

Synthesis of Aromatic and Heteroaromatic Thioaldehydes, Aryl-thioenals, and -thiodienals as their η^1 Complexes with Pentacarbonyltungsten(o) by the Reaction of Aldimines and a new Reagent, $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$

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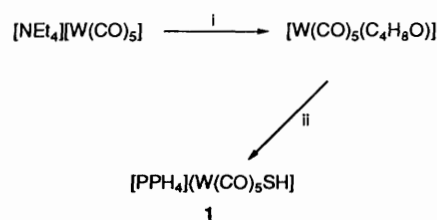
A new reagent, $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ **1** for the synthesis of pentacarbonyltungsten(o) complexes of thioaldehydes has been synthesised from $[\text{PPh}_4]\text{SH}$ and $[\text{W}(\text{CO})_5(\text{C}_4\text{H}_8\text{O})]$. The latter was formed conveniently by a nonphotochemical process. Treatment of each imine **2** with $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ **1** in the presence of equimolar mixture of $\text{BF}_3 \cdot \text{OEt}_2$ and MeCO_2H (2 equiv.) gave complexes of the thiobenzaldehydes **3a–j**, thionaphthaldehydes **4a–b**, thioanthraldehydes **5a–b**, 5-methyl-2-thioformylfuran **6**, 2-thioformylthiophenes **7a–c**, 4-substituted thiocinnamaldehydes **8a–c**, and 4-substituted thiocinnamylideneacetaldehydes **9a–c** with pentacarbonyltungsten(o) in high yields. NMR studies revealed that the above exist as η^1 complexes.

Approaches to the synthesis of simple aliphatic thioaldehydes and thiobenzaldehydes, have been unsuccessful in most cases except for heterocyclic¹ and enamino thioaldehydes.² The only four exceptions are 2,4,6-tri-*tert*-butyl-,³ and 2,4,6-tris[bis(trimethylsilyl)methyl]-thiobenzaldehyde,⁴ tris(trimethylsilyl)ethanethial,⁵ and di-*tert*-butylethanethial.⁶ Although Vedejs *et al.*⁷ synthesised thiopivaldehyde and characterised it as the first aliphatic thioaldehyde, it could not be isolated, owing to its polymerisation on removal of solvent. Several unstable thioaldehydes have been isolated as their metal complexes in recent years.⁸ However, η^1 complexes^{8a,b} which appear to have the properties characteristic of free thioaldehydes much more than η^2 complexes,⁹ have been the subject of very few reports. Since the stepwise synthesis of thioaldehyde complexes would result in polymerisation or decomposition, the formation of a thioaldehyde and its conversion into a complex must be simultaneous.

A possible method for simultaneous R-CHS generation and η^1 complex formation is the exposure of aldehydes or the corresponding imines to a combination of HS^- coordinated to a metal carbonyl, *i.e.* $[\text{M}(\text{CO})_x\text{SH}]^-$ and an appropriate super acid. Gingerich *et al.* developed such a process in which *para*-substituted benzaldehydes were treated with $[\text{N}(\text{Ph}_3\text{P})_2][\text{W}(\text{CO})_5\text{SH}]$ ^{8a} in the presence of $\text{CF}_3\text{SO}_3\text{H}$. They obtained three thiobenzaldehydes as their complexes in fair to low yield. It appears that very pure reagents, appropriate reaction conditions including the use of suitable super acids, and adequate and prompt work-up procedures may be required for the synthesis of the desired complexes. The drastic conditions for the preparation of $[(\text{PPh}_3)_2\text{N}][\text{W}(\text{CO})_5\text{SH}]$, which Gingerich *et al.* synthesised, led to impurities which were difficult to remove.

As a substitute compound for $[(\text{PPh}_3)_2\text{N}][\text{W}(\text{CO})_5\text{SH}]$, we synthesised a new reagent, $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ by the reaction of $[\text{PPh}_4]\text{SH}^\dagger$ and $[\text{W}(\text{CO})_5(\text{C}_4\text{H}_8\text{O})]$.[‡] The latter was prepared nonphotochemically by treatment of $[\text{NET}_4][\text{W}(\text{CO})_5\text{I}]$ with aqueous AgNO_3 in THF.§ $[\text{PPh}_4]$ -

$[\text{W}(\text{CO})_5\text{SH}]$, prepared in quantitative yield, is a stable crystalline compound easy to purify by recrystallisation. This method developed here for the synthesis of $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ **1** is very convenient for large-scale preparation in a short time without the need for any special equipment.



Scheme 1 Reagents and conditions: i, $\text{AgNO}_3\text{-H}_2\text{O}$, THF, room temp., 30 s (*ca.* 100%); ii, $[\text{PPh}_4]\text{SH-EtOH}$, THF, 20 °C, 30 s (95%)

Aromatic thioaldehyde pentacarbonyltungsten(o) complexes were synthesised best by treatment of *N*-phenyl or *N*-cyclohexyl imines of aryl aldehydes with $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ in CH_2Cl_2 or C_6H_6 in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ and MeCO_2H . The resulting solution, after quick treatment with silica gel, was column-chromatographed. Removal of the solvent from the eluent followed by recrystallisation gave the pure thioaldehyde complexes **3**, **4** and **5**.

Similar complexes of some hetero aromatic thioaldehydes were also synthesised. As a result, pentacarbonyl(2-thioformylfuran)tungsten **6** and three examples of pentacarbonyl(parent or substituted 2-thioformylthiophene)tungsten **7a–c** were obtained as stable entities.

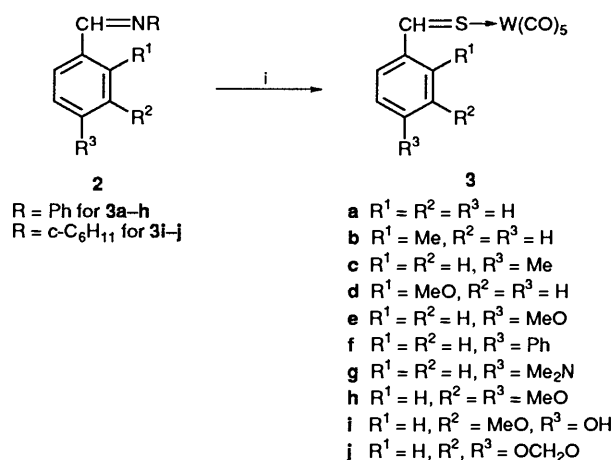
The complexes of the thioarylenals **8a–c** and thioaryldienals **9a–c**, with exception of each parent thioaryl-enal and -dienal, were also synthesised. In the case of complex **8c**, a better yield was attained on treatment of a *N*-(4-substituted cinnamylidene)pyrrolidinium perchlorate with $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$. For the synthesis of other complexes of those thioaldehydes, imines were much superior materials to ylidenepyrrolidinium perchlorates as starting materials; the latter being more crowded around the iminium carbon atom and less reactive with $[\text{W}(\text{CO})_5\text{SH}]^-$ owing to steric hindrance.

The complexes of thiobenzaldehyde and 2-thionaphthal-

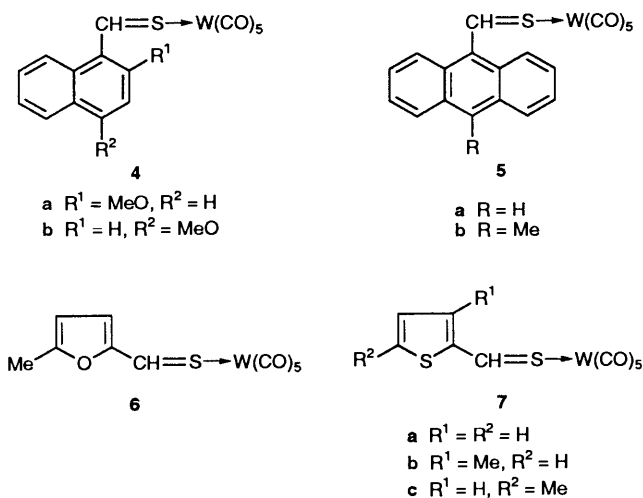
[†] $[\text{PPh}_4]\text{SH}$ was prepared as an ethanolic solution by dissolving an equimolar amount of pure $[\text{PPh}_4]\text{Br}$ and NaSH in ethanol just prior to use.

[‡] $[\text{W}(\text{CO})_5(\text{C}_4\text{H}_8\text{O})]$ has been prepared in low yield by irradiation of $[\text{W}(\text{CO})_6]$ in THF. The product is accompanied by contaminants. See, for example, ref. 10.

§ Gingerich *et al.* have obtained the complex by the reaction of $[\text{NET}_4][\text{W}(\text{CO})_5\text{I}]$ and $\text{Ag}[\text{BF}_4]$ in THF at -40 °C.¹¹



Scheme 2 Reagents and conditions: i, [PPH₄][W(CO)₅SH], 1, BF₃·OEt₂-MeCO₂H, C₆H₆ or CH₂Cl₂, room temp.

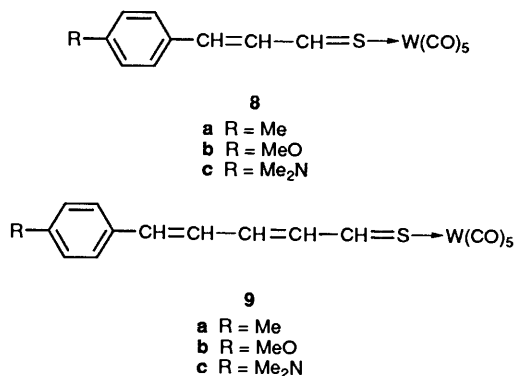


dehyde are stable in benzene at room temperature and their ¹H NMR spectra can be determined. The complexes decompose gradually on removal of the solvent (benzene) at room temperature. Fischer *et al.*^{8b} first isolated the parent pentacarbonyl(thiobenzaldehyde)tungsten(0) complex. They prepared the complex by the reaction of [NEt₄]SCN or S₈ with a carbene complex of pentacarbonyltungsten which was generated *in situ* from [NEt₄][W(CO)₅C(H)(OMe)(Ph)] and HBF₄·Et₂O and isolated by chromatography at -20 °C.

Complex **5** of 9-thioanthraldehyde is very stable, a property which may possibly be due to the effective steric protection of the thioformyl group by the anthracene ring and pentacarbonyltungsten group in this complex. Any stabilisation due to the polarisation of the C=S double bond through conjugation with the anthryl group can be discounted by the observation of its ¹H NMR spectrum, in which only 5 groups of signals based on aromatic protons of the anthryl group are observed. This observation suggests that the C=S double bond and the anthryl group are possibly at right angles to each other.

Complexes of aliphatic thioaldehydes and [W(CO)₅] are regarded as being much more unstable than those of aromatic thioaldehydes. As a matter of fact, the complexes of aliphatic thioaldehydes such as propane- and 2-methylethane-thial have never been formed by the above-mentioned method of preparation for ArCHS-W(CO)₅ complexes.

Although attempts were made to synthesise tungsten(0) complexes of β,β-tetramethylene- and -pentamethylene-α,β-unsaturated thioaldehydes and β,δ-trimethylene-α,β,γ,δ-unsatu-



rated thioaldehyde by the same procedure as those for the above complexes of aromatic thioaldehydes, they could not be isolated due to rapid decomposition at room temperature. Signals of the thioformyl protons of these complexes in ¹H NMR were identified with difficulty.

We are now studying extensively the chemical reactions of these thioaldehyde complexes towards hydrazines, enamines, dienes, dienophiles, diazomethanes, carbanions *etc.* and the results will be published elsewhere in the near future.

Experimental

M.p.s were measured on a Yanagimoto micro melting point apparatus and a Mettler FP62 melting point instrument. M.p.s and b.p.s are uncorrected. ¹H NMR spectra were determined with a JEOL JNM-GX270-FT spectrometer operating at 270 MHz with tetramethylsilane as internal standard.

All solvents used for reactions and column chromatography were dried and distilled prior to use.

Starting Materials.—Known anils formed from the appropriate aromatic and heteroaromatic aldehydes were used for the synthesis of the thioaldehyde complexes **3a-d**, **3f**, **3h-i**, **4b**, **5a-b**, **6** and **7a-c**.

N-Piperonylidene)cyclohexylamine. In a round-bottomed flask, fitted with a reflux condenser and a Dean-Stark trap, was placed a mixture of piperonal (20 mmol), cyclohexylamine (60 mmol), a catalytic amount of toluene-*p*-sulfonic acid and benzene (50 cm³). The mixture was refluxed for 1 day after which the solvent was removed under reduced pressure to give crude crystals of the imine, which was purified by recrystallisation from hot hexane; yield 60%, m.p. 59.5–60.5 °C (Found: C, 72.4; H, 7.6; N, 5.8. C₁₄H₁₇NO₂ requires C, 72.7; H, 7.4; N, 6.1%).

N-[p-(N,N-Dimethylamino)benzylidene]cyclohexylamine. This compound was prepared in a similar manner to the above imine; the crude oil obtained was distilled fractionally *in vacuo* to give the imine which solidified with time; yield 90%, b.p. 212 °C/1.2 mm Hg, m.p. 83.5–84 °C (Found: C, 78.3; H, 9.6; N, 12.1. C₁₅H₂₂N₂ requires C, 78.2; H, 9.6; N, 12.2%).

N-(2-Methoxy-1-naphthylmethylene)cyclohexylamine. This imine was also prepared in a similar manner to *N*-piperonylidene)cyclohexylamine. The crude solid obtained on removal of the solvent from the reaction mixture was collected, washed with hexane, and recrystallised from hot hexane to give the pure title compound, yield 85%, m.p. 94–94.5 °C (Found: C, 80.7; H, 8.0; N, 5.2. C₁₈H₂₁NO requires C, 80.9; H, 7.9; N, 5.2%).

N-(4-Methylcinnamylidene)cyclohexylamine. This compound was prepared from *p*-tolualdehyde and diethyl 2-(cyclohexylimino)ethylphosphonate as the intermediate for the formylation of carbonyl compounds reported by Nagata *et al.*¹²

This imine could not be purified by recrystallisation. For this imine, Nagata's method¹² of purification was carried out; yield 60%, m.p. 66 °C (Found: C, 84.8; H, 9.2; N, 6.0. C₁₆H₂₁N requires C, 84.5; H, 9.3; N, 6.2%).

N-[4-(Methoxycinnamylidene)cyclohexylamine]. This compound was also prepared by Nagata's method¹² as mentioned above; yield 47%, m.p. 82–82.5 °C (Found: C, 78.7; H, 8.5; N, 5.7. C₁₆H₂₁NO requires C, 79.0; H, 8.7; N, 5.8%).

N-[4-(Dimethylamino)cinnamylidene]pyrrolidinium perchlorate. This compound was prepared by a known preparative method¹³ using *p*-(dimethylamino)cinnamaldehyde and pyrrolidinium perchlorate; yield 85%, m.p. 220–220.5 °C (Found: C, 54.8; H, 6.3; N, 8.3. C₁₅H₂₁N₂ClO₄ requires C, 54.8; H, 6.4; N, 8.5%).

N-[5-(*p*-Tolyl)penta-2,4-dienylidene]cyclohexylamine. This compound was prepared from 4-methylcinnamaldehyde and 2-(cyclohexylimino)ethylphosphonate in a similar manner to *N*-(*p*-methylcinnamylidene)cyclohexylamine mentioned above. Nagata's isolation procedure¹² for the imine was repeated three times owing to difficulties in purification by any other method; yield 54%, m.p. 97–98 °C (Found: C, 84.9; H, 9.05; N, 5.4. C₁₈H₂₃N requires C, 85.3; H, 9.15; N, 5.5%).

N-[5-(*p*-Methoxyphenyl)penta-2,4-dienylidene]cyclohexylamine was prepared by the above-mentioned method; yield 53%, m.p. 103 °C (Found: C, 80.4; H, 8.4; N, 5.1. C₁₈H₂₃NO requires C, 80.25; H, 8.6; N, 5.2%).

Synthesis of [PPh₄][W(CO)₅SH] 1.—To a cooled THF (50 cm³) solution of [NEt₄][W(CO)₅I] (5.8 g, 10 mmol) was added 2 mol dm⁻³ aqueous AgNO₃ (5 cm³) under Ar and the mixture was shaken vigorously for 30 s. After the precipitated AgI had been filtered off, the filtrate was chilled to –20 °C and poured into a chilled solution (–20 °C) of [PPh₄]Br (4.2 g, 10 mmol) and NaSH (0.6 g, 10 mmol) in ethanol (20 cm³) with vigorous stirring. Ether (20 cm³), MgSO₄ (ca. 10 g) and active carbon (ca. 0.1 g) were added to this mixture which was then shaken for 30 s. Insoluble matter was filtered off to leave a yellow solution from which yellow crystals of [PPh₄][W(CO)₅SH] separated on addition of hexane (300 cm³). The crystals were collected, washed with hexane and recrystallised from THF–Et₂O–hexane (5:1:10) to give pure yellow crystals of the title compound (6.6 g, 95%); gradually decomposes over 128 °C and rapidly at 134–137 °C; δ_H(CDCl₃) 7.92 (4 H, m, 4-H × 4), ca. 7.8 and ca. 7.6 (each 8 H, each m, ArH) and –2.98 (1 H, s, SH) (Found: C, 50.2; H, 3.2. C₂₉H₂₁O₅PSW requires C, 50.0; H, 3.0%).

Preparation of Pentacarbonyl(aromatic thioaldehyde)tungsten 3a–j.—*General procedure.* To a solution of each of the corresponding anils (1 mmol) (for the complexes 3a–f and 3h–i) or substituted *N*-(benzylidene)cyclohexylamine (1 mmol) (for 3g and 3j) as an imine 2, boron trifluoride–diethyl ether (2 mmol), and acetic acid (2 mmol) in dichloromethane (50 cm³) (for complexes 3b, 3d–g, 3i–j) or benzene (50 cm³) (for 3a, 3c and 3h) was added tetraphenylphosphonium mercaptopentacarbonyltungstate 1 (1 mmol) at room temperature. The solution turned blue–black to purple immediately. The resulting mixture was shaken vigorously for 1 min. after which it was diluted with benzene (100 cm³) to precipitate insoluble matter, which was filtered off. The clear benzene solution was passed through a column of silica gel [Fuji-Davison, BW-235 (150–350 mesh), column: 60Φ × 50 mm] using benzene as eluent. Complexes 3b and 3e–g were obtained pure. Other complexes were further purified by column chromatography or recrystallisation. Most of the complexes obtained in our work are very soluble in common organic solvents, including aliphatic hydrocarbons such as hexane and cyclohexane, but are insoluble only in water.

Pentacarbonyl(thiobenzaldehyde)tungsten 3a. Complex 3a was stable in benzene solution at room temperature but decomposed gradually when most of the solvent was removed. On complete removal of the solvent, it decomposed rapidly at room temperature. Decomposition also occurred much more rapidly in dichloromethane and cyclohexane. A solution in [2H₆]benzene for the measurement of the ¹H NMR spectra of 3a was obtained by passing the reaction mixture in [2H₆]benzene through a silica-packed syringe; δ_H(C₆D₆) 10.43 (s, CH=S) and 7.08–6.76 (m, C₆H₅). Complex 3a was stable for several days in dilute benzene solution.

Pentacarbonyl(o-methylthiobenzaldehyde)tungsten 3b. This complex was obtained as black crystals. Further chromatography on silica gel (above BW-235, column: 20Φ × 200 mm, eluent; benzene) gave pure crystals of complex 3b as thick black plates (82%), m.p. 78–83 °C; δ_H(CDCl₃) 11.69 (1 H, s, CHS), 8.00 (1 H, d, 6-H, *J* 7.7), 7.56–7.25 (3 H, m, 3-, 4- and 5-H) and 2.56 (3 H, s, CH₃) (Found: C, 33.75; H, 2.0; S, 7.0. C₁₃H₈O₅SW requires C, 33.9; H, 1.75; S, 7.0%).

Pentacarbonyl(p-methylthiobenzaldehyde)tungsten 3c. Crude complex 3c was purified by column chromatography on silica gel (above BW-235, column: 20Φ × 200 mm, eluent; hexane) to give pure black crystals (85%), m.p. 73–76 °C [lit.,^{8a} 72–74 °C (decomp.)]; δ_H(C₆D₆) 10.60 (1 H, s, CHS), 7.00 (1 H, d, 6-H), 6.92 (1 H, s, 2-H), 6.87 (1 H, d, 4-H), 6.75 (1 H, t, 5-H) and 1.93 (3 H, s, CH₃) (Found: C, 34.0; H, 2.0; S, 7.3. C₁₃H₈O₅SW requires C, 33.9; H, 1.75; S, 7.0%).

Pentacarbonyl(o-methoxythiobenzaldehyde)tungsten 3d. Pure complex 3d was obtained in the same way as complex 3b; yield 79%, m.p. 153–154 °C (decomp.); δ_H(CDCl₃) 11.56 (1 H, s, CHS), 7.94–6.97 (3 H, m, ArH) and 3.96 (3 H, s, OCH₃) (Found: C, 32.5; H, 1.8; S, 6.4. C₁₃H₈O₆SW requires C, 32.8; H, 1.7; S, 6.7%).

Pentacarbonyl(p-methoxythiobenzaldehyde)tungsten 3e. This complex was purified in the same way as that of complex 3b; yield 88%, m.p. 105–107 °C (decomp.) [lit.,^{8a} 108–110 °C (decomp.)]; δ_H(CDCl₃) 11.10 (1 H, s, CHS), 7.83 (2 H, d, 2- and 6-H), 6.95 (2 H, d, 3- and 5-H) and 3.92 (3 H, s, OCH₃) (Found: C, 33.1; H, 1.8; S, 6.9. C₁₃H₈O₆SW requires C, 32.8; H, 1.7; S, 6.7%).

Pentacarbonyl(p-phenylthiobenzaldehyde)tungsten 3f. This complex was also obtained in crystalline form by a similar procedure to that for complex 3b; yield 84%, m.p. 119–122 °C (decomp.); δ_H(CDCl₃) 11.03 (1 H, s, CHS) and 7.9–7.5 (9 H, m, ArH) (Found: C, 41.1; H, 2.15; S, 6.2. C₁₈H₁₀O₅SW requires C, 41.4; H, 1.9; S, 6.1%).

Pentacarbonyl[p-(dimethylamino)thiobenzaldehyde]tungsten 3g. The optimum yield for this complex was obtained when 4 mol. equiv. of acetic acid and 2 mol. equiv. of boron trifluoride–diethyl ether were used in the reaction with *N*-[*p*-(*N,N*-dimethylamino)benzylidene]cyclohexylamine; the product was isolated as black to purplish black crude crystals which were recrystallised from dichloromethane–hexane to give pure crystals of complex 3g (85%), m.p. 136 °C (decomp.) [lit.,^{8a} 144–146 °C (decomp.)]; δ_H(CDCl₃) 10.55 (1 H, s, CHS), 7.72 (2 H, br s, 2- and 6-H), 6.66 (2 H, d, 3- and 5-H) and 3.15 [6 H, s, N(CH₃)₂] (Found: C, 34.1; H, 2.35; N, 2.6; S, 6.5. C₁₄H₁₁NO₅SW requires C, 34.4; H, 2.3; N, 2.85; S, 6.5%).

Pentacarbonyl(3,4-dimethoxythiobenzaldehyde)tungsten 3h. Complex 3h was obtained as pure crystals in a fashion similar to that for complex 3e; yield 72%, m.p. > 280 °C; δ_H(CDCl₃) 11.01 (1 H, s, CHS), 7.44 (1 H, d, 2-H), 7.40 (1 H, dd, 6-H), 6.92 (1 H, d, 5-H) and 4.00 and 3.97 (each 3 H, each s, OCH₃ × 2) (Found: C, 33.3; H, 2.1; S, 6.5. C₁₄H₁₀O₇SW requires C, 33.2; H, 2.0; S, 6.3%).

Pentacarbonyl(4-hydroxy-3-methoxythiobenzaldehyde)tungsten 3i. Although the isolated crude complex 3i was pure (TLC) it was recrystallised from dichloromethane–hexane to

give black prisms (67%), m.p. 43 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 11.00 (1 H, s, CHS), 7.44 (1 H, s, 2-H), 7.37 (1 H, d, 6-H), 6.97 (1 H, d, 5-H), 6.45 (1 H, s, OH) and 4.00 (3 H, s, OCH_3) (Found: C, 31.5; H, 1.65; S, 6.5. $\text{C}_{13}\text{H}_8\text{O}_7\text{SW}$ requires C, 31.7; H, 1.6; S, 6.5%).

Pentacarbonyl(3,4-methylenedioxythiobenzaldehyde)tungsten 3j. Pure crystals were obtained in a fashion similar to that for complex **3b**; purplish black crystals (74%), m.p. 109 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_3)$ 11.00 (H, s, CHS), 7.41 (1 H, d, 2-H), 7.35 (1 H, dd, 6-H), 6.88 (1 H, d, 5-H) and 6.10 (2 H, s, OCH_2O) (Found: C, 31.6; H, 1.2; S, 6.7. $\text{C}_{13}\text{H}_6\text{O}_7\text{SW}$ requires C, 31.9; H, 1.2; S, 6.7%).

Pentacarbonyl(2-methoxythionaphthaldehyde)tungsten 4a. To a solution of *N*-(2-methoxy-1-naphthylmethylene)cyclohexylamine (1 mmol, 0.267 g) and an equimolar mixture of boron trifluoride–diethyl ether and acetic acid (each 2 mmol, 0.404 g) in dichloromethane (50 cm³), was added [PPh_4][$\text{W}(\text{CO})_5\text{SH}$] (1 mmol, 0.698 g) at room temperature. The mixture was shaken vigorously for 30 s after which it was diluted with benzene and filtered to remove insoluble matter. The clear benzene solution was passed twice through a column of silica gel [Fuji-Davison, BW-235 (150–350 mesh), column: 60 Φ × 50 mm] using benzene as eluent. Removal of solvent gave black crystals which were chromatographically pure (TLC). Recrystallisation from dichloromethane–hexane gave pure crystals of complex **4a** (80%) which gradually decomposed over 132 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 12.22 (1 H, s, CHS), 9.21 (1 H, d, 8-H), 8.18 (1 H, d, 5-H), 7.84 (1 H, d, 4-H), 7.75 (1 H, m, 7-H), 7.49 (1 H, ca. t, 6-H), 7.25 (1 H, d, 3-H) and 4.12 (3 H, s, OCH_3) (Found: C, 38.6; H, 2.0; S, 5.8. $\text{C}_{17}\text{H}_{10}\text{O}_6\text{SW}$ requires C, 38.8; H, 1.9; S, 6.1%).

Pentacarbonyl[(4-methoxy)thionaphthaldehyde)tungsten 4b. To a solution of *N*-(4-methoxy-1-naphthylmethylene)aniline (1 mmol, 0.262 g) in dichloromethane (20 cm³), were added a mixture of boron trifluoride–diethyl ether (2 mmol, 0.284 g) and acetic acid (4 mmol, 0.241 g) in dichloromethane (5 cm³) and then [PPh_4][$\text{W}(\text{CO})_5\text{SH}$] (1 mmol, 0.698 g) in dichloromethane (5 cm³) at room temperature. The resulting mixture was shaken vigorously for a short time then set aside for 1 min. The reaction mixture was then passed through a column of silica gel (Fuji-Davison, BW-235, 60 Φ × 50 mm) and then eluent evaporated to dryness to give black crystals which were pure by TLC; yield 83%. Recrystallisation from dichloromethane–hexane gave pure crystals of complex **4b**, m.p. 123 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_3)$ 11.84 (1 H, s, CHS), 8.55 (1 H, d, 2-H), 8.37 (1 H, d, 8-H), 8.35 (1 H, d, 5-H), 7.79 (1 H, dd, 7-H), 7.66 (1 H, dd, 6-H), 6.94 (1 H, d, 3-H) and 4.14 (3 H, s, OCH_3) (Found: C, 38.5; H, 2.0. $\text{C}_{17}\text{H}_{10}\text{O}_6\text{SW}$ requires C, 38.8; H, 1.9%).

Pentacarbonyl(thioanthraldehyde)tungsten 5a. This complex was prepared by a similar procedure to that employed in the preparation of the thioaldehyde complex **4b**. Crude complex **5a** was washed with hexane to give brilliant brownish red crystals which were recrystallised from hot benzene; yield 66%, m.p. 145.5 °C (decomp.). Chemical shifts for nine aromatic protons on the anthracene ring of complex **5a** were determined by use of the ¹H COSY technique; $\delta_{\text{H}}(\text{CDCl}_3)$ 12.84 (1 H, s, CHS), 8.93 (2 H, ca. d, J 7, 1- and 8-H), 8.84 (1 H, ca. s, 10-H), 8.12 (2 H, dp, J 8.5, 1.5 and 0.7, 4- and 5-H), 7.85 (2 H, ddd, J 9, 7 and 1.5, 2- and 7-H) and 7.58 (2 H, dddd, J 9, 8.5, 1 and 0.5, 3- and 6-H) (Found: C, 44.0; H, 2.0; S, 5.8. $\text{C}_{20}\text{H}_{10}\text{O}_5\text{SW}$ requires C, 44.0; H, 1.85; S, 5.9%).

The thioanthraldehyde complex **5a** is the most stable of all the complexes of aromatic and heteroaromatic thioaldehydes here synthesised and could be recrystallised even from hot benzene.

Pentacarbonyl(10-methylthioanthraldehyde)tungsten 5b. This was prepared in a similar fashion to complex **5a** using benzene as solvent. The complex was recrystallised from tetrahydrofuran–hexane to remove benzene of recrystallisation; yield 55%, m.p. 145 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 12.69 (1 H, s, CHS), 8.95 (2 H, d, 1- and 8-H), 8.45 (2 H, d, 4- and 5-H), 7.84 (2 H, dd, 2- and 7-H),

7.62 (2 H, dd, 3- and 6-H) and 3.05 (3 H, s, CH_3) (Found: C, 45.15; H, 2.2; S, 6.0. $\text{C}_{21}\text{H}_{12}\text{O}_5\text{SW}$ requires C, 45.0; H, 2.2; S, 5.7%). Complex **5b** tends to have benzene of crystallisation which is difficult to remove by drying at 56 °C *in vacuo*.

Pentacarbonyl(5-methyl-2-thioformylfuran)tungsten 6. To a solution of *N*-(5-methylfurfurylidene)aniline (0.185 g, 1 mmol) in benzene (50 cm³), was added a solution of boron trifluoride–diethyl ether (0.284 g, 2 mmol) and acetic acid (0.12 g, 2 mmol) in dichloromethane (5 cm³); [PPh_4][$\text{W}(\text{CO})_5\text{SH}$] (0.697 g, 1 mmol) dissolved in dichloromethane (5 cm³) was then added to this mixture at room temperature. After the resulting mixture had been stirred for 1 min, it was passed through a column of silica gel [Fuji-Davison, BW-235 (150–350 mesh), column: 60 Φ × 50 mm] and then evaporated to dryness under reduced pressure to give blue–black crystals. These were column chromatographed on silica gel with benzene–hexane (1:1) as eluent to give crystals of the pure thioaldehyde complex **6** (86%), m.p. 79–79.5 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 10.36 (1 H, s, CHS) 7.12 (1 H, d, 3-H), 6.34 (1 H, s, 4-H) and 2.30 (3 H, s, CH_3) (Found: C, 29.1; H, 1.5; S, 6.8. $\text{C}_{11}\text{H}_6\text{O}_6\text{SW}$ requires C, 29.4; H, 1.3; S, 7.1%).

Use of FSO_3H instead of mixed acid in the above preparation resulted in the formation of several by-products: these led to a troublesome work-up procedure and a poor yield of product.

N-(5-Methylfurfurylidene)pyrrolidinium perchlorate reacted with [PPh_4][$\text{W}(\text{CO})_5\text{SH}$] to give complex **6** only in low yield, probably as a result of steric hindrance between the reactants.

Pentacarbonyl(2-thioformylthiophene)tungsten 7a. Pure *N*-(2-thienylmethylene)aniline (0.092 g, 0.5 mmol) was dissolved in hexane (19 cm³) and benzene (1 cm³) and to this solution were added solution (A) [a mixture of boron trifluoride–diethyl ether (0.071 g, 0.5 mmol) and acetic acid (0.06 g, 1 mmol) in dichloromethane (2.5 cm³)] and solution (B) [a solution of [PPh_4][$\text{W}(\text{CO})_5\text{SH}$] (0.348 g, 0.5 mmol) in dichloromethane (2.5 cm³)]. After being stirred vigorously for 3 min at 0 °C the resulting reddish purple reaction mixture was passed through a column of silica gel [Fuji-Davison, BW-235 (150–350 mesh), 60 Φ × 50 mm] and then concentrated to afford a thick solution (ca. 5 cm³). This was diluted with cooled hexane (15 cm³) to provide a precipitate which was filtered off; this procedure was repeated three times. Evaporation of the filtrate gave black needles of complex **7a** (59%), m.p. 36.5 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 10.83 (1 H, s, CHS), 7.46 (1 H, ca. d, 3-H), 6.955 (1 H, dq, 4-H) and 2.48 (3 H, s, CH_3) (Found: C, 26.75; H, 1.1; S, 13.8. $\text{C}_{10}\text{H}_4\text{O}_5\text{S}_2\text{W}$ requires C, 26.6; H, 0.9; S, 14.2%). Complex **7a** is extremely soluble in almost all organic solvents.

Pentacarbonyl(3-methyl-2-thioformylthiophene)tungsten 7b. The preparation of this compound was similar to that of complex **7a**, dichloromethane (20 cm³) being employed to dissolve *N*-(3-methyl-2-thienylmethylene)aniline (0.101 g, 1 mmol). After passage of the reaction mixture through the column of silica gel, it contained only the thioaldehyde complex (TLC). Brilliant reddish black crystals, obtained by evaporation of the solvent to dryness, were washed with cold hexane to give pure complex **7b** (87%), m.p. 90–90.5 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 11.04 (1 H, ca. s, CHS), 7.87 (1 H, d, 5-H), 7.04 (1 H, d, 4-H) and 2.42 (3 H, s, CH_3) (Found: C, 28.6; H, 1.5; S, 13.4. $\text{C}_{11}\text{H}_6\text{O}_5\text{S}_2\text{W}$ requires C, 28.3; H, 1.3; S, 13.8%). Complex **7b** is also very soluble in most organic solvents, it is barely soluble in cold liquid alkanes. A small amount of isomer, pentacarbonyl(4-methyl-2-thioformylthiophene)tungsten was observed in the NMR spectrum of **7b** [$\delta_{\text{H}}(\text{CDCl}_3)$ 10.95 (s, CHS), 7.57 (5-H), 7.46 (3-H) and 2.34 (CH_3)], but the isomeric complex could not be separated because of the same *R_f* values of the two isomers.

Pentacarbonyl(5-methyl-2-thioformylthiophene)tungsten 7c. The preparation and purification of this compound were the same as for the complex **7b**. Pure complex **7c** was obtained as lustrous yellowish black crystals (90%), m.p. 112.5–113 °C;

$\delta_{\text{H}}(\text{CDCl}_3)$ 10.83 (1 H, s, CHS), 7.46 (1 H, d, 3-H), 6.955 (1 H, dq, 4-H) and 2.48 (3 H, s, CH_3) (Found: C, 28.2; H, 1.45; S, 13.7. $\text{C}_{11}\text{H}_6\text{O}_5\text{S}_2\text{W}$ requires C, 28.3; H, 1.3; S, 13.8%).

Of these thioformylthiophenetungsten(0) complexes **7a-c**, complex **7c** is the most stable, being almost equal to the thioanthraldehydetungsten(0) complex **5a**.

Preparation of Pentacarbonyl[(4-methyl)thiocinnamaldehyde]tungsten 8a and Pentacarbonyl[(p-methoxy)thiocinnamaldehyde]tungsten 8b.—Freshly prepared *para*-substituted cinnamylidenecyclohexylamines were used for the preparation of these two thioaldehyde complexes. The molar ratio of reactants, conditions, and work-up procedures were similar to those for the preparation of complex **6**.

Complex **8a** (65%), m.p. 94–95 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 10.92 (1 H, dd, CHS), 7.58–7.04 (6 H, m, ArH) and 2.34 (3 H, s, CH_3) (Found: C, 37.2; H, 2.15; S, 6.7. $\text{C}_{15}\text{H}_{10}\text{O}_5\text{SW}$ requires C, 37.1; H, 2.1; S, 6.6%).

Complex **8b** (62%), m.p. 97 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 10.84 (1 H, d, CHS), 7.65 and 6.96 (each 2 H, d and *ca.* d, C_6H_4), 7.54–7.34 (2 H, m, vinylene H) and 3.88 (3 H, s, OCH_3) (Found: C, 36.0; H, 2.1; S, 6.1. $\text{C}_{15}\text{H}_{10}\text{O}_5\text{SW}$ requires C, 35.9; H, 2.0; S, 6.4%).

Pentacarbonyl[4-(N,N-dimethylamino)thiocinnamaldehyde]tungsten 8c.— $[\text{PPh}_4][\text{W}(\text{CO})_5\text{SH}]$ (0.696 g, 1 mmol) dissolved in dichloromethane (5 cm^3) was added to a solution of *N*-[*p*-(*N,N*-dimethylamino)cinnamylidene]pyrrolidinium perchlorate (0.329 g, 1 mmol) and acetic acid (0.15 g, 2.5 mmol) in dichloromethane (50 cm^3), was added. The resulting mixture was set aside for 15 min at room temperature, after which it was diluted with hexane (70 cm^3) and benzene (30 cm^3) and then filtered. The filtrate was passed twice through a column of silica gel and then evaporated to give pure complex **8c** as blue-black crystals (61%), m.p. 95 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_3)$ 10.43 (1 H, dd, CHS), 7.57 and 6.71 (each 2 H, each d, C_6H_4), 7.42–7.26 (2 H, m, vinylene H) and 3.11 (6 H, s, $\text{CH}_3 \times 2$) (Found: C, 37.1; H, 2.7; N, 2.5; S, 6.3. $\text{C}_{16}\text{H}_{13}\text{NO}_5\text{SW}$ requires C, 37.3; H, 2.5; N, 2.7; S, 6.2%).

Preparation of Pentacarbonyl(4-substituted cinnamylidene-thioacetaldehyde)tungsten 9a-c.—These three δ -arylthiodienal-tungsten(0) complexes were also prepared by the same procedure employed for the preparation of complex **6**. Both reaction scale and reaction time were reduced to half. Hexane (25 cm^3) was added immediately to each reaction mixture to precipitate ionic compounds, which were filtered off. The resulting solution was flash-column-chromatographed on silica gel [Fuji-Davison BW-350 (400 mesh), 60 Φ \times 70 mm, eluent; benzene-hexane (1 : 1)] to give black crystals. When the crystals had benzene of crystallisation, the benzene was removed by drying at 40 °C for 6 h *in vacuo*.

Pentacarbonyl(4-methylcinnamylidene-thioacetaldehyde)tungsten 9a; yield 17%, m.p. 222 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_3)$ 10.82 (1 H, d, *J* 12, CHS), 7.47 (1 H, d, *J* 8, 2- and 6-H), 7.34 (1 H, dd, *J* 15 and 15.5, β -H), 7.31 (1 H, d, *J* 11, δ -H), 7.19 (2 H, d, *J* 8, 3 and 5-H), 6.95 (1 H, dd, *J* 12 and 15, α -H), 6.87 (1 H, dd, *J* 11 and 15.5, γ -H) and 2.33 (3 H, s, CH_3) (Found: C, 39.7; H, 2.6; S, 6.1. $\text{C}_{17}\text{H}_{12}\text{O}_5\text{SW}$ requires C, 39.9; H, 2.4; S, 6.3%).

Pentacarbonyl(4-methoxycinnamylidene-thioacetaldehyde)tungsten 9b; yield 57%, m.p. 71–72 °C (decomp.); $\delta_{\text{H}}(\text{CDCl}_3)$ 10.75 (1 H, d, *J* 11, CHS), 7.54 (2 H, d, *J* 8.5, 2- and 6-H), 7.31

[1 H, *ca.* dd, *J* 11 (probably) and 15, β -H], 7.29 (1 H, d, *J* 15.5, δ -H), 6.93 (1 H, dd, *J* 11 and 15, α -H), 6.91 (2 H, d, *J* 8.5, 3- and 5-H), 6.79 (1 H, dd, *J* 11 and 15.5, γ -H) and 3.85 (3 H, s, OCH_3) (Found: C, 38.4; H, 2.55; S, 5.9. $\text{C}_{17}\text{H}_{12}\text{O}_6\text{SW}$ requires C, 38.7; H, 2.3; S, 6.1%).

Pentacarbonyl[4-(N,N-dimethylamino)cinnamylidene-thioacetaldehyde]tungsten 9c; yield 29%, m.p. > 300 °C; $\delta_{\text{H}}(\text{CDCl}_3)$ 10.48 (1 H, d, *J* 12, CHS), 7.57 (1 H, d, *J* 9, δ -H), 7.49 (2 H, d, *J* 9, 2- and 6-H), 7.28 (1 H, dd, *J* 15 and 15.5, β -H), 6.93 (1 H, dd, *J* 12 and 15, α -H), 6.75 (1 H, dd, *J* 9 and 15.5, γ -H), 6.67 (2 H, d, *J* 9, 3- and 5-H) and 3.06 (6 H, s, $\text{CH}_3 \times 2$) (Found: C, 39.6; H, 3.1; N, 2.3. $\text{C}_{18}\text{H}_{15}\text{NO}_5\text{SW}$ requires C, 39.95; H, 2.8; N, 2.6%).

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