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The coordination chemistry of iminooxosulphuranes

IV *. The reactions of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ with iminooxosulphuranes and diiminosulphuranes

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Abstract

The tungsten hydride $[WH(CO)_3(\eta\text{-}C_5H_5)]$ reacts with iminooxosulphuranes, RN=S=O ($R = C_6H_4Me\text{-}2$, $C_6H_4Me\text{-}4$), to give the tungsten sulphinamides $[W\{S(=O)NHR\}(CO)_3(\eta\text{-}C_5H_5)]$. Diiminosulphuranes bearing electron-withdrawing substituents, $R'N{=}S{=}NSO_2C_6H_4Me\text{-}4$ ($R' = C_6H_5$, $SO_2C_6H_4Me\text{-}4$), insert into the metal–hydrogen bond of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ to give $[W\{S(=NR)NHSO_2C_6H_4\text{-}Me\text{-}4\}(CO)_3(\eta\text{-}C_5H_5)]$, whilst bis(*p*-tolylimino)sulphurane, $S(=NC_6H_4Me\text{-}4)_2$, gives the tungstacycle $[W\{S(NHC_6H_4Me\text{-}4)N(C_6H_4Me\text{-}4)C(=O)\}(CO)_2(\eta\text{-}C_5H_5)]$. A comprehensive mechanism is discussed.

Introduction

The interaction of transition-metal hydrides, whether molecular or surfacial in nature, with unsaturated organic systems is of great interest in many branches of chemistry. Multiply-bonded systems involving other main group elements should also combine with transition-metal hydrides. The comparative ignorance about these reactions is presumably due to lack of interest in the past and not a reflection upon the wealth of chemistry likely to be associated with them. We discuss here the interaction of the nitrogen–sulphur double-bond with the model hydride complex $[WH(CO)_3(\eta\text{-}C_5H_5)]$ [2].

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* For part III see Ref. 1.

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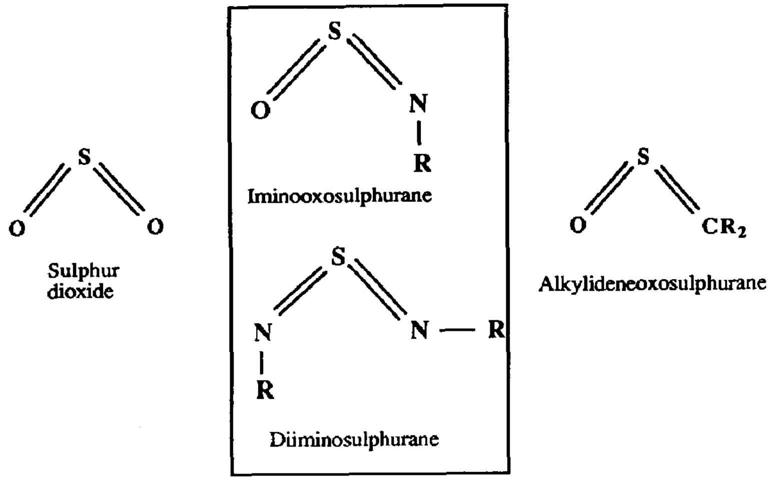


Scheme 1. Derivatives of sulphur dioxide.

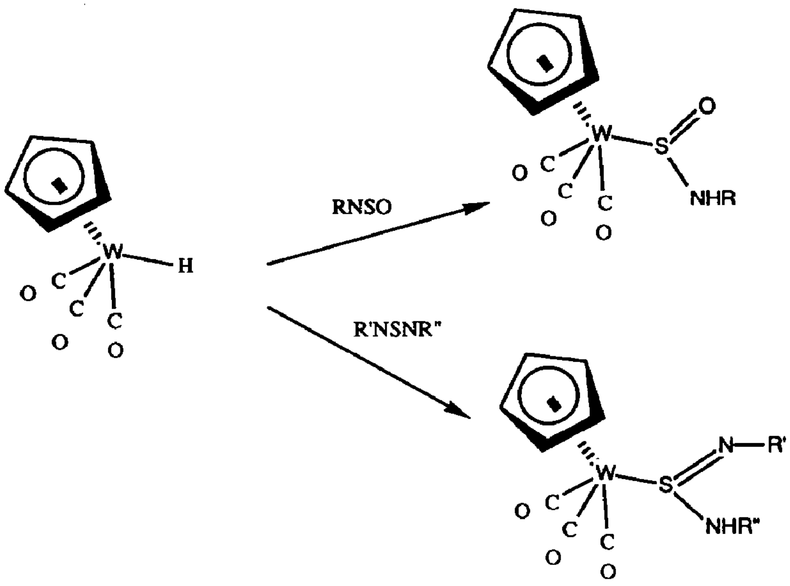
Despite our successful synthesis of complexes incorporating both hydrido ligands and ligands which contain double bonds between nitrogen and divalent sulphur [3], attempts to prepare hydrido complexes of diiminosulphuranes have invariably led to disruption of the –N=S=N– cumulene system [4–7], notable exceptions being provided by $[Os_3H_2\{P^tBu_2(NSNAs^tBu_2)\}(CO)_9]$ [8], and the 2,1,3-benzothiadiazole (BTD) complex *trans, trans*-$[IrHCl_2(BTD)(PPh_3)_2]$ [9]. A consideration of the products of these degradations indicates the operation of multistep processes. To elucidate the primary step in these reactions it is necessary to block subsequent reaction pathways. This may be achieved by using the case of iminooxosulphuranes, tetravalent sulphur cumulenes which contain only one sulphur–nitrogen double bond (Scheme 1).

Results and Discussion

Reactions with iminooxosulphuranes

The model complex $[WH(CO)_3(\eta\text{-}C_5H_5)]$ [2] has been observed to insert sulphur dioxide [10] and sulphine (prepared in situ) [11] to give the complexes $[W\{S(=O)OH\}(CO)_3(\eta\text{-}C_5H_5)]$ and $[W\{S(=O)CH_3\}(CO)_3(\eta\text{-}C_5H_5)]$, respectively. The topological similarity between the products of the reactions of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ with these molecules served to reinforce the idea of an isolobal relationship [12] between the tetravalent sulphur cumulenes SO_2 and CH_2SO. These cumulenes may be further related to the iminooxosulphurane class of compounds, formally obtained by replacing one oxo atom in SO_2 with an imino group (Scheme 1). Consistent with this, we find that the cumulenes RN=S=O ($R = C_6H_4Me\text{-}2$, $C_6H_4Me\text{-}4$) react with $[WH(CO)_3(\eta\text{-}C_5H_5)]$ to give the compounds $[W\{S(=O)\text{-}NHR\}(CO)_3(\eta\text{-}C_5H_5)]$ (Scheme 2).

The retention of the integrity of the S=O multiple bond is evident from the infrared spectra of the complexes (Table 1), with strong bands being observed at 1007 ($R = C_6H_4Me\text{-}2$) or 981 cm^{-1} ($R = C_6H_4Me\text{-}4$). The small variation between these values for the two complexes possibly reflects steric pressures associated with isomerism about the S–N bond, which presumably retains a degree of multiplicity.



Scheme 2. Reaction of a tungsten hydride with iminooxosulphuranes and diiminosulphuranes; R = C_6H_4Me-2, C_6H_4Me-4; R' = C_6H_5, $SO_2C_6H_4Me$-4; R" = $SO_2C_6H_4Me$-4.

The η^1-sulphinamide complexes $[W\{S(=O)NHR\}(CO)_3(\eta\text{-}C_5H_5)]$ show no tendency to rearrange further at room temperature but decompose to intractable products upon warming.

Table 1

Infrared data for the tungsten complexes [a]

Complex [W] = $[W(\eta\text{-}C_5H_5)(CO)_2]$ R = $SO_2C_6H_4Me$-4	Infrared (cm^{-1})	
	ν(CO)	Other
$[W](CO)\{S(=O)NHC_6H_4Me\text{-}2\}$	2025, 1940, 1919	3180(NH), 1237 1110, 1007(SO), 863, 745
$[W](CO)\{S(=O)NHC_6H_4Me\text{-}4\}$	2022, 1944, 1921 812	3287(NH), 1277, 1221, 1012, 981(SO), 864, 850,
$[W](CO)\{S(=NR)NHR\}$	2040, 1965, 1945	3260(NH)
$[W](CO)\{S(=NC_6H_5)NHR\}$	2038, 1957, 1940	3370(NH)
$[W]\{S(NHC_6H_4Me\text{-}4)N\text{-}(C_6H_4Me\text{-}4)C(=O)\}$	1960 1875	3240 1615 (acyl), 1245 (NS)

[a] Infrared data were obtained from KBr pellets of the complexes in the range 4000–400 cm^{-1}.

Table 2

^{1}H NMR data for the tungsten complexes

Complex [W] = $[W(\eta\text{-}C_5H_5)(CO)_2]$ R = $SO_2C_6H_4Me\text{-}4$	$\delta(^1H)$ [a] (ppm)
[W](CO){S(=O)NHC_6H_4Me-2}	2.25 (s, 3H, CH_3), 5.82 (s, 5H,C_5H_5), 6.45 (s, 1H, NH), 7.16, 7.20 (m×2, 4H, C_6H_4)
[W](CO){S(=O)NHC_6H_4Me-4}	2.27 (s, 3H, CH_3), 5.83 (s, 5H, C_5H_5), 6.52 (s, 1H, NH), 6.91, 7.08 [$(AB)_2$, 4H, J(AB) 8 Hz, C_6H_4]
[W](CO){S(=NR)NHR}	[b] 2.37 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 6.14 (s, 5H, C_5H_5), 7.0–7.8 (m, 8H, C_6H_4)
[W](CO){S(=NC_6H_5)NHR}	[b] 2.42 (s, 3H, CH_3), 5.34 (s, 5H, C_5H_5), 6.38 [s(br), 1H, NH], 7.3–7.8 (m, 9H, C_6H_5 and C_6H_4)
[W]{S(NHC_6H_4Me-4)N-(C_6H_4Me-4)C(=O)}	2.21 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 5.67 (s, 5H, C_5H_5), 5.96 [s(br), 1H, NH], 6.9–7.1 (m, 8H, C_6H_4)

[a] ^{1}H NMR data determined from saturated solutions in $CDCl_3$ at 25 °C unless otherwise stated (90 MHz) relative to internal $SiMe_4$. [b] Measured at −8 °C.

The first step in the interaction of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ with nitrogen–sulphur (IV) double bonds having been established, the reactions of diiminosulphuranes were next examined, a second degree of freedom in reactivity thereby being introduced.

Reactions with diiminosulphuranes

The electron-deficient diiminosulphuranes S(=NR)(=N$SO_2C_6H_4$Me-4) (R = C_6H_5, $SO_2C_6H_4$Me-4) react cleanly with $[WH(CO)_3(\eta\text{-}C_5H_5)]$ to provide 1 : 1 adducts reminiscent of those from the iminooxosulphurane reaction, i.e., involving 1,2-addition of tungsten and hydrogen to one nitrogen–sulphur bond, leading to the complexes [W{S(=NR)NH$SO_2C_6H_4$Me-4}$(CO)_3(\eta\text{-}C_5H_5)$] (Scheme 2).

The asymmetry of the diiminosulphurane S(=NC_6H_5)(=N$SO_2C_6H_4$Me-4) raises the possibility of obtaining isomeric adducts with $[WH(CO)_3(\eta\text{-}C_5H_5)]$, depending upon the nitrogen to which the proton becomes ultimately bound. The spectroscopic data available for the adduct (Table 1) are insufficient to distinguish between the two possibilities, but the synthesis of bis(phenylimino)sulphurane from bis(toluenesulphonylimino)sulphurane and analine suggests that the tosyl-substituted double bond is the more reactive. Accordingly, the most likely adduct of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ and S(=NC_6H_5)(=N$SO_2C_6H_4$Me-4) is that in which the phenyl-substituted sulphur–nitrogen bond remains intact. In any event, proton transfer between the two nitrogen sites will be rapid on the synthetic timescale.

The adducts [W{S(NR)NH$SO_2C_6H_4$Me-4}$(CO)_3(\eta\text{-}C_5H_5)$] show no tendency to rearrange. The related adduct [W{S(=NC_6H_4Me-4)NHC_6H_4Me-4}$(CO)_3(\eta\text{-}C_5H_5)$] is, however, not observed in the reaction of the tungsten hydrido complex with bis(tolylimino)sulphurane. Rather, a metallacyclic complex is isolated in which one carbonyl ligand has become incorporated into a nitrogen–sulphur-containing ligand, viz. [W{S(NHR)NRC(=O)}$(CO)_2(\eta\text{-}C_5H_5)$] (R = C_6H_4Me-4) (Scheme 3). Similar cyclisations involving the carbonyl ligand have been observed in reactions of the

Table 3

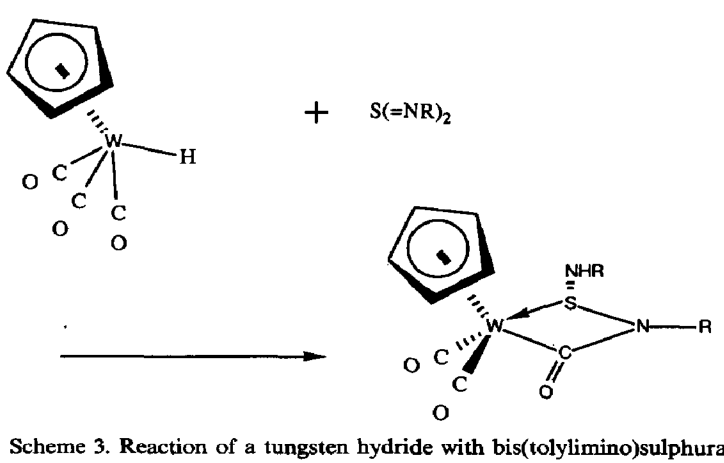
^{13}C-{^{1}H} NMR data for the tungsten complexes

Complex [W] = $[\mathrm{W}(\eta\text{-}\mathrm{C_5H_5})(\mathrm{CO})_2]$ R = $\mathrm{SO_2C_6H_4Me}$-4	$\delta(^{13}\mathrm{C})$ [a] (ppm)
[W](CO){S(=O)NH$\mathrm{C_6H_4}$Me-2}	222.8, 217.6, 216.1 (W*C*O), 143.4, 130.4, 126.9, 122.5, 118.2, 126.5 ($C_6\mathrm{H}_4$), 94.3 ($C_5\mathrm{H}_5$), 17.7 ($C\mathrm{H}_3$)
[W](CO){S(=O)NH$\mathrm{C_6H_4}$Me-4}	223.0, 217.2, 215.7 (W*C*O), 142.8, 131.7, 129.6, 117.8 ($C_6\mathrm{H}_4$), 94.3 ($C_5\mathrm{H}_5$), 20.7 ($C\mathrm{H}_3$)
[W](CO){S(=NR)NHR}	[b] 230.4, 220.3 (W*C*O), 143.7, 142.6, 137.5, 136.3, 129.6, 128.9, 127.9, 126.6 ($C_6\mathrm{H}_4$), 94.8 ($C_5\mathrm{H}_5$), 21.5 ($C\mathrm{H}_3$).
[W](CO){S(=N$\mathrm{C_6H_5}$)NHR}	[b] 229.5 (W*C*O), 148.0, 142.2, 136.9, 129.4, 128.9, 127.7, 121.7, 117.0 ($C_6\mathrm{H}_5$ and $C_6\mathrm{H}_4$), 94.6 ($C_5\mathrm{H}_5$), 21.5 ($C\mathrm{H}_3$)
[W]{S(NH$\mathrm{C_6H_4}$Me-4)N-($\mathrm{C_6H_4}$Me-4)C(=O)}	[c] 243.4, 230.5 (W*C*O), 182.7 (N*C*O), 141.3, 138.5, 135.2, 132.8, 129.6, 129.1, 121.7, 117.3 ($C_6\mathrm{H}_4$), 91.5 ($C_5\mathrm{H}_5$), 20.9, 20.6 ($C\mathrm{H}_3$)

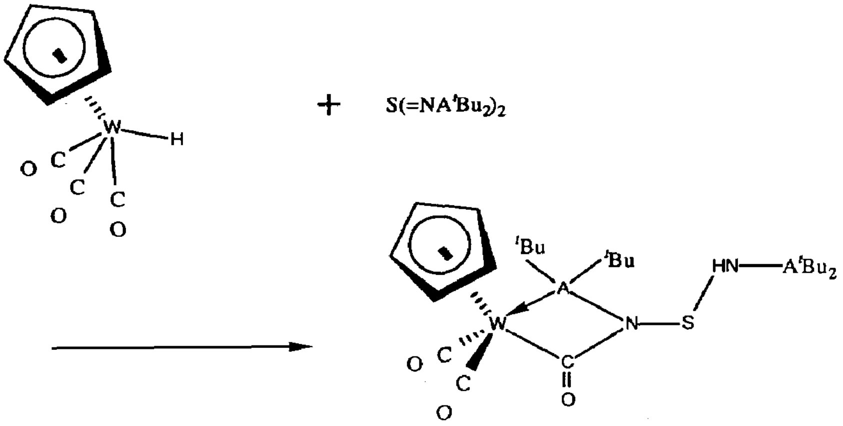
[a] ^{13}C-{^{1}H} NMR data determined from saturated solutions in $\mathrm{CDCl_3}$ at 25 °C unless otherwise stated (90 MHz) relative to $\delta(\mathrm{CDCl_3}) = 77.0$ ppm. [b] Measured at −20 °C. [c] Measured at −40 °C.

tungsten hydride with ynamines [13], and we have previously encountered this type of metallacycle in the related reactions with the diiminosulphuranes S(NR′)(NR″) (R′, R″ = H, SiMe$_3$; R′ = ^{t}Bu, R″ = As^{t}Bu$_2$) [5–7].

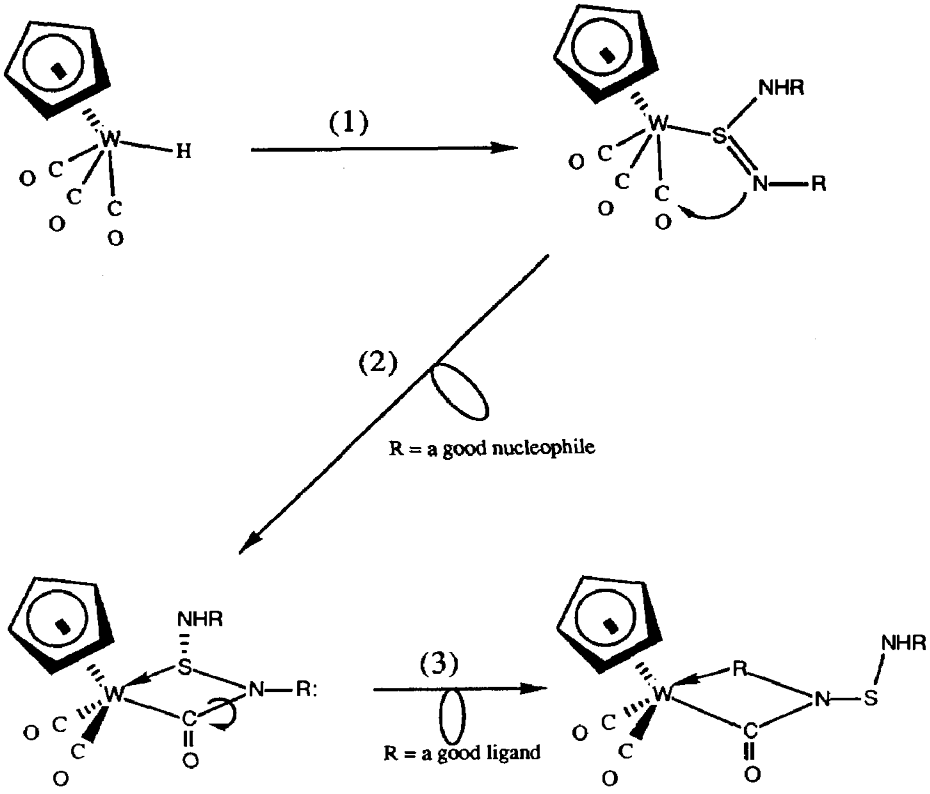
A third possibility has been observed for the reaction of $[\mathrm{WH(CO)_3}(\eta\text{-}\mathrm{C_5H_5})]$ with diiminosulphuranes disubstituted with phosphino or arsino groups [5] (Scheme 4). In these cases one of the pnicogino groups becomes ultimately bound to the tungsten atom, as established for the crystallographically characterised complex $[\mathrm{W\{As^tBu_2N(SNHAs^tBu_2)C(=O)\}(CO)_2}(\eta\text{-}\mathrm{C_5H_5})]$ [5]. This unusual result may be incorporated within a general scheme of reactions for the tungsten hydrido complex with diiminosulphuranes (Scheme 5).



Scheme 3. Reaction of a tungsten hydride with bis(tolylimino)sulphurane; R = $\mathrm{C_6H_4Me}$-4.



Scheme 4. Hydrotungstation of bis(pnicoginoimino)sulphuranes A = P, As.



Scheme 5. A mechanism for the various hydrotungstations.

A comprehensive mechanism is proposed as follows:

(1) Initial adduct formation

In keeping with the known Brønsted acidity of [$WH(CO)_3(\eta\text{-}C_5H_5)$], protonation occurs at a nitrogen of $S(NR)_2$ to give an ion-pair $[W(CO)_3(\eta\text{-}C_5H_5)]^-[RNHS{=}NR]^+$ which collapses via nucleophilic attack by tungsten at sulphur to give

$[W\{S(=NR)NHR\}(CO)_3(\eta\text{-}C_5H_5)]$. This interpretation is supported by the observed retardation or complete suppression of the related reactions between $O{=}S{=}NC_6H_4Me\text{-}4$ and the weaker Brønsted acids $[WH(CO)_3(\eta\text{-}C_5Me_5)]$ and $[WH(PMe_3)(CO)_2(\eta\text{-}C_5H_5)]$. If these reactions were to proceed through electrophilic attack on the tungsten centre by the tetravalent sulphur, these changes would be expected to accelerate the reaction.

(2) Effect of electron-donating substituents, R

If the substituents R are sufficiently electron-releasing, the nitrogen of the imino group becomes nucleophilic and intramolecular attack at carbon monoxide occurs, leading to metallacyclic carboxamido ligands. Alternatively, nucleophilic attack by the amino nitrogen could occur, followed by proton transfer to the free imine.

(3) Effect of ligating substituents, R

If the substituent R contains a functional group which can serve as a better ligand to tungsten than the aminosulphane unit, e.g., phosphino or arsino groups, rotation about the nitrogen–acyl bond delivers the new donor to the tungsten coordination sphere.

We conclude that the reactions of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ with nitrogen–sulphur (IV) heterocumulenes display a high degree of chemoselectivity, which can be rationalised by consideration of the properties of the imino substituents.

We are currently investigating the reactions of nitrogen–sulphur(IV) heterocumulenes with other potentially non-innocent ligand systems, and will discuss these results in due course [9].

Experimental

General experimental procedures and instrumentation have been described previously [3]. The compound $[WH(CO)_3(\eta\text{-}C_5H_5)]$ [2], the diiminosulphuranes [14] and the iminooxosulphuranes [15] were prepared by published procedures.

$[W\{S(=O)NHR\}(CO)_3(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}2$, $C_6H_4Me\text{-}4$)

A suspension of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ (1.00 g, 3.00 mmol) in pentane (25 cm^3) was cooled to −30 °C and treated with *o*-tolyliminooxosulphurane or *p*-tolyliminooxosulphurane (0.50 g, 3.20 mmol) and the mixture was allowed to warm slowly to room temperature and stirred for a further 30 min. The dark orange suspension was cooled again to −30 °C, and freed from solvent by decantation, and the residue was washed with cooled pentane (10 cm^3) and dried in vacuo. The crude product was spectroscopically pure, but better crystals were obtained by recrystallisation from tetrahydrofuran/pentane at −30 °C. $R = C_6H_4Me\text{-}2$: Yield 1.30 g (89%); M.p. 47 °C decomp. $R = C_6H_4Me\text{-}4$: Yield 1.40 g (96%); M.p. 58 °C decomp.

$[W\{S(NR)NHSO_2C_6H_4Me\text{-}4\}(CO)_3(\eta\text{-}C_5H_5)]$ ($R = C_6H_5$, $SO_2C_6H_4Me\text{-}4$)

A suspension of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ (0.26 g, 0.60 mmol) in diethyl ether (30 cm^3) was cooled to −10 °C and treated with $S(NR)(NSO_2C_6H_4Me\text{-}4)$ (0.60 mmol), and the mixture stirred for 1 h. The solvent was removed by decantation, and a suspension of the residue in dichloromethane (40 cm^3) was stirred at 0 °C for a further 2 h. The red solution was concentrated to ca. 5 cm^3 in vacuo and the product precipitated by slow addition of pentane (40 cm^3), isolated by decantation, and dried under high vacuum for 3 h. $[W\{S(NC_6H_5)NHSO_2C_6H_4Me\text{-}4\}(CO)_3(\eta\text{-}C_5H_5)]$: Yield, 0.31 g (81%), M.p. 94°C. Anal. Found: C, 40.1; H, 3.0; N, 4.4; S, 10.6. $C_{21}H_{18}N_2O_5S_2W$ calc: C, 40.3; H, 2.9; N, 4.5; S, 10.2%. $[W\{N(SO_2C_6H_4Me\text{-}4)NHSO_2C_6H_4Me\text{-}4\}(CO)_3(\eta\text{-}C_5H_5)]$: Yield 0.17 g (48%).

$[W\{S(NHC_6H_4Me\text{-}4)N(C_6H_4Me\text{-}4)C(=O)\}(CO)_2(\eta\text{-}C_5H_5)]$

A solution of $[WH(CO)_3(\eta\text{-}C_5H_5)]$ (0.17 g, 0.50 mmol) in pentane (40 cm^3) was cooled to −30°C and treated with a cooled solution of bis(*p*-tolylimino)sulphurane (0.12 g, 0.50 mmol) in pentane (40 cm^3). The resulting mixture was stirred for 3 h at −30°C and the yellow precipitate was then isolated by decantation, washed with cooled pentane (−30°C), and dried for 3 h under high vacuum at 0°C. Yield 0.20 g (75%). M.p. 70–73°C. Further material was obtained by concentrating the decantate and keeping it at −30°C overnight (ca. 15%). Anal. Found: C, 46.0: N, 4.7; S, 5.4; W, 32.0%. $C_{22}H_{20}N_2O_3SW$ calc: C, 45.9; H, 3.5; N, 4.9; W, 31.9%.

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