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Synthesis and structure of bimetallic complexes with σ,π-bridged monocarbene ligands‡

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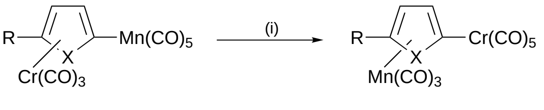
The Fischer method was employed to synthesize bimetallic monocarbene complexes from lithiated $[Cr(SC_4H_4)(CO)_3]$ and metal hexacarbonyls. In addition to the formation of $[M\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ (M = Cr **1** or W **2**) the complexes $[M\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ (M = Cr **3** or W **4**), were also obtained. The formation of **3** and **4** is ascribed to the activation of tetrahydrofuran (thf) by a σ,π-co-ordinated acyl metalate, which triggers the cleavage of the thf ring and leads to its inclusion into the alkoxy substituent of the resulting carbene moiety. In polar solvents the $Cr(CO)_3$ fragments are displaced to give known pentacarbonyl-[ethoxy(thienyl)carbene] complexes and the new mononuclear carbene complexes $[M\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ (M = Cr **5** or W **6**). The analogous benzo[*b*]thienyl carbene complex $[Cr\{C[\eta^6\text{-}C_8H_5SCr(CO)_3]OEt\}(CO)_5]$ **7** was prepared similarly, but did not afford the thf-inserted product and the corresponding conversion into the mononuclear carbene complex $[Cr\{C(C_8H_5S)OEt\}(CO)_5]$ **8**, was much slower.

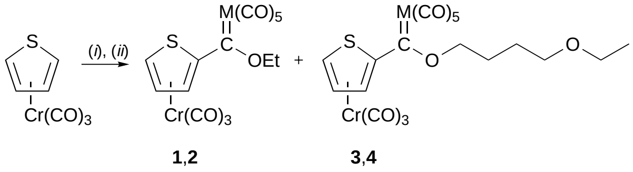
The activation of simple organic molecules by more than one transition-metal constitutes an area of research which has grown in importance over the last decade.[2] Transition-metal complexes with bridging ligands and without metal–metal bonds can be conveniently divided into three classes based on the mode of co-ordination of the ligand. Attachments of ligands to metal centres may consist of (*i*) σ,σ, (*ii*) σ,π or (*iii*) π,π bonds. Small bridging ligands place a second metal fragment in close proximity to the first one and if these ligands contain conjugated π systems electronic contact is established between the two metal centres. Our interest in this area deals with the activation of benzene[3] and thiophene[4] derivatives by more than one metal centre. We have recently shown that an interesting form of activation exists when thiophene is π bonded to $Cr(CO)_3$ and σ bonded to $Mn(CO)_5$ in the 2 position. We discovered that the metal fragments irreversibly exchanged co-ordination sites, which indicated that different metal fragments exhibit preferences for specific co-ordination sites in σ,π-bimetallic complexes,[1,4] Scheme 1. This novel conversion was the result of the metals being in direct electronic contact through the bridging thienyl ligand, the presence of a low-energy pathway facilitating the conversion and the fact that the converted product is thermodynamically more stable than the precursor. Metal–metal communication is also possible *via* π-resonance effects when a second metal fragment is σ bonded *via* a carbene unit to a π-co-ordinated thienyl ligand. This prompted us to investigate the effect of π co-ordination on the properties of such a carbene functionality.

Examples of bimetallic monocarbene complexes with σ,π-bridging benzene and cyclopentadienyl ligands are scarce but have been documented, *i.e.* $[(OC)_5M\{\eta^1{:}\eta^6\text{-}C_6H_5C(OEt)\}\text{-}Cr(CO)_3]$ (M = W, Mo or Cr),[5] $[(OC)_5M\{\eta^1{:}\eta^5\text{-}C_5H_3RC(OEt)\}\text{-}M'(\eta^5\text{-}C_5H_4R)]$ (M = W, Mo or Cr; M′ = Fe or Ru; R = H or Me),[6] a series of ferrocenyl carbene complexes of chromium, tungsten and manganese, which were synthesized to study electronic effects of the ferrocenyl substituent on the carbene ligand,[7] and the modification of the cationic ferrocenyl carbyne complexes of manganese with thiolate, selenolate, tellurolate and $[Co(CO)_4]^-$ to afford the corresponding neutral carbene complexes.[8] The addition of anionic carbene complexes $[M\{C(OMe)CH_2\}(CO)_5]^-$ to cationic complexes with co-ordinated unsaturated hydrocarbons, *e.g.* ethene and tropylium, *etc.*, also afforded bimetallic mononuclear carbene complexes with σ,π-bridging ligands, but without π conjugation.[9]



R = H, Me or $Mn(CO)_5$; X = S or Se

Scheme 1 (*i*) Acetone, 0 °C, 3 d



Scheme 2 (*i*) LiBu, thf, $[M(CO)_6]$; (*ii*) Et_3OBF_4, CH_2Cl_2

In this paper we report results obtained from the reaction of $[Cr(\eta^5\text{-}SC_4H_3Li)(CO)_3]$ and $[M(CO)_6]$ which after subsequent alkylation in dichloromethane with Et_3OBF_4 afforded, not only the expected bimetallic Fischer-type carbene complex **1** or **2**, but a second modified carbene complex **3** or **4** (Scheme 2). The latter involved the incorporation of a cleaved tetrahydrofuran (thf) molecule into the ethoxy substituent of the carbene ligand. The lability of the π-thienyl ligand is demonstrated by the displacement of the $Cr(CO)_3$ fragment in polar solvents.

Results and Discussion

Synthesis

The π-bonded heteroarene ring complex $[Cr(SC_4H_4)(CO)_3]$ can be used advantageously as a precursor in the synthesis of σ,π-bimetallic complexes. It was prepared for the first time in a low yield by Fischer and Öfele[10] in the thermal reaction of $[Cr(CO)_6]$ and thiophene. The synthesis was improved by a two-step procedure, in which the $[Cr(CO)_6]$ was converted into $[Cr(CO)_3(NH_3)_3]$[11] and thereafter treated with an excess of thiophene and 3 equivalents of the Lewis acid, BF_3, in diethyl ether.[12] Metallation of $[Cr(SC_4H_4)(CO)_3]$ at low temperatures is readily achieved.[13]

Another π-bonded heterocycle which could be utilized with

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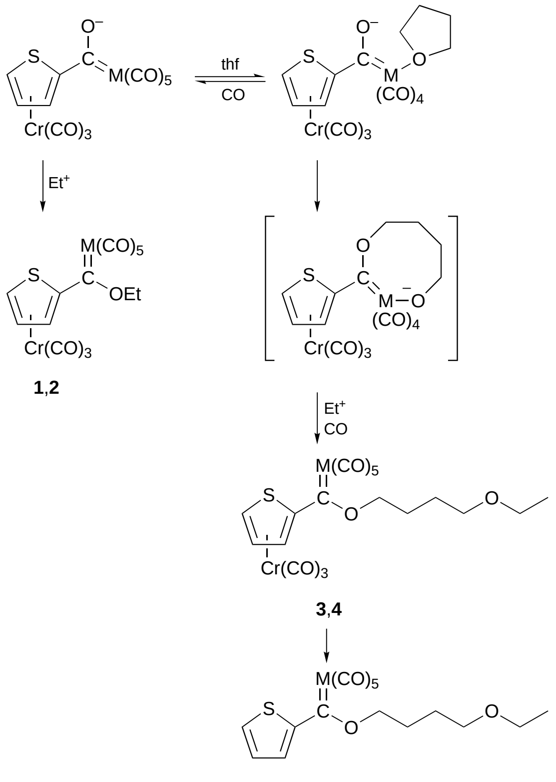
‡ π-Heteroarene complexes. Part 4.[1]

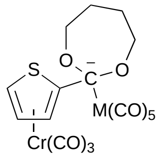
success and has the advantage of being related to the thiophene system is the complex $[Cr(SC_8H_6)(CO)_3]$ (SC_8H_6 = benzo[*b*]thiophene) which can be prepared in a direct procedure by heating the thiophene derivative and chromium hexacarbonyl in dibutyl ether.[14] Complexes with a benzene instead of a π-co-ordinated thiophene ligand are less labile and exhibit greater stability against $Cr(CO)_3$ displacement in polar solvents.

The reaction of chromium and tungsten hexacarbonyl complexes with lithiated $[Cr(SC_4H_4)(CO)_3]$ followed by alkylation with Et_3OBF_4 in dichloromethane afforded, in addition to the desired σ,π-monocarbene complexes $[M\{C[\eta^1{:}\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ (M = Cr **1** or W **2**), a second, more soluble in hexane, bimetallic monocarbene complex, $[M\{C[\eta^1{:}\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ (M = Cr **3** or W **4**). The compounds **3** and **4** were recrystallized from dichloromethane–hexane mixtures. Complexes **1** and **2** are stable under an inert atmosphere in the solid state, but decompose slowly in polar solution giving the known complexes $[M\{C(C_4H_3S)OEt\}(CO)_5]$.[15,16] Complexes **3** and **4** are more soluble in hexane than **1** and **2**, respectively, but less stable owing to faster displacement of the $Cr(CO)_3$ fragment in polar solvents to afford the mononuclear carbene complexes $[M\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ (M = Cr **5** or W **6**). The preparative yields of **3** and **4** were optimized by extending the reaction time at room temperature, but this unfortunately also leads to higher yields of **5** and **6**, respectively. The synthesis of the analogous π-co-ordinated thienyl carbene complexes of $[Mn(\eta^5\text{-}C_5H_5)(CO)_2]$ instead of $[M(CO)_5]$ was attempted, but without success.

The formation of complexes **3** and **4** is very interesting as it represents the cleavage and inclusion of tetrahydrofuran into the ethoxy substituent of the bimetallic carbene complex. Christoffers and Dötz[17] have previously reported a similar insertion of thf into the allyloxy C–O bond of a carbene complex while utilizing a one-pot, Fischer-type nucleophilic/electrophilic addition methodology using allyl triflate (trifluoromethane sulfonate) as alkylating reagent in thf. It was evident that the very strong allyl triflate interacts with the solvent thf whereby the cyclic *O*-allyloxonium ion is generated, which subsequently undergoes ring opening upon nucleophilic attack by the acyl chromate to form the {[(allyloxy)butyl]oxy}carbene side chain. By contrast, in our two-step synthesis the formation of the acyl metalate was achieved in thf, whereafter the solvent was completely removed and the residue washed several times with hexane, before the alkylation was performed in dichloromethane. Therefore, it seems unlikely that thf ring opening was only triggered during the alkylation step by $[C_4H_8O{\cdot}Et]^+$ and that it probably involves an earlier attack of the σ,π-bonded acyl metalate on an activated thf molecule in a bimetallic intermediate species. If so, a different mechanism to that proposed by Christoffers and Dötz[17] involving bimetallic activation is operative. Efforts to isolate, purify and study intermediate acyl metalates spectroscopically were not successful and abandoned. Tetrahydrofuran has been successfully cleaved at low temperatures by reducing agents in the presence of Lewis acids.[18] The reductive cleavage of free thf at −78 °C was easily achieved by using lithium powder or even lithium 4,4′-di-*tert*-butylbiphenyl and $BF_3{\cdot}OEt_2$ in the presence of a catalytic amount of arene, *e.g.* naphthalene, biphenyl, 4,4′-di-*tert*-butylbiphenyl or anthracene. Scheme 3 presents a possible explanation for the formation of the products **1**–**6**.



Scheme 3



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In the first step, a carbonyl ligand of the parent acyl metalate, which leads to the formation of **1** or **2**, is substituted by a thf solvent molecule. Under the prevailing reaction conditions the π-bonded thienyl is fairly labile and the gradual decomplexation of $Cr(CO)_3$ can occur. This is also evident from the formation of the known thienyl carbene complexes $[M\{C(C_4H_3S)OEt\}(CO)_5]$[15,16] during the reaction. Electron-withdrawing effects and steric implications of the π-co-ordinated $Cr(CO)_3$ unit facilitates the co-ordination of a thf molecule at an appropriate position close to the acylate's oxygen atom. Furthermore, the co-ordination of thf induces a formal positive charge on the oxygen atom, leading to greater polarization of the C–O bond. The higher electron density on the metal can be distributed effectively *via* stronger π-back bonding to its carbonyl ligands and will also affect the carbene carbon atom by stronger interaction with the metal, resulting in an enhanced nucleophilic character on the adjacent oxygen atom. Attack by the acylate oxygen atom on the α-carbon of co-ordinated thf in the second step induces cleavage of the thf ring. We propose as key intermediates either one where the metal centre accommodates the excess of negative charge and is part of an eight-membered ring or a second, rearranged formulation resulting from migration of the oxygen from the metal onto the carbene carbon atom giving an anionic seven-membered ring intermediate as is shown in **I**. In the final step the alkylation of the oxygen with Et_3OBF_4 leads to the final products **3** and **4**. Important features are the favourable electronic situation and arrangement of ligands in the π-bonded thienyl acylate which promote and facilitate the attack on a *cis* co-ordinated thf molecule. By contrast, as these conditions did not prevail for $Li(C_4H_3S)$,[15,16] the π-bonded phenyl precursors $[(Cr(\eta^6\text{-}C_6H_5Li)(CO)_3]$[5] or $[Cr(\eta^6\text{-}SC_8H_5Li)(CO)_3]$, when treated in the same way and under similar reaction conditions the insertion of thf was not observed.

In spite of the fact that co-ordination of $Cr(CO)_3$ is through the benzene ring in $[Cr(\eta^6\text{-}SC_8H_6)(CO)_3]$ activation by co-ordination towards metallation is at the 2 position on the thiophene ring.[19] As a result of its separation the $Cr(CO)_3$ fragment is sterically less influenced by the substituents at the 2 position of the thiophene ring. The dark purple-blue ethoxycarbene complex $[Cr\{C[\eta^6\text{-}C_8H_5SCr(CO)_3]OEt\}(CO)_5]$ **7** was obtained in excellent yield and was purified by crystallization from dichloromethane–hexane. Although very stable in the solid state, the $Cr(CO)_3$ fragment was lost very slowly to give $[Cr\{C(C_8H_5S)OEt\}(CO)_5]$ **8** in polar solvents.

Spectroscopic properties of complexes

Complexes **1**–**8** were fully characterized by elemental analyses, mass, infrared (Table 1), ^1H and $^{13}C\text{-}\{H\}$ NMR (Tables 2 and 3) spectroscopy. General features displayed in the infrared spectra are well resolved bands in hexane allowing assignments to the $M(CO)_5$ and $M(CO)_3$ fragments and the lifting of the degeneracy of the E band (A′, A″) of the $Cr(CO)_3$ fragment for π-co-ordinated thienyl complexes.

Two characteristic features of the σ,π-bimetallic monocarbene complexes are the upfield shifts of the thienyl protons in the ^1H NMR spectra of **1**–**4** by more than 1 ppm compared to those of free thiophene[20] and **5** or **6** and the duplication of the methylene resonances of the $C(carbene)OCH_2$ unit. Localization of the π bonds by co-ordination to a transition-metal affects the proton resonances to such an extent that upfield shifts are observed in the ^1H NMR spectra.[21] The ^1H NMR data for **1**–**4** and in particular the methylene resonances of the alkoxy substituent are affected by the lack of a plane of symmetry imposed on the complexes by π co-ordination to the $Cr(CO)_3$ fragment. The methylene protons $C(carbene)OCH_2R$ are prochiral and the chemical shifts are duplicated with resonances at δ 4.99 and 4.88 for **1**, 4.83 and 4.77 for **2**, 4.97 and 4.96 for **3**, and 4.80 and 4.77 for **4**. Other resonances of the alkoxy substituents are broad. In addition, a second set of resonances having the same pattern as the above, but of lower intensity (the ratio based on peak integrations of the ^1H NMR data is *ca.* 1 : 3 for **1**–**4**), are observed indicating the existence of a second isomer in solution. The two components are believed to be diastereoisomers, which can formally be related by a simple rotation around the thienyl–carbon(carbene) bond. The presence of a second diastereoisomer is also indicated by an additional resonance in the ^{13}C NMR spectra of **1**–**3** in the carbene region (not observed for **4**). Restricted rotation around the carbene–thienyl carbon bond will sustain the two different orientations **A** and **B** for the $W(CO)_5$ fragment and the alkoxy substituents. Restricted rotation originating from electronic features is not supported by comparison of the observed resonances of the thienyl protons. Support for steric effects is found in the structure determined for **2** which displays a very compact arrangement of $W(CO)_5$ and (π-thienyl)$Cr(CO)_3$ units. The bond distances (see below) in the solid state show very little multiple bond character in any of the bonds around the carbene carbon atom. However, once formed, the bulky metal carbonyl fragments may inhibit conversion of one diastereoisomer into the other. We observed no change in the diastereoisomeric ratios by recording the NMR spectrum at different temperatures. The corresponding methylene resonances for **5** and **6** reduce to single triplets on removing the chirality caused by the planar ring and the $Cr(CO)_3$ fragment. Furthermore, the barrier to rotation has been lifted by removal of the $Cr(CO)_3$ fragment and allowing free rotation around the C (thienyl)–C (carbene) bond. Support is found in the spectrum of the σ,π-bimetallic complex **7** where the metal carbonyl fragments are far apart and restricted rotation around the C (thienyl)–C (carbene) bond is lifted. In fact, the effect on the resonances of the carbene methylene protons due to planar chirality imposed by the $Cr(CO)_3$ fragment on one side of the benzothiophene

Table 1 Infrared data* ($\tilde{\nu}_{CO}/cm^{-1}$) for the carbene complexes **1**–**8**

	$M(CO)_5$				$Cr(CO)_3$	
Complex	$A_1^{(1)}$	B	E	$A_1^{(2)}$	A_1	E(A′,A″)
1	2062	1978	1952	1963	1990	1935, 1920
2	2069	—	1947	1952	1989	1947
	2067		1941	1941	1981	1895
3	2062	—	1951	1964	1989	1947, 1919
	2061		1945	1945		
4	2080	—	1953	1942	1984	1915, 1895
	2069		1941	1941	1935	1941
5	2069	1988	1948	1978		
	2059	1972	1940	1940		
6	2082	—	1942	1984		
7	2060	—	1980	1980	1980	1893
8	2069	2009	1987	1987		

* The first set of values was recorded in hexane and the second in dichloromethane. In some instances bands of the $M(CO)_3$ fragment were obscured by those of the $M(CO)_5$ fragment.

Table 2 Proton NMR data (δ, *J*/Hz) in $CDCl_3$ for the carbene complexes $[M\{C(R)OR'\}(CO)_5]$ **1**–**8**

	R				R′	
	Thienyl					
Complex	H^3	H^4	H^5	Other	Alkoxy CH_2	Other CH_3
1	5.81 (d) $^3J_{HH}$ 3.7	5.79 (t) $^3J_{HH}$ 3.7	6.54 (d) $^3J_{HH}$ 3.7		4.99 (q), 4.88 (q) 5.02 (q), 4.82 (q) $^3J_{HH}$ 7.2	1.53 (t) $^3J_{HH}$ 7.1
2	5.95 (d) $^3J_{HH}$ 3.8	5.79 (t) $^3J_{HH}$ 3.8	6.49 (d) $^3J_{HH}$ 3.7		4.83 (q), 4.77 (q) 4.89 (q), 4.72 (q) $^3J_{HH}$ 7.2	1.51 (t) $^3J_{HH}$ 7.1
3	5.81 (d)	5.75 (t)	6.54 (d)		4.97 (t), 4.96 (t) 5.02 (t), 4.89 (t) $^3J_{HH}$ 6.3	3.47 (t), 3.49 (q), 2.02–1.93 (m), 1.78–1.69 (m), 1.21 (t)
4	5.89 (d)	5.75 (t)	6.48 (d)		4.80 (t), 4.77 (t) 4.83 (t), 4.74 (t)	3.47 (q), 3.46 (t), 2.00–1.91 (m), 1.87–1.72 (m), 1.20 (t)
5	7.67 (d)	7.21 (t)	8.24 (d)		5.13 (t)	3.51 (t), 3.48 (q), 2.11 (q), 1.83 (q), 1.20 (t)
6	7.79 (d)	7.20 (t)	8.14 (d)		4.95 (t)	3.51 (t), 3.47 (q), 2.09 (q), 1.84 (q), 1.20 (t)
7	8.14 (s)			6.29 (d), 6.07 (d), 5.24 (dt), 5.62 (dt)	5.20 (q)	1.68 (t)
8	8.47 (s)			7.97 (d), 7.78 (d), 7.47 (dt), 7.39 (dt)	5.24 (q)	1.71 (t)

Table 3 Carbon-13 NMR data[a] for complexes **1–4**, **7** and **8**

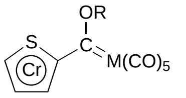
Complex	δ $M(CO)_5$	$M(CO)_3$	C_{carb}	Thienyl[b]	Other
1	222.2 (*trans*)	232	312.3	108.8, 93.5, 88.1,	76.6
	215.8 (*cis*)		268.8	6.8	15.1
2	201.6 (*trans*)	232.6	311.2	111.8, 93.1, 88.4,	78.2
	196.4 (*cis*)		285.7	7.8	14.9
3	222.1 (*trans*)	232.4	312.8	123.5, 93.0, 83.3,	83.2, 69.9
	216.9 (*cis*)		303.5	6.5	66.3, 29.4, 29.4, 15.4
4	201.7 (*trans*)	232.5	312.0	113, 92.8, 88.1,	82.1, 69.6
	196.6 (*cis*)		—	7.4	66.2, 26.2, 26.2, 15.1
7	223.3 (*trans*)	231.4	318.1	167.0, 138.0, 124.0,	92.3, 84.3
	216.5 (*cis*)			106.0	89.8, 88.9, 76.6, 15.1
8	222.0 (*trans*)	—	320.1	176.0, 155.1, 139.0,	126.7, 122.8
	216.9 (*cis*)			128.9	125.0, 123.5, 76.6, 15.1

[a] Recorded in $CDCl_3$. [b] Thienyl carbons are given in the sequence C^2 to C^5.

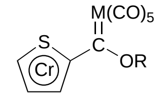
Table 4 Selected bond lengths (Å)* and bond angles (°) for complex **2**

W–C(5) (carbene)	2.173(9)	C(1)–S–C(4)	90.6(5)
W–C (carbonyl) *trans*	2.011(15)	S–C(4)–C(3)	111.8(7)
cis	2.039(15)	S–C(4)–C(5)	117.3(7)
Cr–C (carbonyl)	1.858(13)	C(1)–C(2)–C(3)	112.7(9)
Cr–C(1)	2.176(10)	C(2)–C(3)–C(4)	112.1(8)
Cr–C(2)	2.205(10)	S–C(1)–C(2)	112.4(7)
Cr–C(3)	2.183(9)	C(3)–C(4)–C(5)	131.0(8)
Cr–C(4)	2.152(9)	C(4)–C(5)–O(1)	104.2(7)
Cr–S	2.360(3)	W–C(5)–C(4)	124.6(6)
C(1)–C(2)	1.420(15)	W–C(5)–O(1)	131.2(6)
C(2)–C(3)	1.416(13)	C(5)–O(1)–C(7)	122.7(8)
C(3)–C(4)	1.404(13)	C(21)–Cr–C(31)	91.8(5)
S–C(1)	1.726(11)	C(11)–Cr–C(31)	91.3(5)
S–C(4)	1.780(9)	C(11)–Cr–C(21)	90.9(6)
C(4)–C(5)	1.499(13)	C(5)–W–C(41)	93.8(4)
C(5)–O(1)	1.311(11)	C(5)–W–C(61)	92.5(4)
C(7)–O(1)	1.458(12)	C(5)–W–C(71)	91.0(4)
		C(5)–W–C(81)	89.6(4)

* Carbonyl distances are averaged values.



A



B

(Cr) = $Cr(CO)_3$; M = W or Cr

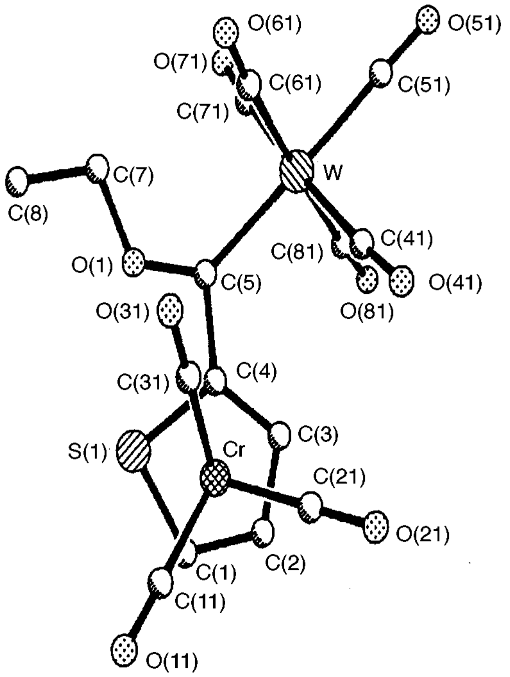


Fig. 1 Molecular structure of complex **2** with the atom numbering scheme

ring has been greatly reduced and the signal appears as a slightly broadened quartet. The $Cr(CO)_3$, $Cr(CO)_5$ and $W(CO)_5$ chemical shifts in the ^{13}C NMR spectra are insensitive to changes in substituents and compare well with those reported.[22] As is the case for the ^1H NMR chemical shifts, the ^{13}C shifts of the thienyl carbons are downfield (*ca.* 40 ppm) for the π-co-ordinated thienyl complexes **1–4** compared to monocarbene thienyl complexes.[15]

Crystal structure

The crystal structure of complex **2** was determined and selected bond distances and angles are given in Table 4. Fig. 1 displays the molecular structure with the atom labelling used. The molecular structure shows the typical three-legged piano-stool arrangement for the thienyl ring and $Cr(CO)_3$ fragment linked *via* the carbene unit to an octahedrally co-ordinated tungsten centre. Although relatively crowded, the carbonyl ligands are orientated in their normal, electronically favoured positions. The $Cr(CO)_3$ tripod is arranged with one of the carbonyl ligands *trans* to the thienyl sulfur[23] and three of the four *cis*-carbonyl ligands of the $W(CO)_5$ fragment displaced marginally out of the plane, away from the carbene ligand. The thienyl ring is planar and the ring carbons are at approximately equal distances from the chromium with the *ipso*-carbon closest and the adjacent carbon furthest away from the chromium. The only sign of possible crowding is found in a relative long W–C (carbene) bond distance of 2.17 Å which is significantly longer than the corresponding distance of 2.05 Å in $[W\{C(OMe)Ph\}(CO)_5]$,[24] but shorter than the corresponding distance of 2.23 Å recorded for a similarly crowded σ,π-bimetallic complex $[(OC)_5W\{C(OEt)C_5H_4\}Ru(C_5H_5)]$.[25] The C (carbene)-O bond of 1.311(11) Å is significantly shorter than the O(1)–C(7) distance of 1.458(12) Å. The three C–C distances in the ring are the same, indicating delocalization of electron density in the ring. By contrast, free thiophene displays localized bonds with two exhibiting double-bond character (1.370 Å) and one single-bond character (1.424 Å).[26]

Experimental

All reactions were performed under an inert atmosphere using standard Schlenk-tube techniques.[27] Solvents were dried by the usual procedures and distilled under nitrogen prior to use. The starting materials, $[Cr(CO)_6]$, $[W(CO)_6]$, LiBu and benzo[*b*]thiophene, were used as obtained from Aldrich and thiophene was purified as described previously.[28] The starting compounds were prepared according to literature methods, $[Cr(NH_3)_3(CO)_3]$,[11]

$[Cr(SC_4H_4)(CO)_3]$,[12] $[Cr(SC_8H_6)(CO)_3]$[14] and triethyloxonium tetrafluoroborate.[29] Column chromatography was performed on silica gel (0.063–0.200 mm) and the column cooled by recycling (−20 °C) Pr^{i}OH through the column jacket. The NMR spectra were recorded at −20 °C on a Bruker AC-300 spectrometer with reference to the deuterium signal of the solvent employed; ^{1}H and ^{13}C spectra were measured at 300.135 and 75.469 MHz, respectively, unless specified otherwise. The NMR solvents were degassed by several freeze–pump–thaw cycles, and NMR sample tubes sealed under nitrogen. Infrared spectra were recorded as liquid solutions on a Bomem Michelson-100 FT spectrophotometer, and wavenumbers (cm^{-1}) were assigned relative to a polystyrene standard. Mass spectra were recorded on a Perkin-Elmer RMU-6H instrument operating at 70 eV (*ca.* 1.12×10^{-17} J). Elemental analyses were obtained from the Analytical Division (PCMT) of the Council for Scientific and Industrial Research, Pretoria, South Africa. Melting points were recorded in capillaries on a Gallenkamp hot-stage apparatus and are uncorrected.

Preparations

$[Cr\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ 1, $[Cr\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ 3 and $[Cr\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ 5. The dropwise addition a 1.6 mol dm^{-3} hexane solution (4–5 cm^3) of LiBu (5.5 mmol) to a cooled (−50 °C) thf solution (60 cm^3) containing $[Cr(SC_4H_4)(CO)_3]$ (1.09 g, 5 mmol) afforded the lithiated thienyl complex in high yields after 30 min. Addition of $[Cr(CO)_6]$ (1.1 g, 5 mmol) in small portions over 10 min resulted in a gradual change from yellow to dark red-brown. After stirring for 30 min in the cold, the reaction mixture was warmed to room temperature and stripped of solvent under reduced pressure. The brown residue was washed several times with hexane, redissolved in dichloromethane, cooled to −30 °C and carefully treated with Et_3OBF_4 (0.91 g, 5.0 mmol) dissolved in dichloromethane (20 cm^3). After stirring for 1 h and allowing the reaction mixture to warm to room temperature, the cerise pink solution was filtered through silica gel and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel (0.063–0.200 nm) and five bands separated. The first yellow product was the known mononuclear carbene complex $[Cr\{C(C_4H_3S)(OEt)\}(CO)_5]$ (0.1 g, 10.1%). The second product, yield 0.55 g (50.2%), was purple and was identified as the σ,π-bimetallic carbene complex $[Cr\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ **1**. The third orange band gave unchanged starting complex (0.06 g, 5.2%), and the fourth orange product was identified as the modified mononuclear carbene complex $[Cr\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ **5** (0.1 g, 10.1%). The last blue band was characterized as the modified σ,π-carbene complex $[Cr\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ **3** (0.2 g, 20.5%). The yield of **3** was increased to 30% by stirring the thf reaction mixture at room temperature for 2 h.

Complex **1** (Found: C, 33.35; H, 2.70. $C_{15}H_8Cr_2O_9S$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 468 (M^+), 328 ($M^+ - 5CO$) and 244 ($M^+ - 8CO$). Complex **3** (Found: C, 33.35; H, 2.7. $C_{19}H_{16}Cr_2O_{10}S$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 540 (M^+), 400 ($M^+ - 5CO$) and 316 ($M^+ - 8CO$). Complex **5** (Found: C, 33.35; H, 2.7. $C_{16}H_{16}Cr_2O_7S$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 407 (M^+) and 267 ($M^+ - 5CO$).

$[W\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ 2, $[W\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ 4 and $[W\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ 6. A 1.6 mol dm^{-3} solution (8.4 cm^3) of butyllithium (13.5 mmol) in hexane was added to a solution (30 cm^3) of $[Cr(SC_4H_4)(CO)_3]$ (2.70 g, 12.3 mmol) in thf. The reaction was effected in the same manner as for the chromium analogue with the addition of $[W(CO)_6]$ (4.32 g, 12.4 mmol) and the alkylation done with triethyloxonium tetrafluoroborate (2.26 g, 13.9 mmol). Five compounds analogous to the chromium products above were purified by column chromatography and fully characterized: known yellow mononuclear carbene complex $[W\{C(C_4H_3S)(OEt)\}(CO)_5]$, yield 0.46 g (10.7%), blue σ,π-carbene complex $[W\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]OEt\}(CO)_5]$ **2**, yield 2.26 g (54.6%), unreacted starting material (0.2 g, 5.1%), the carbene complex $[W\{C(C_4H_3S)O(CH_2)_4OEt\}(CO)_5]$ **6**, yield 0.4 g (10.2%), and the σ,π-carbene complex $[W\{C[\eta^5\text{-}C_4H_3SCr(CO)_3]O(CH_2)_4OEt\}(CO)_5]$ **4**, yield 0.8 g (18.6%). The yield of **4** was increased by stirring the thf reaction mixture at room temperature for 2 h.

Complex **2** (Found: C, 33.35; H, 2.7. $C_{15}H_8CrO_9SW$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 599 (M^+), 459 ($M^+ - 5CO$) and 375 ($M^+ - 8CO$). Complex **4** (Found: C, 33.35; H, 2.7. $C_{19}H_{16}CrO_{10}SW$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 671 (M^+), 531 ($M^+ - 5CO$) and 477 ($M^+ - 8CO$). Complex **6** (Found: C, 33.35; H, 2.7. $C_{16}H_{16}CrO_7SW$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 535 (M^+) and 395 ($M^+ - 5CO$).

$[Cr\{C[\eta^6\text{-}C_8H_5SCr(CO)_3]OEt\}(CO)_5]$ 7 and $[Cr\{C(C_8H_5S)OEt\}(CO)_5]$ 8. Benzo[*b*]thiophene (0.42 g, 2.2 mmol) was dissolved in thf, the solution cooled to −50 °C and butyllithium (1.4 cm^3, 2.2 mmol) was added to the stirred solution. The mixture was stirred for 30 min after which it was cooled to −70 °C, and $[Cr(CO)_6]$ (0.48 g, 2.2 mmol) was added, upon which the solution changed to dark red. The temperature was allowed to rise to −50 °C and stirred at this temperature for 2 h. The solvent was removed under reduced pressure and the residue redissolved in dichloromethane. The stirred solution was cooled to −30 °C and triethyloxonium tetrafluoroborate (0.40 g, 2.2 mmol) dissolved in dichloromethane was added. The solution was stirred at room temperature for 30 min during which time it changed to a dark purple. It was filtered through silica gel and the solvent was removed under reduced pressure. An almost quantitative yield of 0.45 g (95.2%) of $[Cr\{C[\eta^6\text{-}C_8H_5SCr(CO)_3]OEt\}(CO)_5]$ **7** and 0.013 g (3.1%) of an orange product, $[Cr\{C(C_8H_5S)OEt\}(CO)_5]$ **8**. The yield of **8** could be increased by stirring a thf solution of **7** for 24 h at room temperature.

Complex **7** (Found: C, 33.35; H, 2.7. $C_{18}H_{10}Cr_2O_9S$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 468 (M^+), 328 ($M^+ - 5CO$) and 244 ($M^+ - 8CO$). Complex **8** (Found: C, 33.35; H, 2.7. $C_{15}H_{16}CrO_{10}S$ requires C, 33.95; H, 2.4%): mass spectrum *m/z* 540 (M^+), 400 ($M^+ - 5CO$) and 316 ($M^+ - 8CO$).

Crystallography

Purple crystals of complex **2**, grown from dichloromethane–hexane mixtures, were suitable for single-crystal X-ray diffraction studies. A dark plate single crystal of approximate size 0.40 × 0.15 × 0.05 mm was mounted on a glass fibre. All geometric and intensity data were taken from this sample using an automated four-circle diffractometer (Nicolet R3mV) equipped with Mo-Kα radiation ($\lambda = 0.710\,73$ Å). Important crystallographic parameters are summarized in Table 5.

The lattice vectors were identified by application of the automatic indexing routine of the diffractometer to the positions of 28 reflections taken from a rotation photograph and centred by the diffractometer. The ω–2θ technique was used to measure 3666 reflections (3313 unique) in the range $5 \leqslant 2\theta \leqslant 50°$. Three standard reflections (remeasured every 97 scans) showed no significant loss in intensity during data collection. The data were corrected for Lorentz-polarization effects, and empirically for absorption. The 2460 unique data with $[I \geqslant 3.0\sigma(I)]$ were used to solve and refine the structure in the triclinic space group $P\bar{1}$.

The structure was solved by Patterson methods and developed by using alternating cycles of least-squares refinement and Fourier-difference synthesis. The non-hydrogen atoms were refined anisotropically while hydrogens were placed

Table 5 Crystal and data-collection parameters for complex **2**

Formula	$C_{15}H_8CrO_9SW$
Crystal symmetry	Triclinic
Space group	$P\bar{1}$
a/Å	6.938(2)
b/Å	10.855(4)
c/Å	12.847(3)
α/°	88.92(2)
β/°	82.39(2)
γ/°	86.44(2)
U/Å^3	957
Z	2
F(000)	568
D_c/g cm^{-3}	2.08
μ(Mo-Kα)/cm^{-1}	68.2
no. Orientation reflections	28
2θ Range/°	14–24°
T/K	293
Data measured	3666
Unique data	3313
No. unique with $I \geqslant 3.0\sigma(I)$	2460
No. parameters	244
R^a	0.0409
R'^b	0.0435
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.000\,961F^2$
Largest shift/e.s.d. in final cycle	0.001
Largest peak/e Å^{-3}	0.6

[a] $R = \Sigma||F_o| - F_c||\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

in idealized positions (C−H 0.96 Å) and assigned a common isotropic thermal parameter ($U = 0.08$ Å^2). The final cycle of least-squares refinement included 244 parameters for 2460 variables [weighting scheme applied: $w^{-1} = \sigma^2(F) + 0.000\,961\,F^2$] and did not shift any parameter by more than 0.001 times its standard deviation. The final $R = 0.0409$ and $R' = 0.0435$, and the final Fourier-difference map was featureless with no peaks greater than 0.60 e Å^{-3}. Structure solution used the SHELXTL PLUS program package[30] on a microVax II computer.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/473.

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