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Synthesis and X-Ray Structure Determination of the First Chelated Phenylsulfinyl Fischer Carbene Complex

Roy L. Beddoes, James E. Painter, and Peter Quayle*[a]

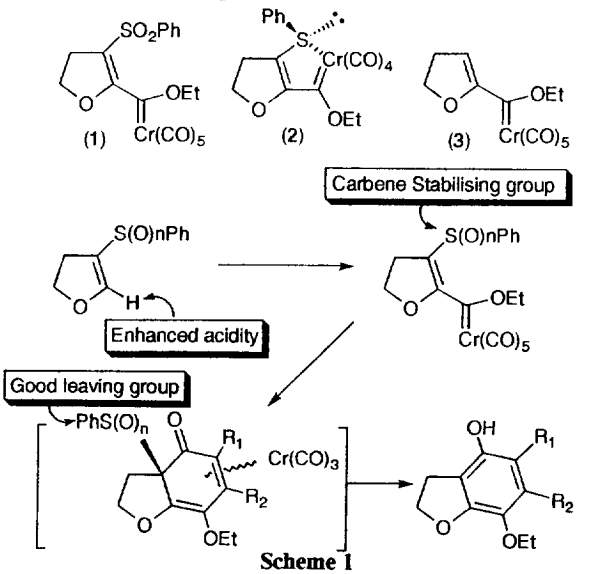
Department of Chemistry.
The Victoria University of Manchester.
Manchester M13 9PL. UK.

Prakash Patel

Zeneca Specialties.
PO Box 42. Hexagon House.
Blackley, Manchester M9 8ZS. UK.

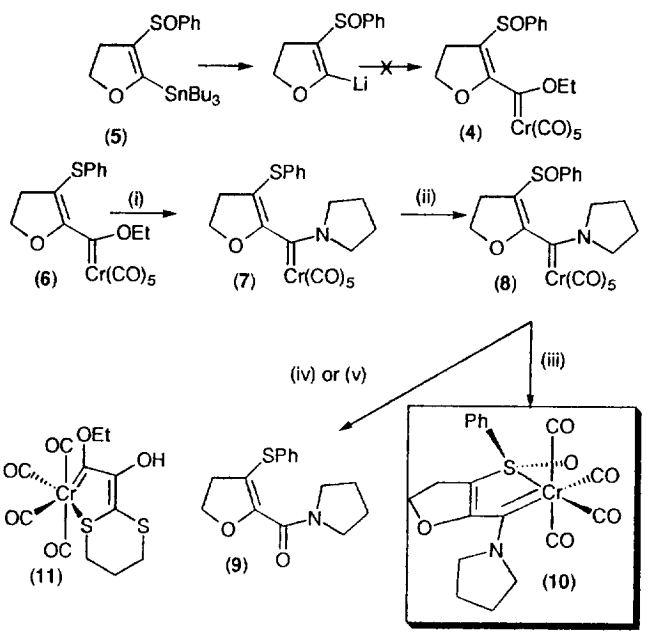
Abstract: Chemoselective oxidation of the phenylthio-substituted Fischer carbene complex (**7**) generates the corresponding sulfinyl complex (**8**) in high yield, which upon mild thermolysis affords the chelated tetracarbonyl complex (**10**). The structure of both (**8**) and (**10**) have been unambiguously assigned by single crystal X-ray diffraction studies. © 1997 Elsevier Science Ltd.

During the course of our recent investigations into the use of Fischer carbene complexes in organic synthesis[1] we have shown that the phenylsulfonyl complex (**1**) and the chelated thioether complex (**2**) provide a practical alternative to the parent carbene complex (**3**) in Dötz benzannulation reactions[2a]. In our modification[2a] of the Dötz reaction we have purposefully incorporated a β - sulfur substituent[2b] into the carbene component which not only facilitates formation and isolation of the carbene complexes but also acts as a leaving group in the final aromatisation step of the benzannulation sequence, **Scheme 1**.



Scheme 1

Further studies have naturally focused upon the preparation of the sulfinyl complex (**4**), which at the outset was deemed to be unstable with respect to oxidation at the metal centre. The preparation of sulfenyl and sulfonyl substituted transition metal complexes is an area of much current interest,[3] although there is only one report[2,4] concerning the preparation of Fischer carbene complexes substituted in this manner. Attempts to prepare the carbene complex (**4**) from (**5**) using the standard Fischer protocol[5] ((i) n-BuLi, THF, -78 °C; (ii) $Cr(CO)_6$, THF, -78 °C to 0 °C; (iii) Et_3OBF_4, H_2O) afforded a complex mixture of products. Likewise, oxidation of the thioether complex (**6**) with oxidising agents such as MCPBA afforded intractable reaction mixtures. Given that aminocarbene complexes have been observed to be more stable than the corresponding alkoxycarbene complexes,[6] oxidation of the pyrrolidino complex (**7**) was next attempted.



Reagents and conditions: (i) Pyrrolidine, 2 eq., CH_2Cl_2, 20 °C, 79%; (ii) a. MCPBA, 1 eq., CH_2Cl_2, -78 °C, ~ 100%; b. DMDO, 1.1 eq., THF, -78 °C, 57%; (iii) Δ, PhH, 70 °C, 56%; (iv) H_2O_2, MeOH-CH_2Cl_2, 78%; (v) DMSO, 40 °C, 84%.

Scheme 2

Exposure of the complex (**6**) to pyrrolidine (2 eq.; CH_2Cl_2; 20 °C) generated the pyrrolidino complex (**7**) as an air-stable, crystalline solid (m.pt. 103-105 °C) in 79% yield after column chromatography. Gratifyingly, treatment of the pyrrolidino complex (**7**) with MCPBA (1.1 eq.; CH_2Cl_2; -78 °C; 1.5 hrs.) afforded the sulfinyl complex (**8**) as a flaky orange-red crystalline solid (m.pt. 106-108 °C) in essentially quantitative yield after purification by column chromatography, **Scheme 2**. The identity of the sulfinyl complex (**8**) was established upon the basis of spectroscopic measurements, and finally by way of a single crystal X-ray analysis , **Figure**

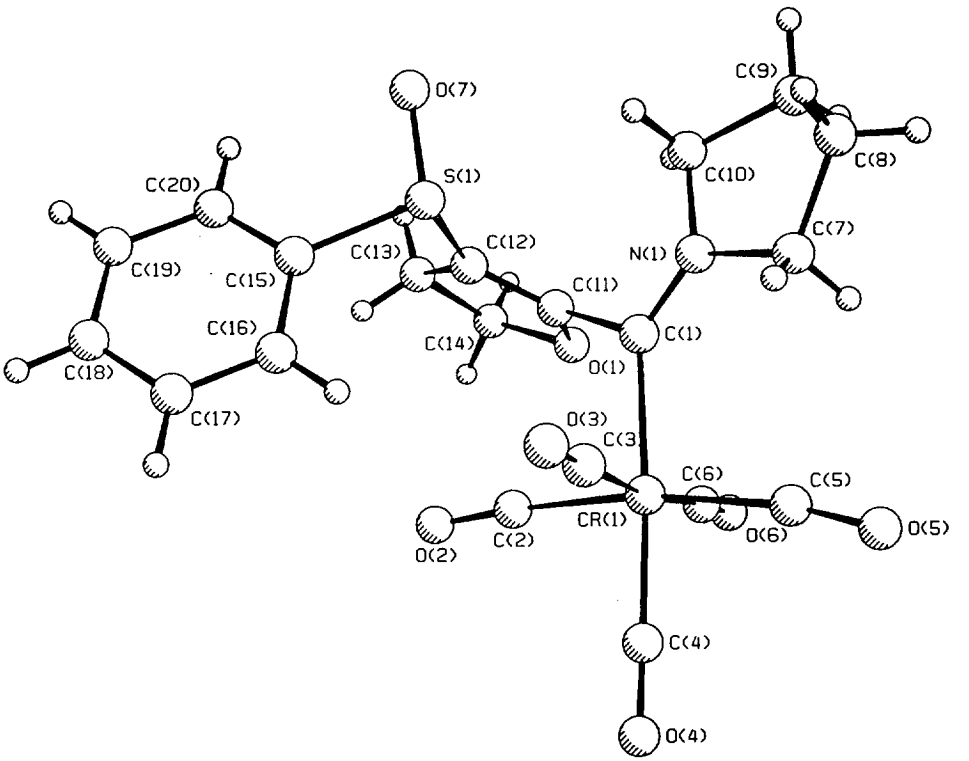
1. The X-ray crystal structure (pertinent experimental details are listed below in the **Table**) clearly demonstrates that oxidation at sulfur had taken place, that the S_1 - O_7 bond is almost antiperiplanar with respect to the Cr_1 - C_1

	Complex (8)	**Complex (10)**
Empirical Formula	$C_{20}H_{17}CrNO_7S$	$C_{19}H_{17}CrNO_6S$
Formula weight	467.41	439.40
Crystal dimensions (mm)	0.20 x 0.30 x 0.40	0.03 x 0.45 x 0.50
Crystal system	monoclinic	monoclinic
Lattice parameters	a = 7.378(2) (Å) b = 12.368(2) (Å) c = 25.548 (Å) β = 94.53 (2)°	a = 10.248(3) (Å) b = 12.972(3) (Å) c = 14.692(7)(Å) β = 90.57(3)°
Space group	$p2_1/c$ (#14)	$p2_1/n$ (#14)
D_{calc}	1.449 g/cm^3	1.494 g/cm^3
Temperature	21 °C (± 1 °C)	19 °C (± 1 °C)
Scan type	ω/2θ	ω/2θ
Scan rate	8°/min.	8°/min.
$2\theta_{max}$	120.1°	120.2°
No. refelections measured	Total = 3639 unique = 3346	Total = 3251 unique = 3061
Ranges of h, k, l	-8 to 8; -11 to 13; -26 to 26	0 to 11; 0 to 14; -16 to 16
Solution structure	Direct methods	Direct methods
Refinement	Full-matrix least-squares	Full-matrix least-squares
Function minimized	$\Sigma w(\|Fo\| - \|Fc\|)^2$	$\Sigma w(\|Fo\| - \|Fc\|)^2$
Least-squares weights	$4Fo^2/\sigma^2(Fo^2)$	$4Fo^2/\sigma^2(Fo^2)$
No. observations (I>3.00 σ(I))	1619	1648
No. variables	272	253
R	0.104	0.072
R_w	0.110	0.076
Max. shift /error in final cycle	<0.01	0.01
Max. peak in final diff. map	0.59e$^-$/Å^3	0.42e$^-$/Å^3
Min. peak in final diff. map	-0.53e$^-$/Å^3	-0.66e$^-$/Å^3

Table

bond, with the plain containing the carbene moiety being essentially orthogonal to that containing the heterocyclic ring. In solution, the ^{13}C nmr spectrum of (**8**) at 20 °C is consistent with rapid rotation about the

Cr_1-C_1 bond giving rise to two resonances for the four carbon monoxide ligands (δ 222.9 (axial CO) and 216.8 (equatorial CO) ppm in a ratio of *ca.* 1:4).

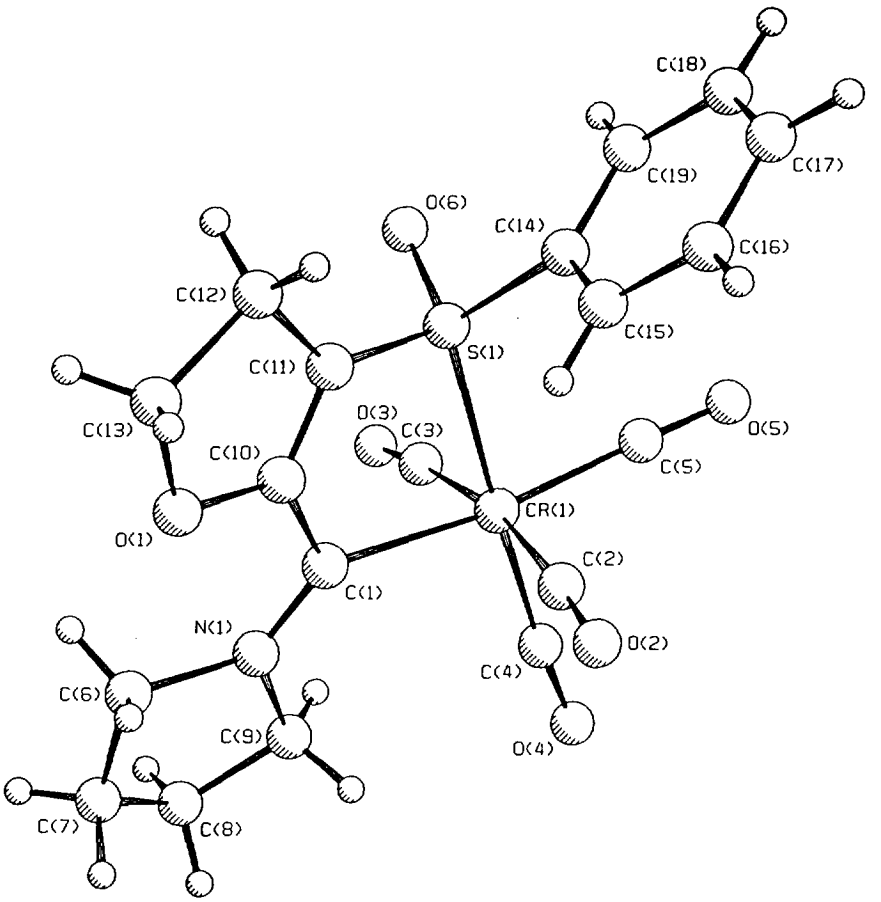


X - ray crystal structure of (**8**). Selected bond lengths (Å) and angles (°): N_1 - C_1 1.28(1), C_1 - Cr_1 2.09(1), C_1 - C_{11} 1.52(2), C_{12} - S_1 1.72(1), S_1 - O_7 1.48(1); Cr_1 - C_1 - N_1 134(1), Cr_1 - C_1 - C_{11} 114.0(9), C_{12} - S_1 - O_7 107.3(7). Torsion angles (°):O_7 - S_1 - C_{12} - C_{11} 117(1), C_{12} - C_{11} - C_1 - Cr_1 103(2).

Figure 1

Other oxidising agents were also screened and found effective in the oxidation of (**7**) to the sulfinyl complex (**8**). Dimethyldioxirane, a reagent which has been previously used to good effect for the selective *oxidative demetallation* of Fischer carbene complexes,[7] afforded the sulfinyl complex (**8**) in 57% isolated yield. The current interest in developing oxidation procedures which utilise a catalytic quantity of an active oxidising agent in conjunction with a stoichiometric re-oxidant[8] also led us to investigate the use of the Griffith-Ley TPAP-NMO reagent.[9] Unfortunately only minor amounts of the chelated complex (**2**) were isolated when adopting Kende's[10] procedure for sulfide oxidation using TPAP. Oxidation of (**7**) using hydrogen peroxide (1 eq. H_2O_2; MeOH-CH_2Cl_2 (1:1), 3 days, 20 °C) merely resulted in the formation of the amide (**9**) in 78% isolated yield. During the course of these oxidation reactions a second minor component (5-8%) was also isolated, which on the basis of spectroscopic measurements, was assigned as being the chelated sulfinyl complex (**10**). Indeed mild thermolysis of (**8**) in dry benzene for four hours led to the isolation of the stable, chelated complex

(10) as a red crystalline solid, (m.pt. with decomposition 157 °C). An unambiguous structural assignment in the case of **(10)** was obtained by way of a single crystal X-ray analysis, **Figure 2**.



X-ray crystal structure of **(10)**. Selected bond lengths (Å) and angles (°): N_1 - C_1 1.27(1), C_1 - Cr_1 2.13(1), C_1 - C_{10} 1.49(1), C_{11} - S_1 1.740(9), S_1 - O_6 1.479(7), Cr_1 - S_1 2.316(3); Cr_1 - C_1 - N_1 129.7(7), Cr_1 - C_1 - C_{10} 110.7(7), C_{11} - S_1 - O_6 111.1(5), C_1 - Cr_1 - S_1 95.7(3) . Torsion angle (°):O_6 - S_1 - C_{11} - C_{10} 112.0(8).

Figure 2

This X-ray study clearly demonstrates that the phenylsulfinyl moiety is bound to the chromium atom of the carbene through sulfur, having a S - Cr bond length of 2.316(3)Å with a $Cr_1S_1O_6$ bond angle of 120.1(3)°. These structural features should be compared to those of the related complex **(11)** which has a Cr -S bond length of 2.38Å.[11] The chromium atom in **(10)** adopts a distorted octahedral geometry, the bond angles around chromium falling between 82.0(3)° to 101.5(4)°. The S-O bond length does not appear to be significantly perturbed upon co-ordination to the chromium in **(10)** ((**8**), S-O bond length 1.479(7) Å; **(10)** S-O bond length

1.48(1) Å). In solution in $CDCl_3$ at 20 °C the ^{13}C nmr spectrum of (**10**) is, as to be expected, much more complex than in (**8**). In particular the equatorial carbon monoxide ligands in (**10**) are now no longer equivalent and combined with the remaining axial CO ligand appear as four signals of equal intensity at δ 229.7, 227.7, 219.8 and 217.8 ppm. In the ^1H nmr spectrum of (**10**), the allylic CH_2 protons appear as a well dispersed AB system at 3.02 ppm (1H, ddd, J = 16, 10, 9, Hz) and 2.57 ppm (1H, ddd, J = 16, 10, 9, Hz), which is similar to the appearance of this methylene group in the sulfinyl complex (**8**) (δ 2.95 ppm, 1H, ddd, J = 16, 10, 9 Hz; δ 2.40 ppm, overlapping multiplet). The chelated thioether complex (**2**) also possess a stereogenic centre, that at sulfur. However, both the ^1H and ^{13}C nmr spectra of (**2**) at 20 °C suggest that there is rapid inversion at sulfur[12a]: the allylic methylene group appears as a pseudo triplet at 2.90 ppm with the carbon monoxide ligands in the ^{13}C spectrum appearing as three signals[12b] at δ 232.2; 231.1 and 216.4 ppm. Unfortunately all attempts to conduct variable temperature nmr experiments on these compounds has so far been hampered by excessive line broadening.

The formation of (**10**) from (**8**) and its stability in the solid state is notable given that dimethylsufoxide is commonly used as a decomplexing agent in the conversion of aminocarbene complexes to amides.[13] Indeed, in a blank experiment dissolution of the complex (**7**) in DMSO at 40 °C for 4 days resulted in the isolation of the amide (**9**) in 84% yield.

In conclusion we have demonstrated the kinetic stability of phenylsulfinyl substituted Fischer carbene complexes and report the first example of an internally co-ordinated complex. The structural identity of these complexes has been conclusively established by single crystal X-ray diffraction analysis.

Experimental

All reactions, except oxidation reactions, were carried out under an atmosphere of dry argon or nitrogen. Melting points (m.pt.) were obtained on a Kofler block and are uncorrected. Infrared spectra (IR) were recorded on a ATI Mattson Genesis FTIR; proton nuclear magnetic resonance spectra were recorded on a Gemini 200 (at 200MHz), a Bruker AC300 or a Varian XL300 (at 300MHz); ^{13}C nuclear magnetic resonance spectra were recorded on a Gemini 200 (at 50MHz), a Bruker AC300 or a Varian XL300 (at 75MHz). All spectra were recorded in deuterated chloroform or dichloromethane and referenced to a residual solvent peak. Mass spectra were recorded on a Kratos Concept or a Fisons VG Trio 2000. Chemical ionisation (CI) was performed using NH_3. Combustion microanalyses were conducted in the microanalytical laboratory at the University of Manchester Chemistry Department. Thin layer chromatography (TLC) was carried out using Polygram G/UV_{254} pre-coated plastic plates. Visualisation was achieved by ultraviolet irradiation and by development in an ethanolic solution of dodecamolybdophosphoric acid. "Flash" column chromatography was carried out using the solvent system indicated using Silica Gel 60 230-400 mesh as the stationary phase. Tetrahydrofuran (THF) was dried by refluxing over sodium metal, using benzophenone as an indicator. Dichloromethane (DCM) was freshly redistilled from phosphorus pentoxide. Petroleum ether, 40-60 fraction, was redistilled prior to use. t-Butyllithium (1.7M soln. in hexanes) and n-butyllithium (1.6M soln. in hexanes) were purchased from Aldrich.

[(Ethoxy)({3-phenylthio}4,5-dihydrofuran-2-yl)carbene]pentacarbonylchromium (6)

To a solution of 3-phenylthio-4,5-dihydrofuran[14] (**1**) (10.052g, 56.5mmol) in dry THF (150ml) at -78 °C argon was cautiously added t-butyllithium (33ml, 1.7M soln. in hexane, 56.1mmol). The reaction mixture was stirred at -78 °C temperature for 35 minutes before the addition of chromium hexacarbonyl (12.501g, 57.0mmol). The mixture was allowed to warm up to 20 °C and stirred at this temperature for 2 hours, at which time the solvent was concentrated *in vacuo*, followed by addition of degassed DCM (150ml) and degassed water (150ml). Triethyloxonium tetrafluoroborate (10.803g, 56.9mmol) was then added and the deep red organic phase was separated and dried ($MgSO_4$). The solvent was removed *in vacuo* at room temperature and the residue purified (flash silica, 1% EtOAc/ petrol 40/60 eluent) affording the *title compound* as a waxy red solid (12.359g, 53%).

^{1}H NMR, δ (ppm): (300MHz, $CDCl_3$) 7.65 (2H, m, Ar); 7.40 (3H, m, Ar); 5.20 (2H, q, *J*=7Hz, $OC\underline{H}_2CH_3$); 4.30 (2H, t, *J*=9Hz, ring $C\underline{H}_2O$); 2.65 (2H, t, *J*=9Hz, ring $C\underline{H}_2$-C=C); 1.80 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$). **^{13}C NMR, δ (ppm):** (50MHz, CD_2Cl_2) 313.1; 225.7; 157.7; 153.1; 135.0; 130.0; 129.8; 127.6; 120.6; 77.1; 68.1; 37.4; 16.1. **IR υ_{max} (cm^{-1}):** (EF) 2056 (m); 1987 (w); 1920 (s). **MS:** (CI, NH_3, MW=426) 427 (M^++1, 48%); 426 (M^+, 2%). **MM:** (EI) $C_{18}H_{14}O_7CrS$ requires 426.9944; found 426.9949.

[(Ethoxy)({3-phenylthio}4,5-dihydrofuran-2-yl)carbene]tetracarbonylchromium (2)

A solution of carbene (**6**) (1.605g, 3.8mmol) in dry benzene (40ml) was brought to reflux under argon for 3 hours. After cooling to ambient temperature the solvent was removed *in vacuo* to afford a deep purple residue. Purification of this residue (flash silica, 8% EtOAc/ petrol 40/60 eluent) afforded the *title compound* as a waxy purple solid (1.145g, 76%).

^{1}H NMR, δ (ppm): (300MHz, $CDCl_3$) 7.40 (5H, m, Ar); 5.20-4.95 (4H, m, $OC\underline{H}_2CH_3$ + ring CH_2O); 2.90 (2H, t, *J*=9Hz, ring $C\underline{H}_2$-C=C); 1.70 (3H, t, *J*=7Hz, $OCH_2C\underline{H}_3$). **^{13}C NMR, δ (ppm):** (50MHz, CD_2Cl_2) 320.8; 232.2; 231.1; 216.4; 173.6; 135.0; 134.4; 130.3; 128.6; 128.5; 78.6; 77.5; 32.4; 15.5. **IR υ_{max} (cm^{-1}):** (EF) 2014 (m); 1909 (s); 1858 (s); 1251 (m). $C_{17}H_{14}O_6CrS$ requires C 51.3%, H 3.5%, S 8.0%; found C 52.4%, H 3.8%, S 7.5%.

[(Pyrrolidino({3-phenylthio}4,5-dihydrofuran-2-yl)carbene]pentacarbonylchromium (7)

To a solution of carbene (**6**) (0.270g, 0.63mmol) in dry DCM (20ml) under argon at 20 °C was added pyrrolidine (0.1ml, 1.2mmol) and the mixture stirred at this temperature for 15 minutes. The solvent was then removed *in vacuo* and the resultant orange/brown residue purified (flash silica, 10% DCM/ petrol 40/60 eluent) to afford the *title compund* as a yellow crystalline solid (0.225g, 79%); m.pt. 103-105 °C .

^{1}H NMR, δ (ppm): (200MHz, $CDCl_3$) 7.35-7.10 (5H, m, Ar); 4.70 (1H, m, NC$\underline{H}$); 4.55 (1H, m, NC$\underline{H}$); 4.25-4.05 (2H, m, $NC\underline{H}_2$); 3.70 (2H, m, ring $C\underline{H}_2O$); 3.00-2.80 (2H, m, CH_2C=C); 2.25-1.95 (4H, m, 2x$NCH_2C\underline{H}_2$). **^{13}C NMR, δ (ppm):** (75MHz, $CDCl_3$) 257.9; 224.2; 217.8; 164.8; 135.6; 129.7; 128.4; 126.6; 90.6; 71.3; 59.7; 57.2; 34.6; 26.0;25.8. **IR, υ_{max} (cm^{-1}):** (EF) 2926 (w); 2056 (w); 1914 (s).

MS: (CI, NH_3, MW=451) 424 (M^+-CO+1, 12%); 396 (M^+-2xCO, 69%). (EI) 451 (M^+, 4%); 423 (M^+-CO, 14%); 395 (M^+-2xCO, 56%); 367 (M^+-3xCO, 15%); 339 (M^+-4xCO, 62%); 311 (M^+-5xCO, 26%). **MM:** (EI) $C_{20}H_{17}NO_6CrS$ requires 451.0260; found 451.0190. $C_{20}H_{17}NO_6CrS$ requires C 53.2%, H 3.8%, N 3.1%, S 7.1%; found C 52.84%; H 4.0%; N 3.0%; S 6.8%.

[(Pyrrolidino)({3-phenylsulfinyl}4,5-dihydrofuran-2-yl)carbene]pentacarbonylchromium (8)

a. Using MCPBA as oxidant.

To a solution of carbene (**7**) (0.502g, 1.11mmol) in DCM (15ml) under Ar at -78°C was added slowly a solution of MCPBA (0.202g, 1.17mmol of purified commercial material) in DCM (10ml) and the mixture stirred at this temp. for 1.5 hours. After being allowed to warm to RT, the solvent was removed *in vacuo* and the residue purified (flash silica, 30% EtOAc/ petrol 40/60 eluent) affording the *title compound* as a flaky orange/red solid (0.520g, 100%); m.pt. 106-108 °C.

^{1}H NMR, δ (ppm): (200MHz, $CDCl_3$) 7.65 (2H, m, Ar); 7.55 (3H, m, Ar); 4.70-4.50 (2H, m, ring $C\underline{H}_2O$); 4.45-4.10 (3H, m, $C\underline{H}NC\underline{H}_2$); 3.75 (1H, m, $NC\underline{H}$); 2.95 (1H, ddd, J = 16, 10, 9, Hz, ring $C\underline{H}C{=}C$); 2.45-2.06 (5H, m, 2x$NCH_2C\underline{H}_2$ + ring $C\underline{H}C{=}C$). **^{13}C NMR, δ (ppm):** (75MHz, $CDCl_3$) 256.0; 222.9; 216.8; 169.5; 141.9; 130.6; 129.1; 124.4; 103.2; 72.2; 59.6; 57.7; 26.5; 25.5; 25.3. **IR, υ_{max} (cm^{-1}):** (EF) 2056 (m); 1912 (s)

MS: (CI, NH_3, MW=467) 468 (M^++1, 26%); 452 (M^+-O+1, 50%); 424 (41%); 396 (M^+-pyrrolidine, 79%); 276 (100%). **MM:** (CI) $C_{19}H_{18}NO_6CrS$ (M^+-CO+H) requires 440.0260; found 440.0152. $C_{20}H_{17}NO_7CrS$ requires C 51.4%, H 3.7%, N 3.0%, S 6.7%; found C 51.5%, H 3.63%, N 3.27%, S 6.75%.

b. Using Davis oxaziridine as oxidant

To a solution of carbene (**7**) (95mg, 0.21mmol) in DCM (5ml) under argon at 20 °C was added a solution of (1R)-(-)-(10-camphorsulfonyl)oxaziridine (48mg, 0.21mmol) in DCM (2ml) and the mixture stirred at this temperature for 3 days. TLC showed only a small amount of starting material had been converted to desired product. The solvent was removed *in vacuo* and the *title compound* isolated (flash silica, 30% EtOAc/ petrol 40/60 eluent), (11.7mg, 12%).

c. Using dimethyldioxirane as oxidant.

To a solution of carbene (**7**) (0.139g, 0.31mmol) in dry THF (8ml) at -78°C under argon was added a freshly prepared solution of dimethyldioxirane in acetone[15] (6.7ml, approx. 0.05M soln., approx. 0.32mmol). This mixture was stirred at -78 °C for 1.5 hours, then allowed to warm to RT before being washed with sat. sodium metabisulphite solutionn (10ml). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo* and the residue purified (flash silica, 30% EtOAc/ petrol 40/60 eluent) affording the *title compound* (82mg, 57%).

[(Pyrrolidino)({3-phenylsulfinyl}4,5-dihydrofuran-2-yl)carbene]tetracarbonylchromium (10)

A solution of carbene (**8**) (0.116g, 0.25mmol) in dry benzene (8ml) was brought to reflux under argon for 4 hours, allowed to cool to ambient temperature and then concentrated *in vacuo*. The residue was purified

(flash silica, 40% EtOAc/ petrol 40/60 eluent) affording the *title compound* as a red solid (61mg, 56%). Decomposes at 157 °C.

^{1}H NMR, δ (ppm): (200MHz, $CDCl_3$) 7.75 (2H, m, Ar); 7.55 (3H, m, Ar); 5.0 (2H, m, ring $C\underline{H}_2O$); 4.25 (2H, m, $C\underline{H}_2N$); 4.00 (2H, m, $C\underline{H}_2N$); 3.02 (1H, ddd, J = 16, 10, 9, Hz, ring $C\underline{H}C{=}C$); 2.57 (1H, ddd, J = 16, 10, 9, Hz, ring $C\underline{H}C{=}C$); 2.15 (4H, m, $2xNCH_2C\underline{H}_2$). **^{13}C NMR, δ (ppm):** (75MHz, $CDCl_3$) 250.1, 229.7, 227.7, 219.8, 217.8, 173.4, 145.1, 141.0, 131.3, 129.5, 125.0, 78.2, 64.3, 59.0, 27.0, 26.0, 24.9. **IR, υ_{max} (cm^{-1}):** (EF) 2011 (m); 1893 (s); 1858 (s); 1501 (w); 1441 (w). **MS:** (CI, NH_3, MW=439) 457 (M^++NH_4^+, 3%); 440 (M^++1, 3%); 396 (M^+-O-CO, 24%). **MM:** (EI) $C_{19}H_{17}NO_6CrS$ (M^+) requires 439.0182; found 439.0176.

[(Pyrrolidino)({3-phenyltio}4,5-dihyrofuran-2-yl)carbene]tetracarbonylchromium (12)

A solution of carbene (7) (0.317g, 0.7mmol) in dry benzene (20ml) was heated at reflux under Ar for 3 hours after which time the solvent was removed *in vacuo* and the residue purified (flash silica; 10% DCM/ petrol 40/60 eluent) to afford the *title compound* as an oily red solid (0.202g, 68%).

^{1}H NMR, δ (ppm): (200MHz, $CDCl_3$) 7.40 (5H, m, Ar); 4.85 (2H, m, ring $C\underline{H}_2O$); 4.30 (2H, m, $NC\underline{H}_2$); 4.00 (2H, m, $NC\underline{H}_2$); 2.80 (2H, m, ring $C\underline{H}_2C{=}C$); 2.05 (4H, m, $2xNCH_2C\underline{H}_2$). **^{13}C NMR, δ (ppm):** (75MHz, $CDCl_3$) 250.8, 231.5, 229.6, 216.7, 169.8, 136.0, 131.2, 129.7, 128.8, 128.3, 75.8, 63.7, 58.0, 31.8, 27.0, 24.9. **MS:** (CI, NH_3, MW=423) 424 (M^++1, 6%); 396 (M^+-CO+1, 15%). (EI) 423 (M^+, 1%); 395 (M^+-CO, 7%); 339 (M^+-3xCO, 6%); 311 (M^+-4xCO, 65%). **MM:** (EI) $C_{19}H_{17}NO_5CrS$ requires 423.0233; found 423.0623.

X- Ray crystallography

Structure determinations[16] of (**8**) and (**10**) were conducted on a Rigaku AFCR X-ray diffractometer with graphite-monochromated CuKα radiation.

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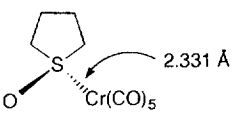

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