Transition Metal Complexes with Sulphur Ligands. Part 67.[1] A Novel Type of Reaction: Nucleophilic Alkylation of Thiolato Ligands by Carbanions *via* Intramolecular Electron Transfer. Alkylation and Reduction of $[W(S_2C_6H_4)_3]$ by Lithium Alkyls

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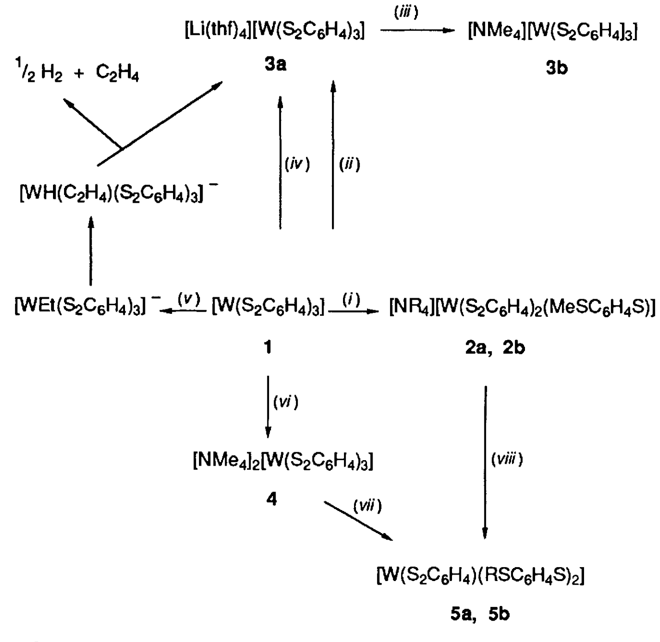
The reaction of $[W(S_2C_6H_4)_3]$ **1** with LiMe depends on the concentration of the latter and yields either the anionic tungsten(IV) complex $[NR_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ (R = Me, **2a**; or Et, **2b**) or the anionic tungsten(V) complex $[NMe_4][W(S_2C_6H_4)_3]$ **3b**. This novel type of reaction demonstrates the reactive versatility of transition-metal sulphur centres and is of importance for the understanding of *trans*-methylation reactions catalysed by oxidoreductases with sulphur-co-ordinated transition-metal centres, *e.g.* CO dehydrogenase. When **1** is treated with LiEt, $LiCH_2Bu^t$ or LiPh only a reduction of **1** takes place yielding **3b**. The reaction of complex **1** with 2 equivalents of $LiBu^n$ affords the dianionic tungsten(IV) complex $[NMe_4]_2[W(S_2C_6H_4)_3]$ **4**. The electrophilic alkylation of **4** by 2 equivalents of R_3OBF_4 (R=Me or Et) or of **2b** by 1 equivalent of Me_3OBF_4 leads to the doubly alkylated complexes $[W(S_2C_6H_4)(RSC_6H_4S)_2]$ (R = Me, **5a**; or Et, **5b**).

The active centres of numerous oxidoreductases contain transition metals in a co-ordination sphere dominated by sulphur donors, *e.g.* nitrate reductase, hydrogenases, CO dehydrogenase or nitrogenases.[2–5] In order to elucidate the chemical processes, which are catalysed by these enzymes, at the molecular level, a basic knowledge of the specific properties and elementary reactions of transition-metal complexes with sulphur ligands that act as model compounds is required.

We have described the first complex in which hydride is bound to a metal having solely sulphur compounds as coligands:[6] $[MoH(S_2C_6H_4)_3]^{3-}$ ($C_6H_4S_2$ = benzene-1,2-dithiolate) is obtained from $[Mo(S_2C_6H_4)_3]$ and $LiBu^n$ *via* several intermediates. However, when we tried to synthesise the analogous tungsten complex by the same method we observed reduction reactions only, and no hydride species. Consequently, we investigated the reaction of $[W(S_2C_6H_4)_3]$[7] with LiMe, aiming at species such as $[W(Me)(S_2C_6H_4)_3]^{n-}$ (n = 1, 2 or 3). Totally unexpectedly, we observed that the carbanion of LiMe acts as an alkylation agent not towards the metal but towards the nucleophilic thiolato atoms of the ligand, yielding the reduced species $[NMe_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$, in which one benzenedithiolato ligand has become methylated. Whereas alkylation of thiolato ligands by electrophilic carbenium ions is a typical and well known reaction of metal thiolato complexes as shown by others[8] and ourselves,[9,10] as far as we are aware the alkylation of such species by carbanions is not known.

Results and Discussion

Preparative Results.—On adding a diethyl ether solution of LiMe to a turquoise suspension of $[W(S_2C_6H_4)_3]$ **1** in tetrahydrofuran (thf) [Scheme 1, (*i*)] a red solution is obtained immediately. The complex $[NR_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ **2a** or **2b**, respectively, precipitates as red crystals upon addition of a methanol solution of NMe_4Cl or NEt_4Cl. Tables 1 and 2 list the microanalytical and spectroscopic properties of **2a** and **2b**. The ^1H and $^{13}C-\{^1H\}$ NMR spectra (Fig. 1) in dimethylformamide (dmf) display signals at δ 3.6 or 55.4, respectively, characteristic for monomethylated benzenedithiolato complexes. Although we could isolate single crystals of the monoanion, *e.g.* as the NMe_4^+ or (4,7,13,16,21-pentaoxa-1,10-diazabicyclo[8.8.5]tricosane) lithium salt, it was impossible to solve their structure by X-ray structure analysis. The crystals were always disordered probably because the methyl group in the $[W(S_2C_6H_4)_2(MeSC_6H_4S)]^-$ anion is statistically distributed among all six sulphur atoms.



Scheme 1 (*i*) LiMe, NR_4Cl (R = Me or Et); (*ii*) LiMe (dropwise), $LiCH_2Bu^t$ or LiPh; (*iii*) NMe_4Cl; (*iv*) Li (powder); (*v*) LiEt; (*vi*) 2 $LiBu^n$; (*vii*) 2 R_3OBF_4 (R = Me or Et); (*viii*) Me_3OBF_4

Reaction (*i*) in Scheme 1 shows that alkylation of one thiolato sulphur atom takes place when complex **1** is treated with LiMe; simultaneously the tungsten centre is reduced by two units from formally W^{VI} to W^{IV}. In order to explain this unexpected reaction, we assume that the Me^- ion primarily attacks the tungsten centre of **1** giving a seven-co-ordinate species as shown in equation (1). Seven-co-ordinate tungsten or molybdenum

$$1 + Me^- \longrightarrow [W^{VI}Me(S_2C_6H_4)_3]^- \longrightarrow [W^{IV}(S_2C_6H_4)_2(MeSC_6H_4S)]^- \quad (1)$$

Table 1 Analytical data for the tungsten complexes

Complex		Analysis (%)[a] C	H	N
2a	$[NMe_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$	39.8 (39.8)	3.9 (3.9)	2.2 (2.0)
2b	$[NEt_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$	43.4 (43.25)	4.8 (4.7)	1.7 (1.9)
3a	$[Li(thf)_4][W(S_2C_6H_4)_3]$	45.0 (45.4)	5.1 (4.9)	
3b	$[NMe_4][W(S_2C_6H_4)_3]$	38.8 (38.9)	3.9 (3.6)	2.0 (2.1)
4	$[NMe_4]_2[W(S_2C_6H_4)_3]$	41.6 (41.5)	5.0 (4.8)	3.5 (3.7)
5a	$[W(S_2C_6H_4)(MeSC_6H_4S)_2]$	36.9 (37.85)	2.7 (2.9)[b]	
5b	$[W(S_2C_6H_4)(EtSC_6H_4S)_2]$	39.5 (39.9)	3.3 (3.35)	

[a] Required values given in parentheses. [b] Compound could not be isolated analytically pure.

Table 2 Spectroscopic data for the tungsten complexes

Complex	^1H[a]	$^{13}C-\{^1H\}$[b]	m/z (M^+)
2a	3.1 [12 H, s, $N(CH_3)_4^+$][c] 3.6 (3 H, s, SCH_3) 6.7–7.9 (12 H, m, $3C_6H_4$)	16.2 (SCH_3)[c] 55.4 [$N(CH_3)_4^+$] 122.6, 123.7, 126.7, 128.0, 128.5, 129.5, 138.3, 156.9, 158.2 (C_6H_4)	693[d]
2b	0.8–1.3 [12 H, t, $N(CH_2CH_3)_4^+$][e] 2.9–3.3 [8 H, q, $N(CH_2CH_3)_4^+$] 3.6 (3 H, s, SCH_3) 6.7–7.9 (12 H, m, $3C_6H_4$)	—	749[d]
3b	3.1 [12 H, s, $N(CH_3)_4^+$][e] 2.5, 18 (6 H, br m, $1.5C_6H_4$) 6.4–7.7 (6 H, m, $1.5C_6H_4$)	—	678[d]
4	2.85 [24 H, s, $2N(CH_3)_4^+$][e] 6.5, 7.5 (12 H, br m, $3C_6H_4$)	54.0 [$N(CH_3)_4^+$][e] 120–130 (br, not resolved, C_6H_4)	752[d]
5a	2.35, 2.4, 3.35, 3.95 (6 H, s, $2SCH_3$)[f] 6.6–8.3 (12 H, m, $3C_6H_4$)	33.2, 33.3 (SCH_3)[f] 125.8, 126.0, 126.4, 126.7, 128.2, 128.3, 128.5, 128.7, 128.8, 128.9, 129.0, 129.2, 130.1, 130.3, 130.7, 140.3, 157.6, 161.0 (C_6H_4)	634[g]
5b	1.0 (6 H, t, $2SCH_2CH_3$)[h] 3.5 (4 H, q, $2SCH_2CH_3$) 6.7–7.9 (12 H, m, $3C_6H_4$)		662[g]

[a] At 270 MHz; standard $SiMe_4$. [b] Standard $SiMe_4$. [c] Solvent [$^2H_7$]dmf. [d] Field desorption. [e] Solvent [$^2H_6$]dmso. [f] Solvent CD_2Cl_2. [g] Electron impact. [h] Solvent $CDCl_3$.

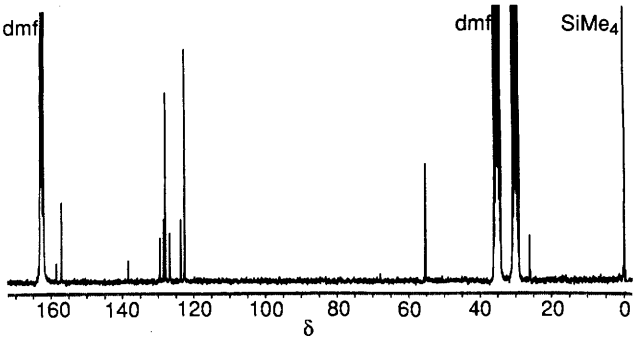


Fig. 1 $^{13}C-\{^1H\}$ NMR spectrum of $[NMe_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ **2a** in [$^2H_7$]dmf

complexes are not unusual and are also found with sulphur ligands, $[WH_2(CO)_3(PR_3)_2]$ [$R_3 = (C_6H_{11})_3$, Pr^i_3 or $(C_6H_{11})_2Pr^i$][11] or $[Mo(MeSC_6H_4S)_3(NO)]$[9] being examples.

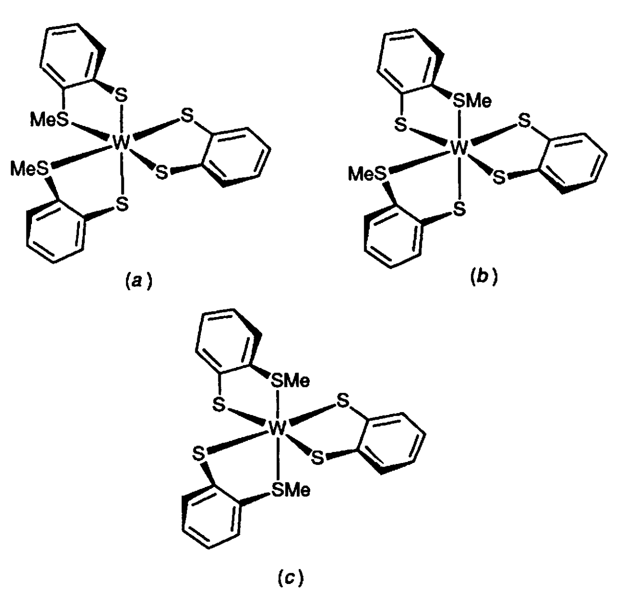
The closest analogue to reaction (*i*) (Scheme 1) we could find in literature is the alkyl-group migration found in $[Rh(COR)(PPh_3)(thf)(mnt)]$ [R = Et or Pr^n; mnt = maleonitriledithiolate(2−)],[12] which gives $[Rh(CO)(PPh_3)(R\text{-}mnt)]$ when heated in thf. In this case, however, the R group originates from EtI or Pr^nI when $[Rh(COR)(PPh_3)(thf)(mnt)]$ is synthesised from $[NBu^n_4][Rh(CO)(PPh_3)(mnt)]$ and EtI or Pr^nI.

With respect to electron counting, also the addition of olefins to dithiolene complexes of the nickel triad may be considered related.[13] Treatment of $[Ni\{S_2C_2(CF_3)_2\}_2]$ with norbornadiene affords an adduct with two new C–S bonds in which the two $S_2C_2(CF_3)_2$ ligands are connected by a C–C bond of the norbornadiene unit. Whereas the nickel centre in the adduct is regarded as Ni^{IV}, it has become Ni^{II} in the product, two electrons having been formally transferred from norbornadiene.

In order to achieve reaction (*i*) in Scheme 1 a relatively rapid addition of LiMe to the suspension of complex **1** is necessary. If, however, the LiMe solution is added dropwise a different reaction takes place [Scheme 1, (*ii*)]. The colour of the suspension slowly changes from turquoise to deep purple and deep purple microcrystals precipitate. They were identified by elemental analysis and IR spectra to be $[Li(thf)_4][W(S_2C_6H_4)_3]$ **3a**, which was obtained from **1** by treating it with lithium powder [Scheme 1, (*iv*)]. Complex **3a** can be converted into $[NMe_4][W(S_2C_6H_4)_3]$ which was characterized by elemental analysis, IR and mass spectra [Scheme 1, (*iii*); see Tables 1 and 2].

As expected, the tungsten(V) species **3b** is paramagnetic and exhibits a magnetic moment of μ_{eff} = 2.04 (Gouy balance, 295 K), which corresponds approximately to one unpaired electron. In the ^1H NMR spectrum of **3b** in dimethylsulphoxide (dmso) we observed in addition to the singlet for the NMe_4^+ protons at δ 3.1 a multiplet at δ 6.4—7.7 and two shifted broad signals at δ 2.5 and 18 for the aromatic protons (relative to $SiMe_4$, Table 2).[14]

If Me^- is present in low concentration it obviously functions as a one-electron reducing agent only, giving rise to the



(a) (b) (c)

Fig. 2 Stereoisomers of complex **5a**

tungsten(v) complex and probably a methyl radical; the latter traps a hydrogen atom of the solvent, as shown in equation (2), to give methane which was detected by gas chromatography.

$$\mathbf{1} + Me^- \longrightarrow [W(S_2C_6H_4)_3]^- + Me^\bullet \xrightarrow{\text{solvent}} CH_4 \quad (2)$$

After we had found the unexpected and novel reactions between complex **1** and LiMe, we investigated reactions of **1** with different lithium organyls: $LiCH_2Bu^t$ as well as LiPh react as one-electron reducing agents only [Scheme 1, (*ii*)], yielding again **3a** and the corresponding organic radicals. The neopentyl radicals react not only with the solvent to give neopentane, but they also dimerize and form 2,2,4,4-tetramethylhexane; both species were detected in the reaction solution by mass spectroscopy. In the case of LiPh only the dimer biphenyl is formed which was again detected by mass spectroscopy.

Ethyllithium functions slightly differently [Scheme 1, (*v*)]. Here, again **3a** is formed, but neither ethane nor butane could be found in the solution. Instead, dihydrogen and ethylene were detected by gas chromatography. They possibly form by decomposition of ethyl radicals, but we think them more likely to result from the sequence of reactions outlined in Scheme 1, (*v*). It includes the typical reactions of transition-metal ethyl units and is consistent with the reactions observed for the lithium organyls described above.

The reversible stepwise polarographic reduction of complex **1** and the related tris(toluene-3,4-dithiolato)tungsten(vi) complex $[W(S_2C_6H_3Me)_3]$[7,15] was reported previously. The final step of reduction yielded the dianionic tungsten(iv) complexes, but only the monoanionic tungsten(v) toluenedithiolate complex could be isolated as $[PHPh_3]^+$, $[Hphen]^+$ (phen = 1,10-phenanthroline) and $[NEt_4]^+$ salts;[16,17] in the latter case, however, the tungsten species was obtained in low yield by treating WO_2Cl_2 with potassium–toluene-3,4-dithiol.

When complex **1** is treated with 2 equivalents of $LiBu^n$ a comparable reaction to that with $[Mo(S_2C_6H_4)_3]$[6] takes place yielding a red solution of the tungsten(iv) species $[W(S_2C_6H_4)_3]^{2-}$. This dianion could be isolated as its NMe_4^+ salt **4** and was completely characterized by elemental analysis, IR, mass and NMR spectroscopy [Scheme 1, (*vi*); see Tables 1 and 2]. In contrast to the corresponding molybdenum complex, however, it was not possible to reduce $[W(S_2C_6H_4)_3]^{2-}$ further in order to give species such as $[WH(S_2C_6H_4)_3]^{3-}$.

In order to verify the suggested reaction pathway leading from complex **1** to **2**, we also investigated reactions of **4** and **2b** with typical alkylating agents such as Me_3OBF_4. Indeed, we obtained, in both cases, products $[W(S_2C_6H_4)(RSC_6H_4S)_2]$ (R = Me, **5a**; or Et, **5b**) respectively [Scheme 1, (*vii*), (*viii*)], which clearly differ from **2**. Even, when **4** was treated very slowly with 1 equivalent of Me_3OBF_4 only, no monomethylation could be achieved, and no **2** was formed. Only **5a** and unreacted **4** were recovered from the reaction solution.

Spectroscopic data for complexes **5a** and **5b** are listed in Table 2. As in the case of $[Mo(MeSC_6H_4S)_2(NO)_2]$,[9] three stereoisomers of **5a**, differing with respect to the position of the Me groups, could occur (Fig. 2). Two of them have C_2 symmetry [(*a*) and (*c*)] and one has C_1 symmetry [(*b*)]. They should give rise to one or two, respectively, signals for the MeS group in the ^1H and $^{13}C-\{^1H\}$ NMR spectra and nine or 18, respectively, signals for the aromatic carbon atoms in the $^{13}C-\{^1H\}$ NMR spectrum. The ^1H NMR spectrum of **5a** in CD_2Cl_2 shows four signals for the MeS group: two major singlets at δ 2.35 and 2.4 and two further singlets of lower intensity at δ 3.35 and 3.95. The $^{13}C-\{^1H\}$ NMR spectrum shows two signals for the MeS group and 18 signals for the aromatic carbon atoms. We assume this to be due to the occurrence of stereoisomer **2b** above all.

Properties.—Complexes **2a**, **2b** and **4** are extremely sensitive to air in solution, but are stable under an inert atmosphere or in the solid state. Complexes **5a** and **5b** are soluble in dmso, dmf, CH_2Cl_2, $CHCl_3$, thf and acetone and slightly soluble in methanol and hydrocarbons; **2a**, **2b**, **3b** and **4** are also soluble in dmso and dmf, but only slightly soluble or even insoluble in CH_2Cl_2, $CHCl_3$, thf, acetone, methanol and hydrocarbons.

Experimental

All the reactions were carried out in dried Schlenk tubes under nitrogen; the solvents were dried and distilled under a nitrogen atmosphere before use. The IR spectra were recorded on a Zeiss IMR 16 spectrometer, NMR spectra on a JEOL JNM-PX60 (^1H, 60 MHz) or FTJNM-GX270 (^1H, ^{13}C, 270 MHz) spectrometer. The C, H and N analyses were carried out with a Carlo Erba 1106 elemental analyzer. Hydrogen, CH_4 and C_2H_4 were determined by gas chromatography using a Philips PU 4500 instrument fitted with an activated carbon column and a thermal conductivity detector. The mass spectra were recorded on a Varian 212 MAT spectrometer. The compounds $[W(S_2C_6H_4)_3]$ **1**,[7] LiEt[18] and $LiCH_2Bu^t$[19] were prepared by published procedures; LiMe and $LiBu^n$ were purchased from Merck, PhLi from Janssen, Me_3OBF_4 and Et_3OBF_4 from Fluka. The microanalytical, NMR (^1H, $^{13}C-\{^1H\}$), and mass spectral data for the complexes are listed in Tables 1 and 2.

Preparation of $[NR_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ **2a** *and* **2b**.—A solution of LiMe in diethyl ether (1.6 mol dm^{-3}, 1.66 cm^3, 2.65 mmol) was added rapidly to a suspension of complex **1** (1.6 g, 2.65 mmol) in thf (25 cm^3) at −70 °C. The colour changed immediately from turquoise to red. The temperature was allowed to increase, the red solution was filtered and treated with a methanol solution of NMe_4Cl (1 mol dm^{-3}, 2.7 cm^3, 2.7 mmol). The red crystals were filtered off, washed with warm methanol (2 × 20 cm^3), and dried *in vacuo*. The product was analytically pure $[NMe_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ **2a** (1.57 g, 85%). The preparation of **2b** was carried out by the same method using a methanol solution of NEt_4Cl (yield: 70%).

Reaction of Complex **1** *with* LiMe *yielding* $[NMe_4][W(S_2C_6H_4)_3]$ **3b**.—A solution of LiMe in diethyl ether (1.6 mol dm^{-3}, 0.85 cm^3, 1.36 mmol) was added dropwise to a suspension of complex **1** (0.82 g, 1.36 mmol) in thf (25 cm^3). Methane was evolved. The resulting dark purple precipitate of complex **3a** was recrystallized from thf (66, 20 °C). Yield 1.04 g (85%). The microcrystals of **3a** were dissolved in CH_2Cl_2 (30 cm^3) and a solution of NMe_4Cl in methanol (1 mol dm^{-3}, 1.36 cm^3, 1.36 mmol) was added, giving dark purple microcrystals of **3b** which were washed with CH_2Cl_2 (3 × 5 cm^3) and dried in *vacuo* (0.66 g, 73%).

Reaction of Complex **1** *with* LiR (R = Et, CH_2Bu^t *or* Ph) *giving* $[NMe_4][W(S_2C_6H_4)_3]$ **3b**.—A solution of LiR [in benzene (R = Et) (0.58 mol dm^{-3}, 1.7 cm^3, 1 mmol), in hexane (R = CH_2Bu^t) (0.228 mol dm^{-3}, 4.4 cm^3, 1 mmol), or in cyclohexane–diethyl ether (70:30) (R = Ph) (2 mol dm^{-3}, 0.5 cm^3, 1 mmol)] was added to a suspension of complex **1** (0.61 g, 1 mmol) in thf (30 cm^3) yielding deep purple microcrystals of **3a**. Hydrogen and ethylene were evolved in the case of LiEt. When $LiCH_2Bu^t$ or LiPh was added to **1**, neopentane and 2,2,4,4-tetramethylhexane or biphenyl, respectively, were afforded. The solvent was removed *in vacuo* to leave a solid which was dissolved in CH_2Cl_2 (30 cm^3). The solution was filtered and a solution of NMe_4Cl in methanol (1 mol dm^{-3}, 1 cm^{-3}, 1 mmol) added. The resulting dark purple precipitate of complex **3b** was filtered off, washed with warm acetone (20 cm^3), and dried *in vacuo* (yield in each case 0.5 g, 75%).

Preparation of $[NMe_4]_2[W(S_2C_6H_4)_3]$ **4**.—To a suspension of complex **1** (1.02 g, 1.68 mmol) in thf (30 cm^3) was added a solution of $LiBu^n$ in hexane (1.6 mol dm^{-3}, 2.1 cm^3, 3.36 mmol). The colour changed slowly from turquoise to red. After filtration of the solution the complex was precipitated by adding a solution of NMe_4Cl in methanol (1 mol dm^{-3}, 3.36 cm^3, 3.36 mmol). The red microcrystals were filtered off, washed with methanol (3 × 20 cm^3) and warm acetone (30 cm^3), and dried *in vacuo* (1.8 g, 67%).

Preparation of $[W(S_2C_6H_4)(MeSC_6H_4S)_2]$ **5a**.—(*a*) *From* $[NMe_4]_2[W(S_2C_6H_4)_3]$ **4**. To a suspension of complex **4** (1.72 g, 2.28 mmol) in CH_2Cl_2 (40 cm^3) was added Me_3OBF_4 (0.67 g, 4.56 mmol). A dark yellow solution resulted which was stirred for 4 h then evaporated to dryness. The brown residue was washed with methanol (30 cm^3), filtered off, and dried *in vacuo* to give complex **5a** as a brown solid (0.42 g, 64%).

(*b*) *From* $[NEt_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ **2b**. Addition of Me_3OBF_4 (0.14 g, 0.95 mmol) to a suspension of complex **2b** (0.71 g, 0.95 mmol) in CH_2Cl_2 (20 cm^3) yielded a dark yellow solution. After 3 h of stirring the solvent was removed *in vacuo*, the brown residue washed with methanol (30 cm^3), filtered off, and dried *in vacuo* to give complex **5a** as a brown solid (0.48 g, 80%).

Preparation of $[W(S_2C_6H_4)(EtSC_6H_4S)_2]$ **5b**.—Addition of a solution of $LiBu^n$ in hexane (1.6 mol dm^{-3}, 1.25 cm^3, 2 mmol) to a suspension of complex **1** (0.61 g, 1 mmol) in thf (25 cm^3) gave a red solution. After filtration a solution of Et_3OBF_4 in CH_2Cl_2 (1 mol dm^{-3}, 2 cm^3, 2 mmol) was added. The colour changed from red to dark yellow. The solvent was evaporated to dryness, the brown residue washed with methanol (30 cm^3), filtered off, and dried *in vacuo* to give complex **5b** as a brown solid (0.4 g, 61%).

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References

1 Part 66, D. Sellmann, W. Kern, A. Holzmeier, G. Pöhlmann and M. Moll, *Z. Naturforsch.*, submitted for publication.
2 T. R. Hawkes, P. A. McLean and B. E. Smith, *Biochem. J.*, 1984, **217**, 317.
3 E. I. Stiefel, *Prog. Inorg. Chem.*, 1977, **22**, 1.
4 J. Okura, *Coord. Chem. Rev.*, 1985, **68**, 59.
5 *Molybdenum Enzymes, Metal Ions in Biology*, ed. T. G. Spiro, Wiley, New York, 1985, vol. 7.
6 D. Sellmann and L. Zapf, *Z. Naturforsch., Teil B*, 1985, **40**, 380.
7 E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and R. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 2956.
8 E. Deutsch, M. J. Root and D. L. Nosco, in *Advances in Inorganic and Bioinorganic Mechanisms*, ed. A. G. Sykes, Academic Press, London, 1982, vol. 1, p. 269.
9 D. Sellmann, L. Zapf, J. Keller and M. Moll, *J. Organomet. Chem.*, 1985, **289**, 71.
10 D. Sellmann, M. Waeber, G. Huttner and L. Zsolnai, *Inorg. Chim. Acta*, 1986, **118**, 49.
11 G. J. Kubas, C. J. Unkefer, B. I. Swanson and E. Fukushima, *J. Am. Chem. Soc.*, 1986, **108**, 7000.
12 C.-H. Cheng and R. Eisenberg, *Inorg. Chem.*, 1979, **18**, 2438.
13 R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.
14 (*a*) T. J. Swift, in *NMR of Paramagnetic Molecules*, eds. G. N. La Mar, W. De W. Horrocks and R. H. Holm, Academic Press, London, 1973, p. 53; (*b*) I. Bertini, C. Luchinat and L. Messoni, in *Metal Ions in Biological Systems*, ed. H. Sigel, Marcel Dekker, Basel, 1987, vol 21, p. 47.
15 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.
16 M. Kawashima, M. Kayama and T. Fujinaga, *J. Inorg. Nucl. Chem.*, 1976, **38**, 801.
17 E. J. Wharton and J. A. McCleverty, *J. Chem. Soc. A*, 1969, 2258.
18 T. V. Talalaeva and K. A. Kocheshkov, *J. Gen. Chem. USSR* (*Engl. Transl.*), 1953, **23**, 399.
19 R. R. Schrock and F. D. Fellmann, *J. Am. Chem. Soc.*, 1978, **100**, 3359.

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