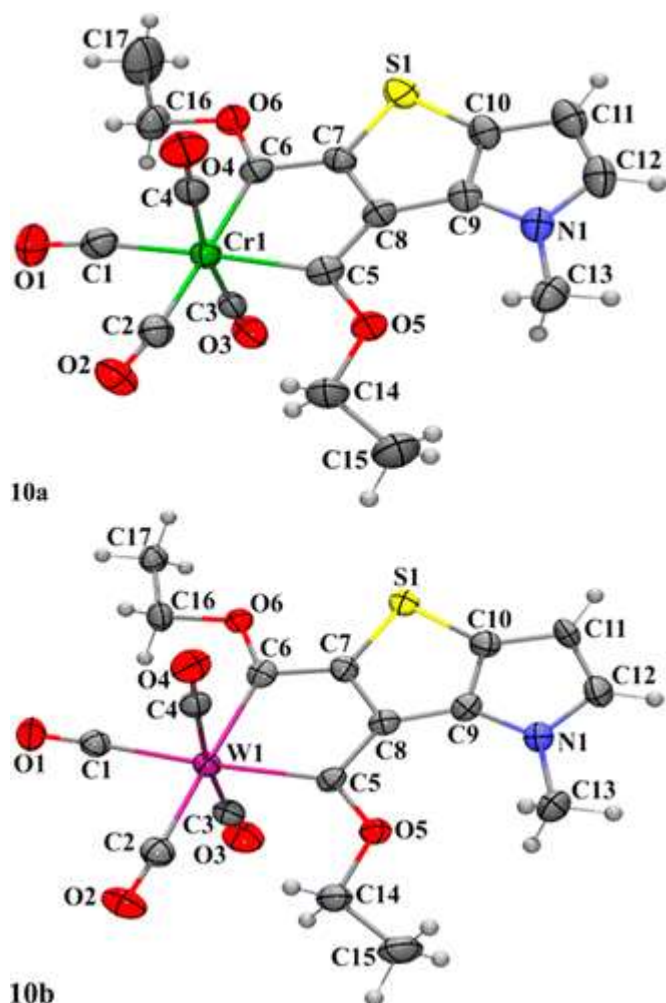**Figure 8**. ORTEP(28)/POV-Ray(29) drawings of [Cr(CO)$_4${C(OEt)}$_2$C$_6$H$_2$N(Me)S}] (**10a**) (molecule 1) and [W(CO)$_4${C(OEt)}$_2$C$_6$H$_2$N(Me)S}] (**10b**) showing the atom-numbering schemes. For molecules 2 and 3 of **10a** add 20 and 40, respectively, to the labels given for molecule 1. Atomic displacement ellipsoids are shown at the 50% probability level.

Structural Studies

The crystal structure of **1** (Figure 2) shows that the thiophene ring, the carbene carbon atoms, the metal atoms, and the ethoxy substituents are all approximately coplanar. Both of the ethoxy substituents are cis with respect to the sulfur about the C(carbene)–C(thiophene) bonds,(62) giving the structure a crablike appearance.(9) This differs from the structure reported for the bis-carbene furan analogue, which has one ethoxy substituent cis and one trans to the furan oxygen.(10) The molecule has approximate 2-fold rotation symmetry, with the pseudorotation axis intersecting the sulfur and bisecting the C8–C9 bond of the thiophene ring. Bond distances and angles for the atoms attached to the carbene carbon atom and C–C distances in the thienyl ring are summarized and compared in Tables 1 and 2. The monocarbene complexes **8a,b** have orientations of the substituents around the carbene carbon atoms similar to that in **1**, and the carbene carbon and ethoxy substituents in both are approximately coplanar with the thiophene-pyrrole rings. The complexes containing chelate rings **5a**, **7a,b**, and **10a,b** have similar structural features.(63) The metal is embedded in an approximately planar five-membered ring that exhibits some delocalization of electron density in the conjugated thiophene ring, but less so in the five-membered chelate ring.

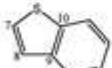**Table 1**. Carbene–Substituent and Thiophene Bond Lengths (Å)
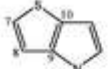
Complex	M	R-group	M=[C]†	O-[C]	R-[C]	C7–C8	C8–C9	C9–C10
1	W		2.176(4)	1.336(5)	1.483(6)	1.382(6)	1.393(6)	1.378(6)
5a	Cr		2.0399(1	1.321(2)	1.455(2)	1.376(3)	1.458(4)	1.342(4)
7a	Cr		2.0435(1	1.3226(1	1.4558(1	1.3780(1	1.4524(1	1.4148(1
7b	W		2.174(3)	1.323(3)	1.463(4)	1.377(4)	1.456(3)	1.420(4)
8a	Cr		2.082(3)	1.332(3)	1.438(4)	1.395(4)	1.394(4)	1.389(4)
8b	W		2.221(5)	1.320(5)	1.437(7)	1.385(6)	1.393(6)	1.405(6)
10a			2.032(2)	1.334(3)	1.442(4)	1.401(3)	1.436(3)	1.387(4)
10a ‡	Cr		2.032(2)	1.333(3)	1.448(4)	1.402(3)	1.431(3)	1.393(4)
10a ‡			2.030(2)	1.338(3)	1.429(4)	1.403(3)	1.441(3)	1.388(4)
10b ‡	W		2.161(5)	1.335(5)	1.460(6)	1.396(6)	1.417(6)	1.394(6)

Table †

[C] is a carbene carbon atom.

Table ‡

Molecule 1, 2 or 3.

Table 2. Selected Bond Angles (deg)

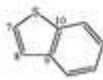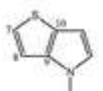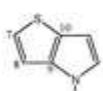| Complex	M	R-group	M–[C]–O	O–[C]–R	R–[C]–M	[C]–M–[C]	(O)C-M-C(O)[a]	(O)C-M-C(O)[b]
1	W		129.5(3)	104.9(4)	125.3(3)		-174.70(18)	–
			128.4(3)	106.0(4)	125.3(3)	–	-176.05(18)	–
5a	Cr		137.55(13)	108.85(15)	113.57(12	81.14(7)	–	+175.71(8)
7a	Cr		136.11(10)	109.64(12)	114.24(9)	81.23(5)	–	+169.88(6)
7b	W		135.39(19)	109.8(2)	114.82(18	77.59(10)	–	+173.29(10)
8a	Cr		128.84(19)	106.3(2)	124.8(2)	–	-175.11(8)	–
8b	W		128.4(4)	106.4(4)	125.2(3)	–	+173.68(18)	–
10a			135.0(2)	110.0(2)	114.86(16	80.74(10)	–	+171.65(12)
10a	Cr		135.9(2)	109.1(2)	114.90(16	80.76(10)	–	+170.99(12)
10a			135.2(2)	109.9(2)	114.90(16	80.66(10)	–	+172.28(12)
10b	W		134.7(3)	109.3(4)	116.0(3)	77.25(17)	–	+173.43(18)

Table a Angles between trans carbonyls cis to a monocarbene.
Table b Angles between trans carbonyls cis to a bis-carbene chelate. Positive angles are bent toward the M–carbene bond(s), and negative angles are bent away from the M–carbene bond.

In the crystal structure of **10a** there are three molecules in the asymmetric unit with the generalized atom numbering scheme X$m+n$ (see Figure 7 for the label values of m). Molecules 1 and 2 ($n = 0, 20$ respectively) are structurally identical (within experimental error) and are related by an approximate (noncrystallographic) pseudo center of inversion; however, in molecule 3 ($n = 40$), the orientation of one ethyl group is different. In general for carbene moieties, and as observed in molecules 1 and 2 and for one ethoxy group (O45, C54, C55) in molecule 3, the ethoxy group tends to lie close to coplanar with the bonding plane of the carbene atom. Thus, the magnitudes of the torsion angles C5+n–O5+n–C14+n–C15+n ($n = 0, 20, 40$) and C6+n–O6+n–C16+n–C17+n ($n = 0, 20$) all lie in the range 173.3(2)–177.0(2)°, whereas for the O46, C56, C57 ethoxy group, the ethyl group is rotated approximately 90° about the O46—C56 bond and is approximately perpendicular to the bonding plane of the carbene atom with a C46–O46–C56–C57 torsion angle of 95.4(3)°. This is illustrated in Figure 9, which shows molecules 1 and 3 of **10a** superimposed on one another. For a mono-carbene complex bonded to a metal pentacarbonyl moiety, the carbene bonding plane and hence the ethoxy group are staggered with respect to the adjacent cis carbonyl ligands, with the methylene CH_2 moiety of the ethoxy group meshing between two carbonyl ligands. However for a bis-carbene chelate bonded to a metal tetracarbonyl moiety, the plane of the carbene and ethoxy groups has to, perforce, adopt an eclipsed orientation with respect to the two carbonyl ligands trans to the two carbene ligands. This is a sterically strained configuration, as evidenced by the opening of the relevant C(carbonyl)–M–C(carbene) bond angles from ca. 90° to close to 100°. The five-membered chelate rings are strained, with bite angles of the carbene ligands at the metal of approximately 81° (Cr) and 77° (W). The preferred configuration appears to be with the ethoxy group approximately coplanar with the bonding plane of the carbene and with the carbonyl ligand meshed between the two hydrogen atoms of the methylene moiety of the ethoxy group (cf. Figure 9, m1). However, it is possible during the reaction with triethyloxonium tetrafluoroborate that an ethyl group is added in a different orientation

such that the carbonyl ligand meshes between the two C atoms of the ethyl group (as observed in molecule 3 of **10a** for carbonyl C41,O41 and ethyl group C56,C57; see Figure 9, m3). Once formed, the ethyl group is effectively locked in that orientation and cannot rotate to the preferred orientation. This orientation appears to be fairly rare and has only been observed for one complex (**10a**) and then only for one of the two carbene–ethoxy groups in one in three molecules in the crystal.
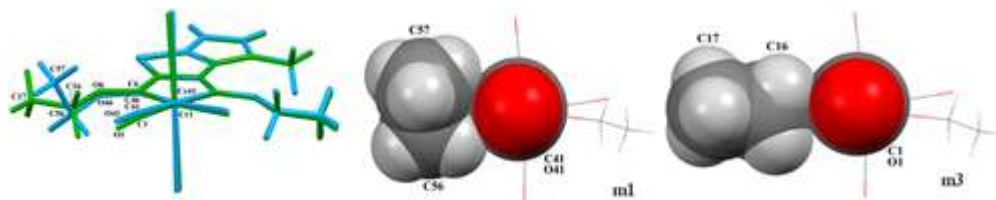

Figure 9. Mercury(66) drawing of molecules 1 (green) and 3 (blue) of **10a** superimposed on one another, showing the difference in orientation of the O6–C16–C17 and O46–C56–C57 ethoxy groups and Mercury(66) partial space-filling drawings of molecules 1 (m1) and 3 (m3) of **10a**, showing the differing steric interactions of ethyl group C16,C17 with carbonyl C1,O1 (in m1) and ethyl group C56,C57 with carbonyl C41,O41 (in m3).

The bond lengths of the five-membered chelated rings display shorter M–C(carbene) distances (average M = Cr 2.03 Å, M = W 2.16 Å) than for the nonchelated carbenes. While there are no significant differences in the C7–C8 distances or the C(carbene)–R distances, this suggests a greater contribution of the localized triene form compared to the diene form. The bond distances in the thiophene rings of the chelated bis-carbene complexes also show double-bond localizations, with C8–C9 being significantly longer than C7–C8 and C9–C10. In contrast, all C–C thiophene ring distances are the same within experimental error for the mono-carbene complexes **1** and **8a,b**. Unlike the case for the pentacarbonyl carbene complexes, the two axial carbonyls in the tetracarbonyl complexes are bent toward the chelate ring and carbene ligands with the C(CO)–M–C(CO) angles deviating from linearity by 6–10° for **5a**, **7a,b**, and **10a,b**. The bending is away from the carbene ligand by 4–5° in **1** and **8a**. Complex **8b** is anomalous in that one pair of trans carbonyls bend toward the carbene ligand and the other pair bend away by 6 and 10°, respectively. Similar features were observed for chelated bis-carbene benzene complexes by Schubert and co-workers.(67)

Conclusion

We have demonstrated with thiophene that it is possible to readily synthesize asymmetrically substituted bis-alkoxycarbene complexes in which the two carbene ligands are part of a chelate ring. Earlier complications recognized for dianion formation in benzene in achieving this goal have been circumvented. Also, complications caused in thiophene by favoring the formation of dinuclear bis-carbene complexes instead of mononuclear chelated complexes have been addressed. In addition to blocking the 2- and 3-positions in thiophene (**C**, **D**) to synthesize bis-carbene chelates of thiophene, it is possible to prepare similar chelates by activating the less active β-positions by lithium–halogen exchange reactions. This can readily be accomplished by using 3-bromothiophene, 2,3- or 3,4-dibromothiophene, or 2,3,4,5-tetrabromothiophene as a precursor substrate for dilithiation.

Experimental Section

General Procedures and Reagents

All operations were performed under an inert gas atmosphere using standard Schlenk techniques. Solvents (hexane, benzene, ether, and tetrahydrofuran (THF)) were dried by distillation from sodium

with benzophenone as an indicator in the case of the ethereal solvents. Chloroform and dichloromethane (DCM) were distilled from phosphorus pentoxide. Bromothiophene derivatives, metal carbonyls, *n*-BuLi (1.6 M solution in hexane), *t*-BuLi (3.2 M solution in heptanes), and other chemicals were obtained commercially and used as supplied. Tetramethylethylenediamine (TMEDA) and diisopropylamine were freshly distilled before use. *n*-BuLi-TMEDA and lithium diisopropylamine (LDA) were freshly prepared before use.(68) Triethyloxonium tetrafluoroborate was prepared according to literature procedures.(69) Thiophene was treated with silver nitrate and distilled from calcium hydride before use.(70) Thieno[2,3-*b*]pyrrole was synthesized according to a modified procedure of Hemetsberger and Knittel that is available as Supporting Information.(55) Product separation was done on a silica gel 60 (0.063–0.200 mm) stationary phase, and the separation time was reduced by using inert-gas pressure to prevent decomposition of especially the chelate carbene analogues. All products were separated by using a gradient elution of hexane and dichloromethane (DCM). ^{1}H NMR spectra were recorded at 300.135 and 500.139 MHz and ^{13}C NMR spectra at 75.49 and 125.75 MHz, respectively, on Bruker ARX-300 and AVANCE 500 spectrometers at ambient temperatures. The signal of the deuterated solvent, either C_6D_6 (7.16, 128.00 ppm) or $CDCl_3$ (7.26, 77.00 ppm), was used as internal reference. IR spectra were recorded in predried hexane on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer, but only vibrations of the carbonyl region (ca. 1600–2200 cm^{-1}) are reported. Elemental analysis was carried out on a Thermoscientific Flash 2000 organic elemental analyzer. Mass spectra were recorded on a Waters SYNAPT G2 high-definition mass spectrometry system in acetonitrile. The CIF files for complexes **1**, **5a**, **7a**,**b**, **8a**,**b**, and **10a**,**b** are available as Supporting Information. The X-ray crystal structure analyses for **1** and **5a** were performed using data collected at 173(2) K on a Nonius kappa CCD diffractometer, those for **7a**,**b** at 173(2) K on a Bruker APEX-II CCD diffractometer, and those for **8a**,**b** and **10a**,**b** at 183(2) K on a Nonius kappa CCD diffractometer using graphite-monochromated Mo Kα radiation by means of combinations of φ and ω scans. Data reductions were performed using SAINT(71) or DENZO and SCALEPACK,(72) and intensities were corrected for absorption using SADABS(71) or SORTAV.(73) The structures were solved by direct methods using SHELXTS(74) or SHELXS-97(74) and refined by full-matrix least squares using SHELXTL(74) and SHELXL-97.(74)

Preparation of [W(CO)$_5${C(OEt)C$_4$H$_2$SC(OEt)W(CO)$_5$}] (1)

Method 1

A solution of 1.40 mL (2.25 mmol) of *n*-BuLi and 0.30 mL (2.25 mmol) of TMEDA in 20 mL of hexane was treated with 0.084 mL (0.084 g, 1 mmol) of thiophene. A white suspension gradually formed, and the conversion was completed by refluxing the mixture for 30 min. The suspension was cooled to −40 °C, and 30 mL of THF was added. While the mixture was stirred vigorously, 0.70 g (2 mmol) of W(CO)$_6$ was gradually added. After warming to room temperature, stirring was continued for a further 30 min, whereby the mixture turned dark brown. All solvents were removed under reduced pressure. The residue was dissolved in 30 mL of DCM, cooled to −30 °C, and treated with 0.45 g (2.3 mmol) of [Et$_3$O][BF$_4$]. The reaction mixture turned very dark purple color on warming to room temperature. The solvent was removed in vacuo, and the residue was absorbed on a minimum amount of silica gel for column chromatography. The products were separated by starting with hexane as the eluent and gradually increasing the polarity by adding DCM. Three fractions were obtained: the first yellow zone contained 0.045 g (0.10 mmol, 10.3%) of [W(CO)$_5${C(OEt)Bu}](41) derived from unreacted *n*-BuLi in the reaction mixture, the second orange fraction contained 0.10 g (0.21 mmol, 21.3%) of the known monocarbene complex [W(CO)$_5${C(OEt)C$_4$H$_3$S}],(33) and the third gave 0.52 g (0.6 mmol, 60.5%) of the violet bis-carbene complex [W(CO)$_5${C(OEt)C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**1**).

Method 2
A solution of 0.13 mL (0.242 g, 1 mmol) of 2,5-dibromothiophene in 20 mL of THF at −78 °C was reacted with 1.3 mL (2.2 mmol) of *n*-BuLi in hexane for 1 h. A 0.70 g portion (2 mmol) of W(CO)$_6$ was then added to the solution in small portions. The reaction mixture gradually turned a dark red-brown after it was stirred at room temperature for 1 h. The solvent was removed in vacuo, and the residue was dissolved in DCM and treated with 0.45 g (2.3 mmol) of [Et$_3$O][BF$_4$] dissolved in DCM

at −30 °C. The reaction mixture turned dark purple. The solvent was removed, and the products were separated by column chromatography as described in Method 1. In this instance 0.72 g (0.78 mmol, 78%) of the violet bis-carbene complex [W(CO)$_5${C(OEt)C$_4$H$_2$SC(OEt)}W(CO)$_5$] (**1**) and very little butylcarbene and monocarbene were obtained.

Data for **1** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.97 (s, 2H, H3/H3′), 5.00 (q, J = 7.0, 2H, CH$_2$), 1.70 (t, J = 7.1, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 294.6 (C1), 202.7 (CO$_{trans}$), 197.0 (CO$_{cis}$), 162.5 (C2/C2′), 137.3 (C3/C3′), 79.1 (CH$_2$), 14.9 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2062 m (A$_1^1$), 1986 w (B$_1$), 1960 s (A$_1^2$), 1951 vs (E). Anal. Calcd for C$_{20}$H$_{12}$O$_{12}$SW$_2$ (844.05): C, 28.46; H, 1.43. Found: C, 28.57; H, 1.54.

Preparation of [M(CO)$_5${C(OEt)C$_4$H$_2$(Me)S}] (M = Cr (2a), W (2b)), [M(CO)$_5$C(OEt)C$_4$H$_2$SCH$_2$C(OEt)M(CO)$_5$] (M = Cr (3a), W (3b)), [M(CO)$_5${C(OEt)C$_4$HBr(Me)S}] (M = Cr (4a), W (4b)), and [M(CO)$_4$C(OEt)}$_2$C$_4$H(Me)S}] (M = Cr (5a), W (5b))

Method 1

A solution of 0.10 mL (0.098 g, 1 mmol) of 2-methylthiophene in THF at −78 °C was reacted with 1.3 mL (2.1 mmol) of *n*-BuLi in hexane for 1 h. A 0.44 g portion (2 mmol) of Cr(CO)$_6$ or 0.696 g (2 mmol) of W(CO)$_6$ was then added to this solution with vigorous stirring. After solvent removal in vacuo the residue was dissolved in DCM and 0.475 g (2.5 mmol) of [Et$_3$O][BF$_4$] in DCM was added at −35 °C. As the temperature was increased, the solution turned dark maroon. The solvent was removed, and the products in the residue were separated using column chromatography on silica gel, first with hexane as eluent and thereafter gradually increasing the polarity by adding DCM. The first fraction containing [W(CO)$_5${C(OEt)Bu}] was discarded. The second orange-red band yielded 0.201 g (29%, mmol) of [Cr(CO)$_5$C(OEt)C$_4$H$_2$(Me)S] (**2a**) or 0.344 g (36%, mmol) of [W(CO)$_5$C(OEt)C$_4$H$_2$(Me)S] (**2b**). The third maroon-purple band yielded 0.44 g (37%) or 0.53 g (31%) of a fraction consisting mostly of the unstable bis-carbene complex [Cr(CO)$_5${C(OEt)C$_4$H$_2$SCH$_2$C(OEt)}Cr(CO)$_5$] (**3a**) or [W(CO)$_5${C(OEt)C$_4$H$_2$SCH$_2$C(OEt)}W(CO)$_5$] (**3b**). ^{1}H NMR studies of **3a,b** revealed that these converted into other carbene products during column chromatography and afterward in solution. Functionalities and compositions of byproducts were deducted by comparing the additional characteristic proton chemical shifts observed and especially resonances of methylene in the ethoxy substituents (4.3–4.1 ppm for esters and ca. 3.8 ppm for the olefinic ethoxy groups).(49)

Method 2

A solution of 0.75 mL (1.2 mmol) of *n*-BuLi was reacted with a solution of 0.11 mL (0.17 g, 1 mmol) of 3-bromo-5-methylthiophene in 30 mL of THF at −78 °C for 1 h. A 0.22 g portion (1 mmol) of Cr(CO)$_6$ or 0.35 g of W(CO)$_6$ was added with vigorous stirring at higher temperatures to allow the metal carbonyl to dissolve and react. A second equivalent, 0.65 mL (1.1 mmol), of *n*-BuLi was added after cooling the reaction mixture to −50 °C. The solution turned bluish-black. After the removal of the solvent by reduced pressure the residue was dissolved in DCM, cooled to −30 °C, and treated with 0.45 g (2.4 mmol) of [Et$_3$O][BF$_4$] in DCM. The solvent was removed in vacuo, and three fractions were collected after column chromatography on silica gel. Eluting with hexane afforded two poorly resolved red zones. The first red fraction gave 0.38 g (11%) of **2a** or 0.067 g (14%) of **2b**, whereas the second yielded 0.098 g (23%) of **4a** or 0.117 g (21%) of **4b**. The third product collected using a 1/4 DCM/hexane mixture, was 0.176 g (47%) or 0.263 g (52%) of the ink blue complexes **5a,b**.

Data for **2a** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.10 (d, J = 4.2, 1H, H3) 6.93 (d, J = 4.1, 1H, H4), 5.14 (q, J = 7.0, 2H, CH$_2$), 2.53 (s, 3H, CH$_3$), 1.64 (t, J = 7.05, 3H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 312.5 (C1), 223.1 (CO$_{trans}$), 217.3 (CO$_{cis}$), 153.0 (C2), 152.2 (C5), 142.3 (C3), 128.2 (C4), 75.5 (CH$_2$), 16.8 (CH$_3$), 15.0 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2056 m (A$_1^1$), 1981 w (B$_1$), 1953 s (A$_1^2$), 1944 vs (E). Anal. Calcd for C$_{13}$H$_{10}$O$_6$SCr (346.26): C, 45.09; H, 2.91. Found: C, 45.21; H, 3.02.

Data for **2b** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.03 (d, J = 4.1, 1H, H3), 6.94 (dd, J = 4.2, 1.1, 1H, H4), 4.96 (q, J = 7.0, 2H, CH$_2$), 2.49 (br, 3H, CH$_3$), 1.63 (t, J = 7.1, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 287.5 (C1), 202.5 (CO$_{trans}$), 197.3 (CO$_{cis}$), 155.9 (C2), 153.4 (C5), 143.1 (C 3), 128.2 (C4), 78.1 (CH$_2$), 16.3 (CH$_3$), 14.9 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2058 w (A$_1^1$), 1981 w (B$_1$), 1955 s (A$_1^2$), 1944 vs (E). Anal. Calcd for C$_{13}$H$_{10}$O$_6$SW (478.11): C, 32.66; H, 2.11. Found: C, 32.82; H 2.21.

Data for **3a** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.07 (d, J = 4.1, 1H, H3), 6.94 (dd, J = 4.2, 1.1, 1H, H4), 5.14 (q, J = 7.0, 2H, CH$_2$), 5.11 (q, J = 7.0, 2H, CH$_2$), 3.2 (s, 2H, CH$_2$–C5), 1.66 (t, J = 7.1, 3H, CH$_3$), 1.64 (t, J = 7.1, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 378.0 (C(carbene)), 314.2 (C1), 223.2, 221.9 (CO$_{trans}$), 217.2, 216.0 (CO$_{cis}$), 153.4 (C2), 147.5 (C5), 141.6 (C3), 127.7 (C4), 78.1, 75.8 (CH$_2$), 15.2, 15.1 (CH$_3$), IR (ν_{CO}, hexane, cm^{-1}): 2065 vw, 2059 m (A$_1^1$), 1983 vw (B$_1$), 1955 s (A$_1^2$), 1945 vs (E).

Data for **3b** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 7.80 (d, J = 4.0, 1H, H3), 6.77 (d, J = 4.0, 1.1, 1H, H4), 4.86 (q, J = 7.1, 2H, CH$_2$), 4.73 (q, J = 7.1, 2H, CH$_2$), 3.18 (dd, J = 7.3,0.9, 2H, CH$_2$–C5), 1.56 (t, J = 7.1, 3H, CH$_3$), 1.55 (t, J = 7.2, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 334.1 (C(carbene)), 287.5 (C1), 204.3, 202.1 (CO$_{trans}$), 197.5, 197.1 (CO$_{cis}$), 155.9 (C2), 153.4 (C5), 143.1 (C3), 128.2 (C4), 78.1 (CH$_2$), 16.3 (CH$_3$), 14.9 (CH$_3$).

Data for **4a** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.77 (s, 1H, H4), 5.13 (q, J = 7.2, 2H, CH$_2$), 2.53 (s, 3H, CH$_3$), 1.73 (t, J = 7.3 Hz, 3H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 319.8 (C1), 223.0 (CO$_{trans}$), 216.2 (CO$_{cis}$), 150.7 (C2), 131.3 (C5), 131.7 (C4), 104.7 (C3), 77.0 (CH$_2$), 15.8 (CH$_3$), 15.4 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2066 m (A$_1^1$), 1980 w (B$_1$), 1953 s (A$_1^2$), 1943 vs (E). Anal. Calcd for C$_{13}$H$_9$BrO$_6$SCr (425.16): C, 36.72; H, 2.13. Found: C, 36.87; H, 2.20.

Data for **4b** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.90 (q, J_4 = 0.9 Hz, 1H, H4), 5.01 (q, J = 7.0, 2H, CH$_2$), 2.49 (d, J_4 = 1.2 Hz, 3H, CH$_3$), 1.73 (t, J = 7.1, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 290.4 (C1), 202.0 (CO$_{trans}$), 197.5 (CO$_{cis}$), 153.1 (C2), 133.2 (C4), 120.3 (C5), 107.6 (C3), 79.7 (CH$_2$), 16.1 (CH$_3$), 15.3 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2066 m (A$_1^1$), 1980 w (B$_1$), 1953 s (A$_1^2$), 1943 vs (E). Anal. Calcd for C$_{13}$H$_9$BrO$_6$SW (557.01): C, 28.03; H, 1.63. Found: C, 28.14; H, 1.77.

Data for **5a** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.60 (s, br, 1H, H4), 4.74 (q, J = 7.1 Hz, 2H, CH$_2$(b)), 4.71 (q, J = 7.1 Hz, 2H, CH$_2$(a)) 2.43 (s, br, 3H, CH$_3$), 1.59 (t, J = 7.1 Hz, 3H, CH$_3$(b)) 1.56 (t, J = 7.1 Hz, 3H, CH$_3$(a)). ^{13}C NMR (126 MHz, CDCl$_3$): δ 320.7 (C1b), 310.2 (C1a), 242.3 (CO$_{trans}$), 242.2 (CO$_{trans}$), 227.1 (CO$_{cis}$), 167.1 (C3), 160.8 (C2), 151.3 (C5), 115.5 (C4), 76.5 (CH$_2$(b)), 76.3 (CH$_2$(a)), 16.7 (CH$_3$) 15.0, (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2015 m (A$_1^1$), 1956 s (A$_1^2$), 1890 s (B$_1$), 1942 s (B$_2$). Anal. Calcd for C$_{15}$H$_{14}$CrO$_6$S (374.31): C, 48.13; H, 3.77. Found: C, 48.37; H, 3.94.

Data for **5b** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 6.71 (d, J = 1.2 Hz, 1H, H4), 4.51 (q, J = 7.1 Hz, 2H, CH$_2$(b)), 4.50 (q, J = 7.1 Hz, 4H, CH$_2$(a)), 2.37 (d, J = 1.2 Hz, 3H, CH$_3$), 1.58 (t, J = 7.1 Hz, 3H, CH$_3$(b)), 1.55 (t, J = 7.1 Hz, 3H, CH$_3$(a)). ^{13}C NMR (126 MHz, CDCl$_3$): δ 294.1 (C1b), 284.2 (C1a), 220.3 (CO$_{trans}$), 220.1 (CO$_{trans}$), 211.6 (CO$_{cis}$), 166.7 (C3), 151.6 (C2), 116.7 (C4), 113.0 (C5), 79.7 (CH$_2$(b)), 79.3 (CH$_2$(a)), 17.2 (CH$_3$), 14.7 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2026 m (A$_1^1$), 1955 s (A$_1^2$), 1889 s (B$_1$), 2004 s (B$_2$). Anal. Calcd for C$_{15}$H$_{14}$O$_6$SW (506.17): C, 35.59; H, 2.79. Found: C 35.71, H 2.88.

Preparation of [(CO)$_5$M{C(OEt)C$_4$H$_2$SCH$_2$C$_4$H$_2$SC(OEt)}M(CO)$_5$] (M = Cr (6a), W (6b))

Method 1

A 3.1 mL portion (5.0 mmol) of *n*-BuLi was added to a solution of 0.41 g (2.25 mmol) of bis(thiophen-2-yl)methane (MDT) in 30 mL of THF at −10 °C, with stirring. After 30 min the mixture was cooled to −50 °C and 0.99 g (4.5 mmol) of Cr(CO)$_6$ or 1.6 g (4.5 mmol) of W(CO)$_6$ was added. The temperature was raised until all the metal carbonyl was dissolved, after which the solvent was removed under reduced pressure at room temperature. The residue was dissolved in DCM and treated

with 0.85 g (4.6 mmol) of [Et$_3$O][BF$_4$] at −35 °C. An immediate color change from light brown to dark red was observed. The solvent was removed in vacuo, and the product was purified by repeated washings through silica gel with hexane and finally collected as a dark red zone after gradually increasing the polarity by adding DCM to give [(CO)$_5$M{C(OEt)C$_4$H$_2$SCH$_2$C$_4$H$_2$SC(OEt)}M(CO)$_5$] (M = Cr (**6a**), W (**6b**)). Yields were 0.9 g (1.35 mmol, 60.2%) for **6a** and 0.59 g (0.63 mmol, 28%) for **6b**.

Method 2

In an alternative method, the lithiation of MDT was achieved by adding 0.21 mL (1.4 mmol) of TMEDA to a solution of 0.25 g (1.4 mmol) of MDT in 30 mL of THF. Addition of 1.75 mL (2.8 mmol) of *n*-BuLi and refluxing the mixture for 15 min resulted in a color change from yellow to very dark brown. The mixture was cooled to −50 °C, and the reaction was further carried out as described in Method 1. Yields were 0.67 g (0.99 mmol, 71%) of **6a** and 1.03 g (1.1 mmol, 78.2%) of **6b**.

Data for **6a** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.11 (d, *J* = 4.1, 2H, H3/H3′), 7.05 (d, *J* = 4.1, 2H, H4/H4′), 5.13 (q, *J* = 7.0, 4H, OCH$_2$), 4.31 (s, 2H, CH$_2$), 1.61 (t, *J* = 7.0, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 314.7 (C1), 223.2 (CO$_{trans}$), 217.1 (CO$_{cis}$), 157.2 (C2/C2′), 151.6 (C5/C5′), 142.0 (C3/C3′), 128.2 (C4/C4′), 76.0 (CH$_2$), 15.1 (CH$_3$). IR (ν$_{CO}$, hexane, cm^{-1}): 2058 m (A$_1^1$), 1983 w (B$_1$), 1954 sh (A$_1^2$), 1947 vs (E). Anal. Calcd for C$_{25}$H$_{16}$O$_{12}$S$_2$Cr$_2$ (676.49): C, 44.38; H, 2.38. Found: C, 44.61; H, 2.59.

Data for **6b** are as follows. ^{1}H NMR (500 MHz, CDCl$_3$): δ 8.02 (d, *J* = 4.1, 2H, H3/H3′), 7.03 (d, *J* = 4.1, 2H, H4/H4′), 4.95 (q, *J* = 7.1, 4H, OCH$_2$), 4.26 (s, 2H, CH$_2$), 1.61 (t, *J* = 7.0, 3H, CH$_3$). ^{13}C NMR (126 MHz, CDCl$_3$): δ 305.2 (C1), 202.4 (CO$_{trans}$), 197.5 (CO$_{cis}$), 157.1 (C2/C2′), 152.3 (C5/C5′), 142.6 (C3/C3′), 128.3 (C4/C4′), 78.4 (CH$_2$), 14.9 (CH$_3$). IR (ν$_{CO}$, hexane, cm^{-1}): 2066 m (A$_1^1$), 1975 w (B$_1$), 1948 s (A$_1^2$), 1941 vs (E). Anal. Calcd for C$_{25}$H$_{16}$O$_{12}$S$_2$W$_2$ (940.19): C, 31.93; H, 1.72. Found: C, 32.29; H, 1.94.

Preparation of [M(CO)$_4${C(OEt)}$_2$C$_8$H$_4$S] (M = Cr (*7a*), W (*7b*))

Method 1

A solution of 0.29 g (1 mmol) of benzothiophene in THF at −78 °C was reacted with a 1.3 mL (1.6 M) solution of *n*-BuLi in hexane for 1 h. A 0.22 g portion of Cr(CO)$_6$ or 0.35 g of W(CO)$_6$ was added to the solution and allowed to react. The solvent was removed under reduced pressure, the residue was dissolved in DCM, and the mixture was cooled to −35 °C. A 0.47 g portion (2.5 mmol) of [Et$_3$O][BF$_4$] was added to this solution, whereby the reaction mixture turned dark red. The solvent was again removed in vacuo before the products were separated on silica gel. Elution with hexane afforded two major products; the first were the yellow butylcarbene complexes [M(CO)$_5$(C(OEt)Bu}][41] (yields 20–30%) and the second the known benzothienyl mono-carbene complexes [M(CO)$_5${C(OEt)C$_8$H$_5$S}] (yields 40–50%).[75]

Method 2

A solution of 0.29 g (1 mmol) of 2,3-dibromobenzothiophene in THF at −78 °C was reacted with 1.3 mL (2.2 mmol) of *n*-BuLi for 30 min. A 0.22 g portion (1 mmol) of Cr(CO)$_6$ or 0.35 g (1 mmol) of W(CO)$_6$ was added to the solution. The solvent was removed in vacuo, and the residue was dissolved in DCM. The mixture was cooled to −35 °C, and 0.47 g (2.5 mmol) of [Et$_3$O][BF$_4$] was added. The mixture turned dark blue on reaching room temperature. The solvent was removed under reduced pressure, and the products were separated by column chromatography on silica gel. Two products were isolated: the first were the monocarbene complexes as minor reaction products and the second, ink blue fraction yielded 0.295 g (0.72 mmol, 72%) of [Cr(CO)$_4${C(OEt)}$_2$C$_8$H$_4$S] (**7a**) or 0.374 g (0.69 mmol, 69%) of [W(CO)$_4${C(OEt)}$_2$C$_8$H$_4$S] (**7b**).

Data for **7a** are as follows. ^{1}H NMR (500 MHz, C_6D_6): δ 8.18 (d, J = 8.2 Hz, 1H, H9), 7.11 (d, J = 8.1 Hz, 1H, H6), 7.06 (dd, br, J = 8.0, 8.15 Hz, 1H7), 6.93 (dd, br, J = 7.8, 7.8 Hz, 1H, H8), 4.45 (q, J = 6.9 Hz, 2H, CH_2(b)), 4.41 (q, J = 6.8 Hz, 2H, CH_2(a)), 1.11 (t, br, J = 7.3 Hz, 6H, CH_3). ^{13}C NMR (126 MHz, C_6D_6): δ 319.8 (C1b), 312.7 (C1a), 245.5 (CO_{cis}), 241.9 (CO_{cis}), 228.9 (CO_{trans}), 165.3 (C3), 160.1 (C2), 144.4 (C4), 129.4 (C5), 128.5 (C8), 126.8 (C9), 126.5 (C7), 124.3 (C6), 77.2 (CH_2), 77.0 (CH_2), 14.7 (CH_3). IR (ν_{CO}, hexane, cm^{-1}) 2018 m (A_1^1), 1962 s (A_1^2), 1946 s (B_1), 1896 m (B_2). Anal. Calcd for $C_{18}H_{14}O_6SCr$ (410.34): C, 52.68; H, 3.44. Found: C, 52.77; H 3.56. MS (*m/z*): 410 (M^+).

Data for **7b** are as follows. ^{1}H NMR (400 MHz, C_6D_6): δ 8.20 (d, 8.1 Hz, 1H, H9), 7.08 (d, J = 8.2, 1H, H6), 7.06 (dd, J = 8.0, 7.2 Hz, 1H, H7), 6.96 (dd, J = 7.4, 7.4 Hz, 1H, H8), 4.22 (q, J = 7.1 Hz, 3H, CH_2(b)), 4.19 (q, J = 7.1 Hz, 3H, CH_2(a)), 1.13 (t, J = 7.1 Hz, 5H, CH_3), 1.13 (t, J = 7.1 Hz, 5H, CH_3). ^{13}C NMR (101 MHz, C_6D_6): δ 293.3 (C1(b)), 285.1 (C1(a)), 222.2 ($CO_{cis(b)}$), 218.7 ($CO_{cis(a)}$), 213.5 (CO_{trans}), 163.2 (C3), 157.5 (C2) 128.5 (C8), 144.3 (C4), 130.1 (C5) 126.9 (C9), 126.8 (C7), 124.4 (C6), 80.6 (CH_2(b)), 80.0 (CH_2(a)), 15.0 (CH_3), 14.4 (CH_3). IR (ν_{CO}, hexane, cm^{-1}): 2026 m (A_1^1), 1955 vs (A_1^2), 1943 s (B_1), 1889 m (B_2). Anal. Calcd for $C_8H_{14}O_6SW$ (542.20): C, 39.87; H, 3.60. Found: C, 40.03; H, 2.81. MS (*m/z*): 540 (M^+).

Preparation of $[M(CO)_5\{C(OEt)C_6H_2N(Me)S\}]$ (M = Cr (8a), W (8b)), $[(CO)_5M\{C(OEt)C_6H_2N(Me)SC(OEt)\}W(CO)_5]$ (M = Cr (9a),(61) W = (9b)), and $[M(CO)_4\{C(OEt)\}_2C_6H_2N(Me)S]$ (M = Cr (10a), W (10b))

Method 1

A 1.66 mL portion (4 mmol) of TMEDA was added to a solution of 0.27 g (2.0 mmol) of *N*-methylthieno[2,3-*b*]pyrrole in hexane at room temperature, followed by 2.75 mL (4.4 mmol) of *n*-BuLi, and the solution was refluxed for 30 min. The reaction mixture was cooled to −40 °C, and 4 mmol of $M(CO)_6$ (0.88 g $Cr(CO)_6$) or 1.40 g $W(CO)_6$) was added. After approximately 15 min the solvent was removed in vacuo and the residue was dissolved in DCM at −35 °C. A 0.80 g portion (4.05 mmol) of $[Et_3O][BF_4]$ was added to the solution, whereby it turned dark purple-black. The solvent was removed under reduced pressure, and the products in the residue were separated on silica gel by gradient elution using hexane and DCM. Four compounds were isolated and characterized: the yellow oil $[M(CO)_5\{C(OEt)Bu\}]$ (3–5%), the red mono-carbene complex $[M(CO)_5\{C(OEt)C_6H_3N(Me)S\}]$ (**8a,b**), the targeted blue chelated bis-carbene complex $[M(CO)_4\{C(OEt)\}_2C_6H_2N(Me)S]$ (**10a,b**), and the purple dinuclear bis-carbene complex $[(CO)_5M\{C(OEt)-C_6H_2N(Me)SC(OEt)\}M(CO)_5]$ (**9a**(61) or **9b**). Yields: for M = Cr, **8a** 0.40 g (1.04 mmol, 52%), **9a** 0.33 g (0.8 mmol, 40%), and **10a** 0.038 g (0.06 mmol, 3%) and for M = W **8b** 0.62 g (1.2 mmol, 60%), **9b** 0.09 g (0.1 mmol, 5%), and **10b** 0.22 g (0.4 mmol, 20%).

Method 2

A 1.25 mL portion (2 mmol) of *n*-BuLi was added to a solution of 0.27 g (2.0 mmol) of *N*-methylthieno[2,3-*b*]pyrrole in THF at −40 °C, and the mixture was stirred for 30 min. This was followed by addition of 2 mmol of $M(CO)_6$ (0.44 g of $Cr(CO)_6$ or 0.70 g of $W(CO)_6$) and vigorous stirring in the cold for 30 min. The temperature was raised to room temperature, and the mixture was stirred for an additional 30 min. The solution turned red-brown. The reaction mixture was cooled to −70 °C and treated with a freshly prepared solution of LDA (2.4 mmol, 1.5 mL of *n*-BuLi and 0.34 mL of diisopropylamine) in THF.(68) Stirring was maintained at this temperature for 1 h. One of two routes was then followed. To optimize the yields of **9a,b**, the reaction mixture was cooled to −40 °C, an additional 2.0 mmol of $M(CO)_6$ was added, and the mixture was stirred in the cold for 30 min and thereafter for 1 h at room temperature. At room temperature the solvent was removed in vacuo and the residue was dissolved in DCM at −35 °C. A 0.78 g portion (4.05 mmol) of $[Et_3O][BF_4]$ was added to the solution at −30 °C, and the solution was stirred, first in the cold and thereafter at room temperature. After removal of the solvent the products were separated by column chromatography as described under Method 1. To optimize the yields of **10a,b**, the solvent was removed under reduced

pressure, the residue was dissolved in 30 mL of DCM, and the solution was cooled to −30 °C and alkylated with 4 equiv (0.78 g, 4.05 mmol) of [Et$_3$O][BF$_4$], as before. After the solvent was removed, the crude residue was separated by column chromatography as described under Method 1. Yields optimized for **9a,b**: **8a**, 0.40 g (1.04 mmol, 35%); **8b**, 0.62 g (1.2 mmol, 46%), **9a**, 0.038 g (0.06 mmol, 19%); **9b**, 0.09 g (0.1 mmol, 15%), **10a**, 0.33 g (0.8 mmol, 38%); **10b**, 0.22 g (0.4 mmol, 25%). Yields optimized for **10a,b**: **8a**, 0.40 g (1.04 mmol, 30%); **8b**, 0.62 g (1.2 mmol, 50%), **9a**, 0.038 g (0.06 mmol, 14%); **9b**, 0.09 g (0.1 mmol, 11%), **10a**, 0.33 g (0.8 mmol, 42%); **10b**, 0.22 g (0.4 mmol, 27%).

Data for **8a** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.07 (d, J = 0.5 Hz, 1H, H3), 7.07 (d, J = 2.8 Hz, 1H, H7), 6.30 (dd, J = 2.8, 0.52 Hz, 1H, H6), 5.08 (q, J = 7.0 Hz, 2H, CH$_2$), 3.84 (s, 3H, NCH$_3$), 1.63 (t, J = 7.0 Hz, 3H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 306.8 (C1), 223.3 (CO$_{trans}$), 217.7 (CO$_{cis}$), 152.5 (C2), 141.9, 133.2 (C4, C5), 124.8 (C3), 134.4 (C7), 100.9 C(6), 75.1 (CH$_2$), 34.8 (NCH$_3$), 15.2 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2054 m (A$_1^1$), 1975 w (B$_1$), 1941 s (A$_1^2$), 1941 vs (E). Anal. Calcd for C$_{15}$H$_{11}$NO$_6$SCr (385.29): C, 46.76; H, 2.88. Found: C, 46.88; H, 2.97. MS (m/z): 385 [M$^+$].

Data for **8b** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.99 (d, J = 0.5 Hz, 1H, H3), 7.11 (d, J = 2.9 Hz, 1H, H7), 6.32 (dd, J = 2.9, 0.5 Hz, 1H, H6), 4.91 (q, J = 7.0 Hz, 2H, CH$_2$), 3.83 (s, 3H, NCH$_3$), 1.61 (t, J = 7.0 Hz, 3H, CH$_3$). ^{13}C NMR (75 MHz, CDCl$_3$): δ 282.5 (C1), 202.5 (CO$_{trans}$), 198.2 (CO$_{cis}$), 155.0 (C2), 141.6, 134.4 (C4, C5), 125.5 (C3), 134.8 (C7), 101.2 C(6), 77.6 (CH$_2$), 34.7 (NCH$_3$), 15.0 (CH$_3$). IR (ν_{CO}, hexane, cm^{-1}): 2062 m (A$_1^1$), 1971 w (B$_1$), 1944 s (A$_1^2$), 1933 vs (E). Anal. Calcd for C$_{15}$H$_{11}$NO$_6$SW (517.15): C, 34.84; H, 2.14. Found: C, 34.90; H, 2.22. MS (m/z): 515 (M$^+$, ^{183}W).

Data for **9b** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.89 (d, J = 0.8 Hz, 1H, H3), 7.59 (d, J = 0.8 Hz, 1H, H6), 5.01 (q, J = 7.0 Hz, 2H, CH$_2$a), 4.97 (q, J = 7.0 Hz, 2H, CH$_2$b), 3.88 (s, 3H, NCH$_3$), 1.71 (t, J = 7.0 Hz, 3H, CH$_3$a), 1.66 (t, J = 7.0 Hz, 3H, CH$_3$b). ^{13}C NMR (75 MHz, CDCl$_3$): δ 289.1 (C1a), 288.6 (C1b) 202.53 (CO$_{trans}$), 202.49 (CO$_{trans}$), 197.6 (CO$_{cis}$), 197.5 (CO$_{cis}$), 161.8 (C2), 129.7, 146.8 (C4, C5), 124.8 (C3), 154.3 (C7), 122.2 C(6), 79.1 (CH$_2$a), 79.1 (CH$_2$b), 37.5 (NCH$_3$), 15.2 (CH$_3$a), 14.9 (CH$_3$b). IR (ν_{CO}, hexane, cm^{-1}): 2061 m (A$_1^1$), 1979 w (B$_1$), 1938 s (A$_1^2$), 1951 vs (E). Anal. Calcd for C$_{23}$H$_{15}$NO$_{12}$SW$_2$ (897.11.): C, 30.79; H, 1.69. Found: C, 30.92; H, 1.81. MS (m/z): 813 [M$^+$ − 3CO].

Data for **10a** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 6.88 (s, 1H, H7), 6.27 (s, 1H, H6), 4.78 (q, J = 7.0 Hz, 2H, CH$_2$b), 4.65 (q, J = 7.2 Hz, 2H, CH$_2$a), 3.91 (s, 3H, NCH$_3$), 1.65 (t, J = 7.0 Hz, 3H, CH$_3$b), 1.57 (t, J = 7.2 Hz, 3H, CH$_3$a). ^{13}C NMR (75 MHz, CDCl$_3$): δ 316.4 (C1a), 305.9 (C1b) 242.9 (CO$_{trans}$), 242.8 (CO$_{trans}$), 228.0 (CO$_{cis}$), 162.3 (C2), 150.3 (C3), 129.4, 134.2 (C4, C5), 101.7 (C6), 133.3 (C7), 77.6 (CH$_2$a), 75.9 (CH$_2$b), 38.6 (NCH$_3$), 15.4 (CH$_3$a), 15.3 (CH$_3$b). IR (ν_{CO}, hexane, cm^{-1}): 2012 m (A$_1^1$), 1954 s (A$_1^2$), 1939 s (B$_1$), 1888 s (B$_2$). Anal. Calcd for C$_{17}$H$_{15}$NO$_6$SCr (413.34): C, 49.40; H, 3.66. Found: C, 49.51; H, 3.75. MS (m/z): 413 [M$^+$].

Data for **10b** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.02 (d, J = 3.0, 1H, H7), 6.27 (d, J = 3.0, 1H, H6), 4.57 (q, J = 7.2 Hz, 2H, CH$_2$b), 4.46 (q, J = 7.2 Hz, 2H, CH$_2$a), 3.94 (s, 3H, NCH$_3$), 1.66 (t, J = 7.2 Hz, 3H, CH$_3$b), 1.57 (t, J = 7.2 Hz, 3H, CH$_3$a). ^{13}C NMR (75 MHz, CDCl$_3$): δ 289.5 (C1a), 280.3 (C1b) 220.6 (CO$_{trans}$), 220.3 (CO$_{trans}$), 212.5 (CO$_{cis}$), 167.6 (CO$_{cis}$), 154.3 (C2), 129.4, 134.5 (C4, C5), 102.1 (C3), 133.4 (C7), 122.2 C(6), 80.1 (CH$_2$a), 78.7 (CH$_2$b), 38.8 (NCH$_3$), 14.9 (CH$_3$a), 14.8 (CH$_3$b). IR (ν_{CO}, hexane, cm^{-1}): 2020 m (A^1), 1947 s (B$_1$), 1936 s (B$_2$), 1882 s (A$_1^2$). Anal. Calcd for C$_{17}$H$_{15}$NO$_6$SW (545.21): C, 37.45; H, 2.77. Found: C, 37.61; H, 2.91. MS (m/z) 545 [M$^+$].

Associated Content

Supporting Information

Text, a figure, tables, and CIF files giving a modified synthesis of 4-methyl-4*H*-thieno[3,2-*b*]pyrrole (**D**) with new intermediates and their characterization, improved NMR spectral data for old intermediates, and single-crystal X-ray diffraction data for complexes **1**, **5a**, **7a,b**, **8a,b**, and **10a,b**.

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Notes

The authors declare no competing financial interest.

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References

(1) Abarca, B.; Asensio, G.; Ballesteros, R.; Varea, T. *J. Org. Chem.* **1991**, *56*, 3224−3229.

(2) Kawase, T.; Ueno, N.; Oda, M. *Tetrahedron Lett.* **1992**, *33*, 5405−5408.

(3) Kawase, T.; Muro, S.; Kurata, H.; Oda, M. *J. Chem. Soc., Chem. Commun.* **1992**, *23*, 778−779.

(4) Shatenshtein, A. I.; Kamrad, A. G.; Shapiro, I. O.; Ranneva, Y. I.; Zvyagintseva, E. N. *Dokl. Akad. Nauk SSSR* **1966**, *168*, 364.

(5) Abraham, R. J.; Fisher, J.; Loftus, P. *Introduction to NMR Sectroscopy*; Wiley: New York, 1988; p 30.

(6) Pretsch, E.; Bühlmann, P.; Badertscher, M. *Tables of Spectral Data for Structure Determinations of Organic Compounds*,4th ed.; Springer-Verlag: Berlin, Heidelberg, 2009.

(7) Fischer, E. O.; Maasböl, A. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 580−581.

(8) Sierra, M. A. *Chem. Rev.* **2000**, *100*, 3591−638.

(9) Terblans, Y. M.; Roos, M. H.; Lotz, S. *J. Organomet. Chem.* **1998**, *566*, 133−142.

(10) Crause, C.; Görls, H.; Lotz, S. *Dalton Trans.* **2005**, 1649−1657.

(11) Landman, M.; Ramontja, J.; van Staden, M.; Bezuidenhout, D. I.; van Rooyen, P. H.; Liles, D. C.; Lotz, S. *Inorg. Chim. Acta* **2010**, *363*, 705−717.

(12) Lotz, S.; Crause, C.; Olivier, A. J.; Liles, D. C.; Görls, H.; Landman, M.; Bezuidenhout, D. I. *Dalton Trans.* **2009**, 697.

(13) Fischer, E. O.; Röll, W.; Hoa Tran Huy, N.; Ackermann, K. *Chem. Ber.* **1982**, *114*, 2951−2964.

(14) Wittig, G.; Bickelhaupt, F. *Angew. Chem.* **1957**, *69*, 883−894.

(15) Wittig, G.; Bickelhaupt, F. *Chem. Ber.* **1958**, *91*, 883−894.

(16) Fischer, E. O.; Röll, W.; Schubert, U.; Ackermann, K. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 611−612.

(17) Poyatos, M.; Mata, J. A.; Peris, E. *Chem. Rev.* **2009**, *109*, 3677−3707.

(18) Xi, Z.; Liu, B.; Lu, C.; Chen, W. *Dalton Trans.* **2009**, 7008−14.

(19) Edwards, P. G.; Hahn, F. E. *Dalton Trans.* **2011**, *40*, 10278−10288.

(20) Barluenga, J.; Trabanco, A. A.; Pérez-Sánchez, I.; De la Campa, R.; Flórez, J.; García-Granda, S.; Aguirre, Á. *Chem.—Eur. J.* **2008**, *14*, 5401−5404.

(21) Hoa Tran Huy, N.; Pascard, C.; Tran Huu Dau, E.; Dötz, K. H.; Hao Tran Huy, N. *Organometallics* **1988**, *7*, 590−592.

(22) Hoa Tran Huy, N.; Fischer, E. O.; Riede, J.; Thewalt, U.; Dötz, K. H. *J. Organomet. Chem.* **1984**, *273*, C29−C32.

(23) Hoa Tran Huy, N.; Lefloch, P.; Louis, J. M.; Fetizon, M. *J. Organomet. Chem.* **1986**, *311*, 79−83.

(24) van Jaarsveld, N. A.; Liles, D. C.; Lotz, S. *Dalton Trans.* **2010**, *39*, 5777−5779.

(25) Schnürch, M.; Spina, M.; Khan, A. F.; Mihovilovic, M. D.; Stanetty, P. *Chem. Soc. Rev.* **2007**, *36*, 1046−1057.

(26) Peyron, C.; Navarre, J.-M.; van Craynest, N.; Benhida, R. *Tetrahedron Lett.* **2005**, *46*, 3315−3318.

(27) Lotz, S.; Landman, M.; Olivier, A. J.; Bezuidenhout, D. I.; Liles, D. C.; Palmer, E. R. *Dalton Trans.* **2011**, *40*, 9394−9403.

(28) Faruggia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(29) Cason, C. J. *POV-RAY for Windows*; Persistence of Vision, 2004.

(30) Mallan, J. M.; Bebb, R. L. *Chem. Rev.* **1969**, *69*, 693−755.

(31) Clayden, J. In *Organolithiums: Selectivity for Synthesis*; Baldwin, J. E., Williams, R. M., Bäckvall, J.-E., Eds.; Pergamon: Oxford, U.K., 2002; Tetrahedron Organic Chemistry Vol. 23, pp 111−119.

(32) Fischer, E. O.; Held, W.; Kreißl, F. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 656−666.

(33) Aoki, S.; Fujimura, T.; Nakamura, E. *J. Am. Chem. Soc.* **1992**, *114*, 2985−2990.

(34) NMR spectra collected for $[W(CO)_5\{C(OEt)C_4H_3S\}]$ (CDCl$_3$) are as follows. ^{1}H NMR (300 MHz): δ 8.14 (d, *J* = 4.2, 1H, H3), 7.20 (d, *J* = 4.1, 1H, H4), 7.80 (d, *J* = 4.1, 1H, H5), 4.99 (q, *J* = 7.0, 2H, CH$_2$), 1.66 (t, *J* = 7.05, 3H, CH$_3$). ^{13}C NMR (75 MHz): δ 312.5 (C1), 205.0 (CO$_{trans}$), 197.6 (CO$_{cis}$), 162.0 (C2), 141.4 (C5), 135.9 (C3), 128.9 (C4), 79.0 (CH$_2$), 14.9 (CH$_3$).

(35) Connor, J. A.; Jones, E. M. *J. Chem. Soc. A* **1971**, 1974−1979.

(36) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 144−145.

(37) Carpenter, A. J.; Chadwick, D. J. *J. Org. Chem.* **1985**, *50*, 4362−4368.

(38) Fraser, R. R.; Mansour, T. S.; Savard, S. *Can. J. Chem.* **1985**, *63*, 3505−3509.

(39) Chadwick, D. J.; Willbe, C. *J. Chem. Soc., Perkin Trans. 1* **1977**, 887−893.

(40) Ogawa, K.; Rasmussen, S. C. *J. Org. Chem.* **2003**, *68*, 2921−8.

(41) Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **1970**, *9*, 32−39.

(42) Gould, N. P.; Lee, T.-J. *J. Org. Chem.* **1980**, *45*, 4528−4530.

(43) Wieber, G. M.; Hegedus, L. S.; Gale, C. *Organometallics* **1995**, *14*, 3574−3577.

(44) Kreiter, C. G.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 761−762.

(45) Farnell, L. F.; Randall, E. W.; Rosenberg, E. *J. Chem. Soc., Chem. Commun.* **1971**, 1078−1079.

(46) Casey, C. P. *J. Chem. Soc., Chem. Commun.* **1970**, 1220−1221.

(47) Gandler, J. R.; Bernasconi, C. F. *Organometallics* **1989**, *8*, 2282−2284.

(48) Kreiter, C. G. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 390−391.

(49) Landman, M.; Görls, H.; Lotz, S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2037−2043.

(50) Fröhlich, J.; Hametner, C.; Kalt, W. *Monatsh. Chem.* **1996**, *127*, 325−330.

(51) Mann, B. E. *J. Chem. Soc., Dalton Trans.* **1973**, 2012−2015.

(52) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: London, 1975; pp 208, 218.

(53) Kawase, T.; Enomoto, T.; Wei, C.; Oda, M. *Tetrahedron Lett.* **1993**, *34*, 8143−8146.

(54) Bezuidenhout, D. I.; van der Watt, E.; Liles, D. C.; Landman, M.; Lotz, S. *Organometallics* **2008**, *27*, 2447−2456.

(55) Hemetsberger, H.; Knittel, D. *Monatsh. Chem.* **1972**, *103*, 194−204.

(56) Aratani, T.; Yoshihara, H.; Suzukamo, G. *Tetrahedron Lett.* **1989**, *30*, 1655−1656.

(57) Gronowitz, S.; Westerlund, C.; Hörnfeldt, A. B. *Acta Chem. Scand.* **1976**, *30*, 391−396.

(58) Soth, S.; Farnierz, M.; Paulmier, C. *Can. J. Chem.* **1978**, *56*, 1429−1434.

(59) Farnier, M.; Soth, S.; Fournari, P. *Can. J. Chem.* **1976**, *54*, 1074−1082.

(60) Landman, M.; Görls, H.; Lotz, S. *Eur. J. Inorg. Chem.* **2001**, *617−618*, 233−238.

(61) Lotz, S.; Landman, M.; Görls, H.; Crause, C.; Nienaber, H.; Olivier, A. J. *Z. Naturforsch.* **2007**, *62*, 419.

(62) Andrada, M. D.; Michoff, M. E. Z.; Fernández, I.; Granados, A. M.; Sierra, M. A. *Organometallics* **2007**, *26*, 5854−5858.

(63) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1−S19.

(64) Bleeke, J. R. *Chem. Rev.* **2001**, *101*, 1205−1228.

(65) Landorf, C. W.; Haley, M. M. *Angew. Chem., Int. Ed.* **2006**, *43*, 3914−3936.

(66) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466−470.

(67) Schubert, U.; Ackermann, K.; Hoa Tran Huy, N.; Röll, W. *J. Organomet. Chem.* **1982**, *232*, 155−162.

(68) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: Berlin, 1987; Vol. *1*, pp 164−165.

(69) Meerwein, H. *Organic Syntheses*; Wiley: New York, 1966; Collect. Vol. *5*, pp 1080−1083.

(70) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897−1903.

(71) *APEX2 (including SAINT and SADABS)*; Bruker AXS Inc., Madison, WI, 2005.

(72) Otwinowski, Z.; Minor, W. In *Macromolecular Crystallography, Part A*; Carter, C. W., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol *276*, pp 307−326.

(73) Blessing, R. H. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1995**, *51*, 33−38.

(74) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *A64*, 112−122.

(75) Bezuidenhout, D. I.; Barnard, W.; van der Westhuizen, B.; van der Watt, E.; Liles, D. C. *Dalton Trans.* **2011**, *40*, 6711−6721.

SUPPORTING INFORMATION

1. *The synthesis of 4-methyl-4H-thieno[3,2-b]pyrrole (**D**)*

The synthesis of (**D**) was based on a modified procedure by Hemetsberger and Knittel.[1] The synthesis of pyrrole-condensed heterocycles mostly involves an alkyl azido-acrylate as key intermediate. This compound undergoes facile thermal cyclization, to yield the condensed thieno[3,2-*b*]pyrrole. In the first step, the condensation of thiophenecarboxaldehyde and ethyl azidoacetate[2] was carried out at lower temperature, which substantially increased the yield. Thermolysis afforded **H**, an orange-red solid. Two possible routes to **D** are shown in Scheme 1. Both involve basic hydrolysis of the ester functionality followed by copper catalyzed decarboxylation. The reported route involved alkylation (of **J**) only at the end of the synthesis. We chose to follow the second route which involved the direct alkylation of **H** to give **K** instead of doing this step only at the end of the synthesis. Following this route, slightly lower yields of **D** (overall 19% *vs* 23%) was obtained but problems associated with the poor solubility of **I** were avoided. The ^{1}H and ^{13}C NMR data of intermediates represent improved data sets (Table 1) compared to those published previously.[1] In earlier work no ^{13}C NMR data were given for **H** and **I**, and as far as we are aware, the N-alkylated derivatives **K** and **L** (our route) have not previously been reported. The observation of several long-range couplings over 5 bonds between H3 and H6 ($J = 0.8$ Hz) and over 4 bonds between H6 and NH ($J = 1.8$ Hz) was previously reported but not assigned.[1,3-5] The ^{1}H NMR spectral data and those obtained from 2D spectra aided assignments of chemical shifts in the spectra. The ^{13}C NMR data were consistent with other condensed pyrroles but no attempt was made to distinguish between the two quaternary carbons C4 and C5. The relative chemical shifts of C7 and C2 are different in the N-

H and N-Me derivatives **J** and **D** where C7 resonate up field from C2 in **J** whilst in **D** the order was reversed.

Scheme 6.
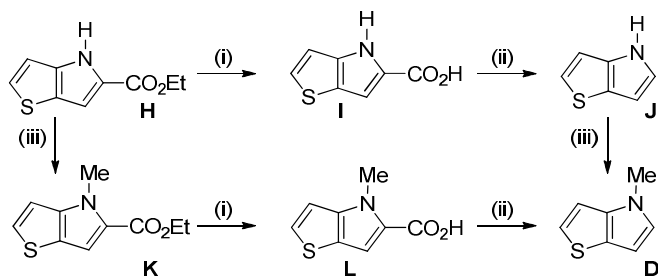
(i) KOH, EtOH, (ii) Cu/quinoline, (iii) *t*-BuOK, MeI.

Experimental:

Preparation of 4-methyl-4*H*-thieno[3,2-*b*]pyrrole (**D**).

Ethyl azidoacetate: 167.0 g (1 mol) of ethyl bromoacetate in ethanol (60 mL) was refluxed for 4 hours with 71.52 g (1.1 mol) of sodium azide in 180 mL H_2O. The reaction mixture was steam distilled and the organic layers combined and washed with H_2O, after which it was dried over anhydrous Na_2SO_4 to afford 104.6 g (0,81 mol, 81%) of a clear oil, ethyl azidoacetate.

Ethyl 2-azido-3-(2'-thienyl)propenoate: 15.49 g (120 mmol) of ethyl azidoacetate and 4.49 g (40 mmol) of 2-thiophenecarboxaldehyde were added to 2.76 g (120 mmol) of sodium in ethanol at -10 to -20°C and stirred vigorously for 90 min. The solution was allowed to warm, but kept below 30°C for an hour and poured over an ice water mixed with 6.4 g (NH_4Cl). The mixture was extracted with 3 portions of ether. The combined organic layers were washed with water and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* after which it was filtered through a small amount of silica gel with a 1:1 hexane:toluene mixture and the solvent was again

removed under reduced pressure to produce 18.48 g (82.3 mmol, 70%) of the yellow-brown oil ethyl 2-azido-3(2'-thienyl)propenoate.

Ethyl 4H-thieno[3,2-b]pyrrole-3-carboxylate (**H**): 6 g (27 mmol) of the azido acrylate (above) was added in small portions to a preheated flask with 250 mL xylene at 130 to 140°C. After the addition the solution was refluxed for a further hour and the solvent removed under reduced pressure. The residue was filtered through silica gel (CH_2Cl_2). 4.72 g (24,2 mmol, 90%) of an orange-red solid **H** was collected upon removal of the solvent.

Ethyl 4-methylthieno[3,2-b]pyrrole-3-carboxylate (**K**): 3.13 g (16.0 mmol) of the N-H ester **H** was dissolved in 30 mL THF and 1.98 g (17.4 mmol) of *t*-BuOK was added at -30°C and stirred for 30 min. After reaching room temperature the solution was again cooled to -30°C and allowed to stir for 20 min where after 2.5 g (17.6 mmol) of MeI was added. After stirring in the cold for 20 min, stirring was continued at room temperature for 1 hour. The mixture was poured over ice and extracted with ether and dried with anhydrous Na_2SO_4 after which the solvent was removed under reduced pressure. The product was purified on a silica gel column with a 1:1 mixture of hexane:DCM affording 2.71 g (13 mmol, 81%) of a red liquid (**K**).

4-methylthieno[3,2-b]pyrrole-3-carboxylic acid (**L**): 1.60 g (28.5 mmol) of KOH was added to a solution of 1.5 g (7.1 mmol) of the N-methyl ester **K** in ethanol:THF:water (25 mL:7 mL:5 mL) and the solution was heated to 40°C for 3 hours. After the removal of the solvent the residue was dissolved in H_2O and acidified to a=pH 2 with concentrated HCl. The mixture was extracted with three portions of ethyl acetate, the combined organic layers were washed with water and dried over anhydrous Na_2SO_4. After removing the solvent 1.15 g (6.3 mmol, 89%) of a greenish white solid **L** was isolated.

4H-thieno[3,2-b]pyrrole-3-carboxylic acid (**I**): 2.84 g (50,6 mmol) of KOH was added to a solution of 2.47 g (12.7 mmol) of the ester **H** in 40 mL of ethanol and 4 mL of water. The solution was heated to 40°C and stirred for three hours. The solvent was removed under reduced pressure, the residue dissolved in water and acidified to pH 2 with concentrated HCl. The mixture was extracted with three portions of ethyl acetate and the combined organic phase was washed with water and dried over anhydrous Na_2SO_4. Removing the solvent yielded 1.59 g (9.5 mmol, 75%) of a light almost white orange-brown solid (**I**).

4H-thieno[3,2-b]pyrrole (**J**): 1.40 g (8.4 mmol) of the acid **I**, along with 20 mL of quinoline and 1.0 g of Cu powder were mixed and heated to 220–230°C for 30 min along with CO_2 evolution. After cooling to room temperature the reaction mixture was poured onto water and acidified to pH 4 with concentrated HCl. The mixture was extracted with five portions of ethyl acetate and the combined organic fractions were washed with solutions of 10% HCl (×5), saturated $NaHCO_3$ (×2) and water (×3) and thereafter dried over anhydrous Na_2SO_4. The crude product was purified on a silica gel column with hexane as the eluent to yield 0.41 g (3.4 mmol, 40%) of a brown oil **J**.
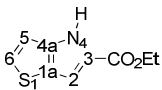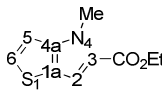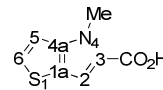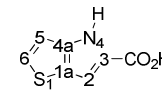
*4-methylthieno[2,3-b]pyrrole (**D**)*
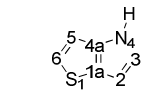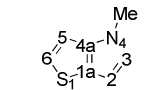
Method 1. A solution of 2.66 g (14.7 mmol) N-methylthieno[3,2-b]pyrrole-3-carboxylic acid (**L**), with 20 mL of quinoline and 1.76 g of Cu powder were heated to 220–230°C for 30 min with CO_2 evolution. After cooling to room temperature the mixture was poured onto ice water and acidified to pH 4 with concentrated HCl. The mixture was extracted with ether, the combined portions were washed with 10% HCl (×5), saturated $NaHCO_3$ (×2), H_2O (×3) and dried over anhydrous Na_2SO_4. The crude product was purified on a silica gel column with

hexane as the eluent to produce 0.99 g (7.2 mmol, 49%) of a light brown oil **D**, which was stored in a dark bottle under argon.

Method 2. 0.39 g (3.5 mmol) of *t*-BuOK was added to 0.38 g (3.1 mmol) of 4H-thieno[3,2-b]pyrrole (**J**) in 10 mL dried THF at -30°C and the light brown suspension was stirred for 20 min. After stirring for a further 10 min at room temperature, the mixture was again cooled to -30°C and 0.49 g (3.5 mmol) MeI was added. After 20 min the solution was allowed to reach room temperature and stirred for an additional hour. The mixture was quenched by the addition of ice water and extracted with ether. The aqueous phase was extracted with two portions of ether and the combined ether fractions were dried over anhydrous Na_2SO_4. The removal of the solvent in vacuo was followed by purification of the crude product on silica gel with a 1:1 mixture of hexane:DCM as the eluent to afford 0.42 g (3.03 mmol, 98%) of a light brown oil **D** which was stored in a dark bottle under argon.

Note: New and improved NMR data for the condensed pyrroles are given in Tables 1.1 (^{1}H) and 1.2 (^{13}C). All spectra were recorded in $CDCl_3$.

Table 1.1 ^{1}H NMR data of condensed pyrroles

Chemical shifts (δ, ppm) and Coupling constants (J, Hz)

Proton assignment	H	K	L	I	J	D
H2	7.13 dd (1.8, 0.8)	7.16 d (0.8)	7.33 d (0.8)	7.09 dd (2.1, 0.8)	6.22 ddd (3.0, 1.8, 0.7)	6.49 dd (2.9, 0.8)
H3	-	-	-	-	6.46 ddd (3.0, 0.5,	6.89 dd (3.0, 0.5,

				1.4)	(2.9, 1.3)
H4	9.40 br s	-	-	3.14 br s	7.32 dd (2.6, 1.8)	-
H5	6.93 dd (5.4, 0.8)	6.90 dd (5.4, 0.8)	6.92 dd (5.4, 0.8)	7.01 dd (5.4, 0.8)	6.48 dd (5.4, 0.7)	7.00 dd (5.2, 0.8)
H6	7.30 d (5.4)	7.33 d (5.4)	7.37 d (5.4)	7.40 d (5.4)	6.84 dd (5.4, 1.4)	7.17 dd (5.2, 1.3)
N-CH$_3$	-	4.03 s	4.05 s	-	-	3.80 s
CH$_2$	4.36 q (7.2)	4.31 q (7.2)	-	-	-	-
CH$_3$	1.48 t (7.2)	1.36 t (7.2)	-	-	-	-
CO$_2$H	-	-	9.40 br s	10.98 br s	-	-

Table 1.2 ^{13}C NMR data of condensed pyrroles

Carbon assignment	Chemical shifts (δ, ppm)					
	H	**K**	**L**	**I**	**J**	**D**
C1a/C4a	127.0	126.8	125.7	127.9	138.6	140.4
	124.7	121.6	122.0	124.3	121.9	122.9
C2	107.5	108.9	110.1	107.3	101.3	100.1
C3	141.4	145.5	146.6	142.2	123.0	126.6

C5	111.1	110.0	111.0	112.1	111.2	109.8
C6	129.4	128.9	130.3	129.2	123.7	123.2
N-**CH**$_3$	-	34.5	34.8	-	-	34.5
CH$_2$	60.7	60.0	-	-	-	-
CH$_3$	14.4	14.4	-	-	-	-
CO$_2$**Et**	161.8	161.7	166.8	162.3	-	-

References

(1) Hemetsberger, H.; Knittel, D. *Monatsh. Chem.* 1972, *103*, 194-204.

(2) Aratani, T.; Yoshihara, H.; Suzukamo, G. *Tetrahedron Lett.* 1989, *30*, 1655-1656.

(3) Gronowitz, S.; Westerlund, C.; Hörnfeldt, A. B. *Acta Chem. Scand.* 1976, *30*, 391-396.

(4) Soth, S.; Farnierz, M.; Paulmier, C. *Can. J. Chem.* 1978, *56*, 1429-1434.

(5) Farnier, M.; Soth, S.; Fournari, P. *Can. J. Chem.* 1976, *54*, 1074-1082.