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SCRAMBLING OF DITHIOACID LIGANDS IN SOME (η-CYCLOPENTADIENYL)NITROSYL-MOLYBDENUM AND -TUNGSTEN DERIVATIVES

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Summary

The complexes $[M(\eta\text{-}C_5H_5)(NO)I_2]_2$ (M = Mo, W) react with dithioacid ligands $(S\text{–}S)^-$ (S–S = $S_2P(OR)_2$, S_2CNR_2, S_2COR, S_2CSR) to produce mono- and di-substituted derivatives $[M(\eta\text{-}C_5H_5)(NO)I(S\text{–}S)]$ and $[M(\eta\text{-}C_5H_5)(NO)(S\text{–}S)_2]$. These compounds have an 18 electron configuration and a "four-legged piano-stool" geometry. Facile intramolecular unidentate-bidentate scrambling of the dithio ligands has been monitored using ^{31}P and ^1H NMR spectroscopy for $[M(\eta\text{-}C_5H_5)(NO)\{PS_2(OR)_2\}_2]$ and $[M(\eta\text{-}C_5H_5)(NO)(S_2COMe)_2]$, and activation parameters obtained for the latter. The complexes $[M(\eta\text{-}C_5H_5)(NO)(S_2CNR_2)\{S_2P(OR)_2\}]$, which contain a bidentate dithiocarbamato ligand and a monodentate dithiophosphato group, are stereochemically rigid. In order to relate the coordination mode of the $PS_2(OR)_2$ ligand to the ^{31}P NMR chemical shift, other complexes including dicarbonyl $[M(\eta\text{-}C_5H_5)(CO)_2(S\text{–}S)]$, tricarbonyl $[M(\eta\text{-}C_5H_5)(CO)_3(S\text{–}S)]$, nitrosyl $[M(NO)(S\text{–}S)_3]$ and dinitrosyl $[M(NO)_2(S\text{–}S)_2]$ derivatives were also studied.

Introduction

Facile intramolecular unidentate-bidentate scrambling of the 1,1-dithioacid ligands has been shown to occur in many transition-metal complexes containing two or three

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(S–S) ligands. Previous studies indicated that simultaneous mono- and bi-dentate coordination of the S–S groups may appear because of (i) geometrical constraints imposed by the central metal atom (usual square-planar coordination of platinum in $[M(PR_3)(S–S)_2]$ and $[M(S–S)_3]^-$ derivatives for instance [1,2]), and (ii) electronic factors. This is the case, for example, for $[ML_n(S-S)_2]$ complexes with a 14-electron ML_n moiety, such as the ruthenium complexes $[Ru(\eta\text{-}C_6H_6)(S–S)_2]$ and the isoelectronic rhodium derivatives $[Rh(\eta\text{-}C_5Me_5)(S–S)_2]$ [3]. In keeping with the 18-electron rule, such compounds contain two S–S groups acting as three- and one-electron ligands respectively.

Our interest in molybdenum and tungsten chemistry prompted us to investigate the behaviour of dithioacid ligands towards Group VI metal complexes. We decided to work with $M(\eta\text{-}C_5H_5)(NO)$ derivatives because: (i) this is a 14-electron unit; (ii) Mo^{IV} and W^{IV} derivatives are wellknown, and therefore $[M(\eta\text{-}C_5H_5)(NO)(S–S)_2]$ complexes seemed likely to be isolable. Among the wide variety of 1,1-dithioacid ligands (S_2CNR_2, S_2COR, S_2CSR, $S_2P(OR)_2$, S_2PR_2, S_2PF_2, etc.) we choose to study mainly the *O,O'*-dialkyldithiophosphate $PS_2(OR)_2$ derivatives because these phosphorus ligands have been less explored than the extensively studied dithiocarbamates and, furthermore, they provided an opportunity to use ^{31}P NMR to gain important structural information.

We describe here the syntheses and properties of $[M(\eta\text{-}C_5H_5)(NO)(S–S)_2]$ (M = Mo, W) complexes. In order to relate the coordination mode of the $PS_2(OR)_2$ ligand to the ^{31}P NMR chemical shift, other related complexes such as carbonyl and dinitrosyl derivatives were also studied.

Results

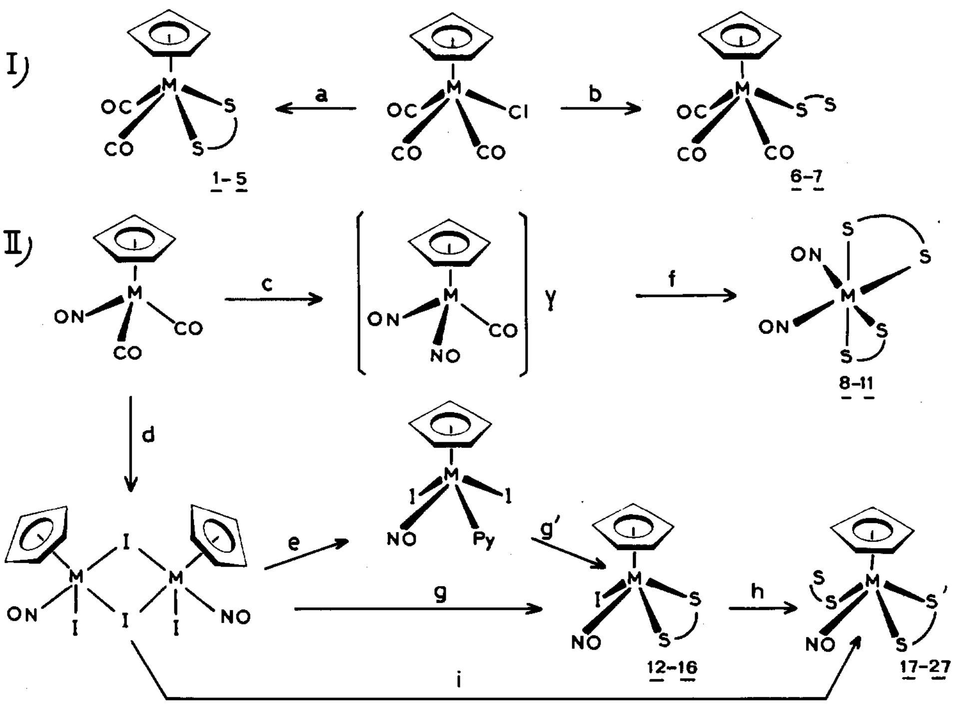
(a) Carbonyl complexes

Treatment of $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ (M = Mo, W) with *O,O'*-dialkyldithiophosphoric acids $HSP(S)(OR)_2$ in the corresponding alcohol ROH afforded the new species $[M(\eta\text{-}C_5H_5)(CO)_2\{PS_2(OR)_2\}]$ (**1–5**) (M = Mo, **1**: R = Me; **2**: R = Et; **3**: R = i-Pr. M = W, **4**: R = Et; **5**: R = i-Pr). The spectral properties of these complexes (Table 1) are consistent with an eighteen electron configuration and a "four-legged piano-stool" geometry (Scheme 1). Thus, IR spectra exhibit $\nu(PS)$ absorptions (ν_s ca. 540 cm^{-1}; ν_{as} ca. 640 cm^{-1}) attributable to bidentate $[PS_2(OR)_2]$ ligand [4] while ^1H and ^{13}C NMR spectra show magnetically inequivalent OR groups at ambient temperature. Surprisingly, use of similar procedures with $HS\overline{P(S)OCH_2CH_2O}$ in ethylene glycol/toluene mixture did not give the corresponding dicarbonyl species but instead gave the new tricarbonyl derivatives $[M(\eta\text{-}C_5H_5)(CO)_3\text{-}\{S_2\underline{POCH_2CH_2O}\}]$ (**6**: M = Mo; **7**: M = W), for which the IR frequency at ca. 790 cm^{-1} was assigned to the PS stretching mode of a monodentate $[PS_2(OR)_2]$ ligand [4].

The *N,N*-dialkyldithiocarbamates, alkylxanthates (*O*-alkyldithiocarbonates) and alkylthioxanthates (*S*-alkyl trithiocarbonates) analogous to complexes **1–7** have been previously described [5–10].

(b) Dinitrosyl complexes

The η-cyclopentadienyl ring in the cationic complexes $[M(\eta\text{-}C_5H_5)(NO)_2(CO)]Y$



SCHEME 1. Syntheses of dithioacid molybdenum and tungsten derivatives. (a) $HPS_2(OR)_2$ in ROH. **1**: M = Mo, R = Me. **2**: M = Mo, R = Et; **3**: M = Mo, R = i-Pr; **4**: M = W, R = Et; **5**: M = W, R = i-Pr. (b) $HSP(S)OCH_2CH_2O$ in ethylene glycol/toluene mixture. **6**: M = Mo; **7**: M = W. (c) NOY (Y = PF_6 or BF_4) [24]. (d) I_2 [22 and 23]. (e) Pyridine [23]. (f) $NaPS_2(OR)_2$ in ROH. **8**: M = Mo, R = Et; **9**: M = Mo, R = i-Pr; **10**: M = W, R = Et; **11**: M = W, R = i-Pr. (g) 2 molar equiv. Na(S–S) (g′: 1 molar equiv. Na(S–S)). **12**: M = Mo, S–S = $PS_2(OEt)_2$; **13**: M = Mo, S–S = $S_2P(O\text{-}i\text{-}Pr)_2$; **14**: M = W, S–S = $PS_2(O\text{-}i\text{-}Pr)_2$; **15**: M = Mo, S–S = S_2COEt; **16**: M = Mo, S–S = S_2CSEt. (h) 2 molar equiv. Na(S–S′) **17**: M = Mo, S–S = S–S′ = $PS_2(OEt)_2$; **18**: M = Mo; S–S = S–S′ = $PS_2(O\text{-}i\text{-}Pr)_2$; **19**: M = W, S–S = S–S′ = $PS_2(OEt)_2$; **20**: M = W, S–S = S–S′ = $PS_2(O\text{-}i\text{-}Pr)_2$; **21**: M = Mo, S–S = S_2CNMe_2, S–S′ = $PS_2(OEt)_2$; **22**: M = Mo, S–S = S_2CNEt_2, S–S′ = $PS_2(OEt)_2$; **23** M = Mo, S–S = S_2CNMe_2; S–S′ = $PS_2(O\text{-}i\text{-}Pr)_2$ **24**: M = Mo, S–S = S_2CNEt_2; S–S′ = $PS_2(O\text{-}i\text{-}Pr)_2$; **25**: M = Mo, S–S = S–S′ = S_2COMe; **26**: M = Mo, S–S = S–S′ = S_2COEt; **27**: M = Mo, S–S = S–S′ = S_2CSEt. (i) 4 molar equiv. of Na(S–S′) when S–S = S–S′.

(M = Mo; Y = PF_6. M = W; Y = BF_4) was readily cleaved by thermal reaction with $NaPS_2(OR)_2$. On the basis of the analytical and spectroscopic data given in Table 1 (two NO stretching frequencies, no ν(PS) frequency in the region 650–800 cm^{-1}, and equivalence of the two phosphorus atoms), we propose for the resulting green compounds $[M(NO)_2\{PS_2(OR)_2\}_2]$ (M = Mo, **8**: R = Et; **9**: R = i-Pr. M = W, **10**: R = Et; **11**: R = i-Pr) a *cis*-octahedral structure (Scheme 1) similar to that reported for the corresponding dithiocarbamato complexes [11].

(c) Mononitrosyl complexes

Treatment of the dinuclear derivatives $[M(\eta\text{-}C_5H_5)(NO)I_2]_2$ with 2 molar equivalents of $NaPS_2(OR)_2$ gave the monomeric $[M(\eta\text{-}C_5H_5)(NO)I\{PS_2(OR)_2\}]$ complexes (M = Mo, **12**: R = Et; **13**: R = i-Pr. M = W, **14**: R = i-Pr). We can reasonably assume (from the ν(PS) frequencies, mass spectra and molar conductivities) that these species have an 18 electron molecular structure with a bidentate dithiolate group, just like the previously known molybdenum dialkyldithiocarbamato complexes [12]. The easy syntheses of complexes **12** and **13** from [Mo(η-C_5H_5)(NO)I_2(C_5H_5N)] were also in agreement with their monomeric structure. Similar reactions occurred when [Mo(η-C_5H_5)(NO)I_2]$_2$ was treated with 2 molar equivalents of KS_2COEt or NaS_2CSEt in ethanol.

In a study of the possible replacement of the iodide ligand of complexes **12–16**, **12** was treated with an excess of $NaPS_2(OEt)_2$. After column chromatography, an orange micro-crystalline powder of compound **17**, [Mo(η-C_5H_5)(NO){$PS_2(OEt)_2$}$_2$], was isolated. ^{31}P NMR data were diagnostic of the scrambling, at room temperature, of a mono- and bi-dentate $PS_2(OR)_2$ ligands. This phenomenom is analysed below. The similar compounds [M(η-C_5H_5)(NO){$S_2P(OR)_2$}$_2$] (M = Mo, **18**: R = i-Pr. M = W, **19**: R = Et; **20**: R = i-Pr) and [Mo(η-C_5H_5)(NO)(S_2CX)$_2$] (**25**: X = OMe; **26**: X = OEt; **27**: X = SEt) were also synthesized. The last three complexes showed temperature dependent ^1H NMR spectra (see (*d*)).

It is noteworthy that when the tungsten derivative **14** [W(η-C_5H_5)(NO)I{PS_2(O-i-Pr)$_2$}] was treated with 1 molar equiv. of $NaPS_2$(O-i-Pr)$_2$ [or when [W(η-C_5H_5)-(NO)I_2]$_2$ was treated with 4 molar equiv. of $NaPS_2(OR)_2$], [W(NO){$PS_2(OR)_2$}$_3$] (**28**: R = Et; **29**: R = i-Pr), arising from η-cyclopentadienyl ring displacement reaction, was separated from the [W(η-C_5H_5)(NO){$S_2P(OR)_2$}$_2$] derivatives by column chromatography. On the basis of ^{31}P NMR data (see below), we assume that compounds **28** and **29** have an octahedral structure, with one monodentate and two bidentate sulphur ligands, while the corresponding dithiocarbamato complexes [M(NO)(S_2CNR_2)$_3$] (M = Mo, W) involve seven coordination with three bidentate sulphur ligands [11–13].

Mixed molybdenum dithioacid complexes [Mo(η-C_5H_5)(NO){$PS_2(OR)_2$} ($S_2CNR'_2$)] (**21**: R = Et, R′ = Me. **22**: R = Et, R′ = Et. **23**: R = i-Pr, R′ = Me. **24**: R = i-Pr; R′ = Et) may be prepared by the reaction between complexes **12** or **13** [Mo(η-C_5H_5)(NO)I{$PS_2(OR)_2$}] and 1 molar equivalent of NaS_2CNR_2. Up to 330 K (the limit of our study), the ^{31}P NMR spectra of these mixed complexes were invariant. They indicated the presence of a monodentate dithiophosphorus ligand, and this was consistent with IR data since a strong ν(PS) absorption was observed in the characteristic region (770–800 cm^{-1}) of a monodentate $PS_2(OR)_2$ group while a strong absorption in the range 1515–1550 cm^{-1} was assigned to the ν(CN) vibration of a bidentate dithiocarbamato ligand [14]. Previously reported mixed complexes such as [Rh(η-C_5Me_5)(S_2PR_2)($S_2CNR'_2$)] [3] and [PtL(S_2PR_2)($S_2CNR'_2$)] [15] also contained bidentate $S_2CNR'_2$ groups and monodentate dithiophosphinato ligands.

(d) NMR study. Scrambling of the S–S ligands

The ^{31}P chemical shifts are given in Table 2. Surprisingly, the sensitivity of $\delta(^{31}P)$ towards the nature of the metal atom depends markedly on the nature of the complexes. It appears very strong in the carbonyl complexes **1–7** (from 11 to 15 ppm) and strong (6 ppm) for the [M(η-C_5H_5)(NO)I {$S_2P(OR)_2$}] derivatives **13** and **14**. In contrast, there is no difference in $\delta(^{31}P)$ between the Mo and W dinitrosyl complexes **8–11**.

According to Glidewell [16], the extreme modes of M–$PS_2(OR)_2$ interaction [ionic interaction, mono-, bi- and bridging coordination] may be distinguished from the ^{31}P chemical shifts, a monodentate group resonance being shielded relative to a bidentate (or a bridging) group signal, both appearing at lower field than the signal of a $PS_2(OR)_2$ anion.

For some complexes reported here, the coordination mode of the $PS_2(OR)_2$ ligand was deduced from IR spectroscopy (ν(PS) frequency) along with the 18 electron rule (complexes **1**–**7**, **12**–**14** and **21**–**24**) or from usual structural considerations (complexes **8**–**11**). For the bidentate coordination, the observed chemical shifts (90–104 ppm) in the molybdenum complexes were broadly consistent with Glidewell's data (97–101 ppm) while, if the $[W(NO)\{PS_2(OR)_2\}_3]$ derivatives **28**–**29** (see below) are excluded, deshielding was found for the tungsten complexes (93–111 ppm). In contrast, we observed that a monodentate $PS_2(OR)_2$ ligand resonates at lower field (105–111 ppm for Mo derivatives) than the bidentate ligand. We previously reported a similar result in niobium chemistry: the complex $[Nb(\eta\text{-}C_5H_5)_2(S_2)\{S_2P(OEt)_2\}]$, which has been shown by X-ray study to contain a monodentate dithiophosphato group, exhibited a ^{31}P NMR signal at δ 108.9 ppm [18]. The relative positions of the doublet and the triplet observed on the ^{31}P NMR spectrum of complexes $[W(NO)\{PS_2(OR)_2\}_3]$ were also in agreement with the above assignment although, for unknown reasons, the doublet appeared at very high field (ca. 75 ppm).

The fluxional behaviour of complexes $[M(\eta\text{-}C_5H_5)(NO)\{PS_2(OR)_2\}_2]$ (**17**–**20**) were monitored by ^{31}P NMR spectroscopy. As an example, ^{31}P NMR spectra for

(Continued on p. 321)

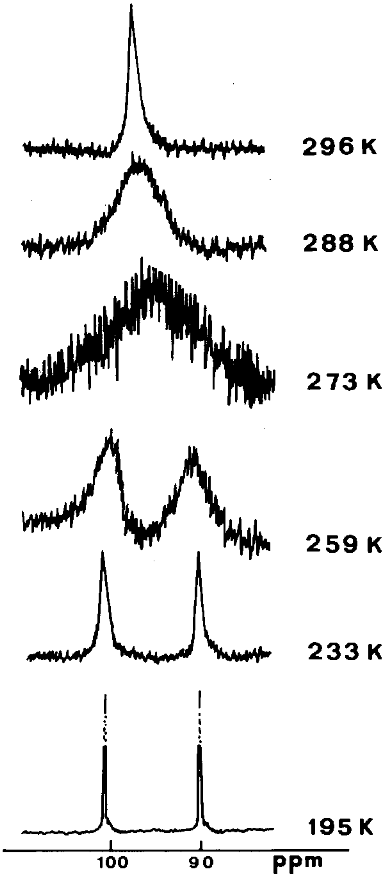


Fig. 1. ^{31}P NMR spectra for complex **18** $[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}_2]$ (solvent: acetone).

TABLE 1

ANALYTICAL AND SPECTROSCOPIC RESULTS

Complexes	Colour	Analysis (Found (calcd.) (%)) ^{a}					IR data ^{a} (cm^{-1}) ν(CO) (CH$_2$Cl$_2$) ν(other) (Nujol mull)	^{1}H and ^{13}C NMR in CDCl$_3$ (δ, ppm; J, Hz)
		C	H	N	P	S		
[M(η-C$_5$H$_5$)(CO)$_2${PS$_2$(OR)$_2$}]								
(**1**, M = Mo, R = Me)	purple	28.9 (28.9)			8.3 (8.3)	17.0 (17.1)	545m and 645 m ν(PS) 1860 vs and 1960 vs ν(CO)	^{1}H: 3.60,d,CH$_3$(^3J(HP) = 14.1);3.78,d,CH$_3$(^3J(HP) 14.2); 5.48,s,C$_5$H$_5$.^{13}C: 53.1,d,CH$_3$(^2J(CP) 5.5);54.5,d,CH$_3$ (^2J(CP) 4.6); 95.1,s,C$_5$H$_5$;254.5,s,CO; 254.8,s,CO.
(**2**, M = Mo, R = Et)	purple	33.0 (32.8)			7.7 (7.7)	15.8 (15.9)	545 m and 645 m ν(PS) 1865 vs and 1960 vs ν(CO)	^{1}H: 1.29,t,CH$_3$(^3J(HH) 7.1; ^4J(HP) 0.6);1.37,t,CH$_3$ (^3J(HH) 7.1;^4J(HP) 0.6); 3.87,d of quad,CH$_2$(^3J(HH) 7.1; ^3J(HP) 9.2); 4.04,d of quad,CH$_2$(^3J(HH) 7.1; ^3J(HP) 9.2); 5.48,s,C$_5$H$_5$. ^{13}C: 15.9,m,2CH$_3$; 63.1,d,CH$_2$ (^2J(CP) 5,5); 64.4,d,CH$_2$(^2J(CP) 5.5); 95.1,s,C$_5$H$_5$; 254.8,s,CO; 255.1,s,CO.
(**3**, M = Mo, R = i-Pr)	purple	36.5 (36.3)			7.2 (7.2)	14.7 (14.9)	545 m and 630 m ν(PS) 1890 vs and 1960 vs ν(CO)	^{1}H: 1.28,d,2CH$_3$(^3J(HH) 6.3); 1.35,d,2CH$_3$(^3J(HH) 6.3); 4.48,m,2CH(^3J(HH) 6.3; ^3J(HP) 12.4); 5.45,s,C$_5$H$_5$. ^{13}C: 23.8,m,4CH$_3$; 72.5,d,CH(^2J(CP) 5.5); 74.1,d,CH (^2J(CP) 5.5); 95.0,s,C$_5$H$_5$; 255.0,s,CO; 255.3,s,CO.
(**4**, M = W, R = Et)	purple	26.9 (26.9)	3.0 (3.1)			13.0 (13.0)	540 m and 645 m ν(PS) 1870 s and 1960 s ν(CO)	^{1}H: 1.31,t,CH$_3$(^3J(HH) 7.0; ^4J(HP) 0.6); 1.36,t,CH$_3$ (^3J(HH) 7.0; ^4J(HP) 0.6); 4.00,m,2CH$_2$(^3J(HH) 7.0; ^3J(HP) 8.7); 5.61,s,C$_5$H$_5$. ^{13}C: 16.0,m,2CH$_3$; 63.2,d,CH$_2$(^2J(CP) 5.0); 65.2,d,CH$_2$(^2J(CP) 5.0); 93.5,s,C$_5$H$_5$; 246.3,s,CO; 246.6,s,CO.
(**5**, M = W, R = i-Pr)	purple	30.0 (30.1)	3.9 (3.7)			12.2 (12.3)	540 m and 635 m ν(PS) 1875s and 1940 s ν(CO)	^{1}H: 1.30,d,2CH$_3$(^3J(HH) 6.2); 1.36,d,2CH$_3$(^3J(HH) 6.2); 4.51,m,2CH(^3J(HH) 6.2; ^3J(HP) 12,3); 5.71,s,C$_5$H$_5$. ^{13}C: 23.8,m,4CH$_3$; 72.8,d,CH(^2J(CP) 6.0); 74.9,d,CH (^2J(CP) 6.0); 93.4,s,C$_5$H$_5$; 246.6,s,CO; 246.9,s,CO.
[M(η-C$_5$H$_5$)(CO)$_3${($S_2\overline{POCH_2CH_2O}$)}]								
(**6**, M = Mo)	purple	30.7 (30.0)			7.9 (7.8)	15.9 (16.0)	660s, 785s and 795s ν(PS) 1845 vs, 1875 vs and 1965 vs ν(CO)	^{1}H: 4.34,d,2CH$_2$(^3J(HP) 13.0); 5.40,s,C$_5$H$_5$. ^{13}C: 65.6,d of d,2CH$_2$(^2J(CP) 2.8); 94.0,s,C$_5$H$_5$; 252.4,s,CO; 252.8,s,CO.
(**7**, M = W)	purple		^{b}				660s, 790 s and 800 sh,ν(PS) 1855 s, 1920 s and 1945 s ν(CO)	^{1}H: 4.43,d,2CH$_2$(^3J(HP) 12,2); 5.65,s,C$_5$H$_5$. ^{13}C: 66.7,d of d,2 CH$_2$(^2J(CP) 3.7); 93.5,s,C$_5$H$_5$; 244.8,s,CO; 245.2,s,CO; 249.8,s,CO.
cis-[M(NO)$_2${PS$_2$(OR)$_2$}$_2$]								
(**8**, M = Mo, R = Et)	green	18.2 (18.3)	3.2 (3.8)	5.3 (5.3)			530s,552w and 645 vs ν(PS) 1650 vs and 1780 vs ν(NO)	^{1}H: 1.30,t,2CH$_3$(^3J(HH) 7.1; ^4J(HP) 0.6); 1.33,t,2CH$_3$ (^3J(HH) 7.1; ^4J(HP) 0.6); 4.10,m,4CH$_2$(^3J(HH) 7.1;^3J(HP) 10.2).

(9, M = Mo, R = i-Pr)	green	25.5 (24.9)	4.9 (4.8)	4.6 (4.8)			530s,555 s and 640 vs ν(PS) 1670 vs and 1785 vs ν(NO)	^{1}H: 1.31,m,8CH$_3$; 4.75,m,4CH.
(10, M = W, R = Et)	green	17.6 (15.6)	3.6 (3.3)	4.2 (4.6)	10.0 (10.1)	21.2 (20.9)	525s,552w,640vs and 660 sh ν(PS) 1635vs and 1765 vs ν(NO)	^{1}H: 1.42,t,4CH$_3$(^{3}J(HH) 7.0; ^{4}J(HP) 0.6); 4.20,m,4CH$_2$ (^{3}J(HH) 7,0); ^{3}J(HP) 10.0); ^{13}C: 16.0,m,4CH$_3$; 64.6,m,4CH$_2$.
(11, M = W, R = i-Pr)	green	22.6 (21.5)	4.2 (4.2)	4.1 (4.2)	8.0 (9.2)	17.0 (19.1)	535s,555w and 640 vsν(PS) 1660vs and 1765 vs ν(NO)	^{1}H: 1.38,m,8CH$_3$(^{3}J(HH) 6.1); 4.85,m,4CH(^{3}J(HH) 6.1); ^{13}C: 23.7,m,8CH$_3$; 74.0,m,4CH.
[M(η-C$_5$H$_5$)(NO)I(S−S)]								
(12, M = Mo; S–S = PS$_2$(OEt)$_2$)	brown	21.4 (21.5)	3.2 (2.9)	2.7 (2.8)		12.3 ^{c} (12.7)	545m and 635s ν(PS) ^{e} 1665 vs ν(NO)	^{1}H ^{f}: 1.34,t,CH$_3$(^{3}J(HH) 7.1; ^{4}J(HP) 0.6); 1.38,t,CH$_3$ (^{3}J(HH) 7.1; J(HP) 0.6); 4.08,d of quad,CH$_2$(^{3}J(HH) 7.1; ^{3}J(HP) 9.7); 4.21, d of quad,CH$_2$(^{3}J(HH) 7.1; ^{3}J(HP) 9.7); 6.19,s,C$_5$H$_5$. ^{13}C: 16.0,m,2CH$_3$; 64.1,d,CH$_2$(^{2}J(CP) 6.1); 65.1,d,CH$_2$(^{2}J(CP) 6.1); 104.7,s,C$_5$H$_5$.
(13, M = Mo; S–S = PS$_2$(O-i-Pr)$_2$)	brown	25.6 (24.9)	3.6 (3.6)	2.6 (2.6)			545 m and 635 vs ν(PS) 1665 vs ν(NO)	^{1}H: 1.36,d,2CH$_3$(^{3}J(HH) 6.0); 1.42,d,2CH$_3$(^{3}J(HH) 6.0); 4.66,m,2CH(^{3}J(HH) 6.1; ^{3}J(HP) 12.5); 5.97,s,C$_5$H$_5$.
(14, M = W; S–S = PS$_2$(O-i-Pr)$_2$)	brown	23.6 (21.3)	3.4 (3.1)	2.3 (2.3)		10.5 (10.3)	542 m and 635 s ν(PS) 1648vs ν(NO)	^{1}H ^{f}: 1.35,m,2CH$_3$; 4.71,m,2CH; 6.11,s,C$_5$H$_5$.
(15, M = Mo; S–S = S$_2$COEt)	orange	22.1 (21.9)	2.1 (2.3)	2.8 (3.2)			1031 m and 1048 s ν(CS) 1131 ν(CO), 1258 vs ν(COR) 1665 vs ν(NO)	^{1}H: 1.48,t,CH$_3$(^{3}J(HH) 7.0); 4.60,quad,CH$_2$(^{3}J(HH) 7.0) 6.04,s,C$_5$H$_5$.
(16, M = Mo; S–S = S$_2$CSEt)	orange	19.9 (21.1)	2.1 (2.2)	2.6 (3.1)			961s and 992s ν(CS) 1650vs ν(NO)	^{1}H: 1.42,t,CH$_3$(^{3}J(HH) 7.0); 3.32,quad,CH$_2$(^{3}J(HH) 7.0); 6.04,s,C$_5$H$_5$.
[M(η-C$_5$H$_5$)(NO)(S−S)(S−S)′]								
(17, M = Mo; S–S = (S–S)′ = PS$_2$(OEt)$_2$)	orange	28.3 (27.8)	4.4 (4.5)	2.4 (2.5)		22.0 ^{d} (22.8)	540 m, 640 sh, 655 s and 770 m ν(PS) 1685 vs ν(NO)	^{1}H ^{f}: 1.32,m,4CH$_3$; 4.12,m,4CH$_2$; 6.20,s,C$_5$H$_5$. ^{13}C: 16.0,m,4CH$_3$(^{3}J(CP) 3.8);63.9,m,4CH$_2$(^{2}J(CP) 6.9); 105.9,s,C$_5$H$_5$.
(18, M = Mo; S–S = (S–S)′ = PS$_2$(O-i-Pr)$_2$)	orange			^{b}			550 m, 565 m, 650 s and 770 s ν(PS) 1685 vs ν(NO)	^{1}H ^{f}: 1.31,m,8CH$_3$; 4.71,m,4CH; 6.15,s,C$_5$H$_5$. ^{13}C: 23.8,quad,8CH$_3$; 73.2,t,4CH; 105.7,s,C$_5$H$_5$.
(19, M = W; S–S = (S–S)′ = PS$_2$(OEt)$_2$)	orange	24.3 (24.0)	3.7 (3.9)	2.2 (2.1)		19.7 (19.7)	545 m, 635 sh, 645 s and 795 s ν(PS) 1655 s νNO	^{1}H ^{f}: 1.31,m,4CH$_3$; 4.11m,4CH$_2$; 6.17,s,C$_5$H$_5$.
(20, M = W; S–S = (S–S)′ = PS$_2$(O-i-Pr)$_2$)	orange	29.3 (28.9)	4.5 (4.7)	1.9 (2.0)		18.0 (18.2)	545 m, 560 s, 740 s and 770 s ν(PS) 1685 s ν(NO)	^{1}H ^{f}: 1.32,m,8CH$_3$;4.75,m,4CH; 6.15,s,C$_5$H$_5$.
(21, M = Mo; S–S = PS$_2$(OEt)$_2$; (S–S)′ = S$_2$CNMe$_2$)	orange	29.2 (29.0)	4.4 (4.2)	4.8 (5.6)			540 m, 555 m, 650 vs and 780 s ν(PS) 1550 s ν(CN); 1645 vs ν(NO)	^{1}H: 1.34,m,2CH$_3$(dtp); 3.33,d,2CH$_3$(dtc); 4.15,m,2CH$_2$(dtp); 6.04,s,C$_5$H$_5$. ^{13}C: 16.2,d,2CH$_3$(dtp); 38.8,d,2CH$_3$(dtc); 62.9,d,2CH$_2$(dtp); 105.2,s,C$_5$H$_5$.

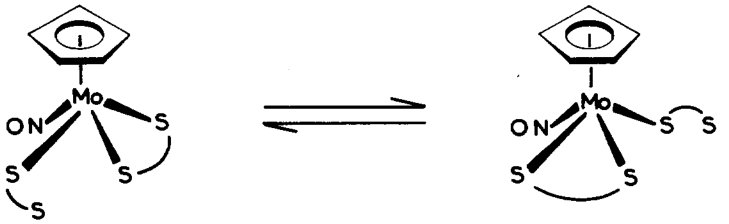
(continued)

TABLE 1 (continued)

Complexes	Colour	Analysis (Found (calcd.) (%)) [a]					IR data [a] (cm^{-1}) ν(CO) (CH_2Cl_2) ν(other) (Nujol mull)	^1H and ^{13}C NMR in $CDCl_3$ (δ, ppm; J, Hz)
		C	H	N	P	S		
(**22**, M = Mo; S–S = $PS_2(OEt)_2$; (S–S)′ = S_2CNEt_2)	yellow	32.5 (32.1)	4.8 (4.8)	4.5 (5.3)		24.1 (24.4)	510 s, 635 vs and 810 sh ν(PS) 1515 s ν(CN); 1645 vs ν(NO)	^1H: 1.32,m,$4CH_3$; 3.72,m,$2CH_2$(dtc); 4.15,m,$2CH_2$(dtp); 6.02,s,C_5H_5. ^{13}C: 12.5,s,$2CH_3$(dtc); 16.0,d,$2CH_3$(dtp); 44.0,d,$2CH_2$(dtc); 63.1,d,$2CH_2$(dtp);105.1,s,C_5H_5.
(**23**, M = Mo; S–S = $PS_2(O\text{-}i\text{-}Pr)_2$; (S–S)′ = S_2CNMe_2)	yellow	31.5 (32.1)	4.7 (4.8)	4.7 (5.3)			545 m, 560 m, 640s and 770 s ν(PS) 1555 s ν(CN); 1615 vs ν(NO)	^1H: 1.37,m,$4CH_3$(dtp); 3.36,d,$2CH_3$(dtc); 4.87,m,2CH(dtp); 6.09,s,C_5H_5. ^{13}C: 31.1,d,$4CH_3$(dtp); 38.8,d,$2CH_3$(dtc); 72.0,d,2CH(dtp); 105.2,s,C_5H_5.
(**24**, M = Mo; S–S = $PS_2(O\text{-}i\text{-}Pr)_2$; (S–S)′ = S_2CNEt_2)	yellow	34.7 (34.8)	5.3 (5.3)	4.6 (5.1)			545 sh, 560 s, 645 vs and 771 s ν(PS) 1520 s ν(CN); 1665 vs ν(NO)	^1H: 1.29,m,$6CH_3$; 3.72,m,$2CH_2$(dtc); 4.82,m,2CH (dtp); 6.02,s,C_5H_5. ^{13}C: 12.5,s,$2CH_3$(dtc); 24.0,m,$4CH_3$(dtp); 43.9,d,$2CH_2$(dtc); 72.2,d,2CH (dtp); 105.1,s,C_5H_5.
(**25**, M = Mo; S–S = (S–S)′ = S_2COMe)	orange	27.5 (26.7)	2.8 (2.7)	3.7 (3.5)			1055 vs ν(CS); 1142 m ν(CO) 1262 vs ν(COR); 1660 vs ν(NO)	^1H [f]: 4.10,s,$2CH_3$; 6.20,s,C_5H_5.
(**26**, M = Mo; S–S = (S–S)′ = S_2COEt)	orange	30.6 (30.4)	3.4 (3.5)	3.2 (3.2)			1035 vs ν(CS); 1130 m ν(CO) 1260 vs ν(COR); 1662 vs ν(NO)	^1H: 1.48,t,$2CH_3$(^3J(HH) 7.0);4.62,quad,$2CH_2$(^3J(HH) 7.0); 6.02,s,C_5H_5.
(**27**, M = Mo; S–S = (S–S)′ = S_2CSEt)	orange	28.3 (28.4)	3.2 (3.2)	3.0 (3.0)			845 w, 960 s and 986 s ν(CS); 1672 vs ν(NO)	^1H: 1.36,t,$2CH_3$(^3J(HH) 7.0);3.25,quad,$2CH_2$(^3J(HH) 7.0); 6.07,s,C_5H_5.
[M(NO)(S–S)₃]								
(**28**, M = W; S–S = $PS_2(OEt)_2$)	brown	18.8 (18.7)	3.8 (3.9)	1.8 (1.8)		25.0 (25.0)	546 m, 645 s, 655 sh and 768 s ν(PS); 1640 s ν(NO)	^1H [f]: 1.32,m,$6CH_3$; 4.28,m,$6CH_2$.
(**29**, M = W; S–S = $PS_2(O\text{-}i\text{-}Pr)_2$)	brown	26.0 (25.3)	4.9 (4.9)	1.7 (1.6)		22.7 (22.5)	540 s, 635 m, 650 m and 795 s ν(PS); 1635 s ν(NO)	^1H [f]: 1.35,m,$12CH_3$; 5.02,m,6CH.

[a] Hydrogen analysis was not considered necessary in some cases in which other analyses and ^1H NMR data were unambiguous. [b] No analytical data. [c] I, 25.1; calcd. 25.2. [d] Decomposition during mass spectroscopy, highest peak at m/e = 533, corresponding to ($P^+ - NO$) with ^{98}Mo. [e] Mass spectrum shows parent ion P^+ at m/e = 505 (calcd. for a monomeric unit 505); other selected peaks at 378 ($P^+ - I$) and 348 ($P^+ - I - NO$). Molar conductivity (10^{-3} M, CH_3NO_2, 20°C) 5 Ω^{-1} cm^2 mol^{-1}; for $NH_4PS_2(OEt)_2$ 71 Ω^{-1} cm^2 mol^{-1}. [f] Solvent $(CD_3)_2CO$.

complex **18** (M = Mo, R = i-Pr) are given Fig. 1. At 195 K the spectrum consisted of two sharp singlets at 90.9 and 103.4 ppm which, on the basis of the above considerations, were respectively attributed to bi- and mono-dentate dithiophosphato ligands. On increasing the temperature, broadening of these two singlets occurred, followed by coalescence. At room temperature, a broad singlet approximatively situated midway between the original signals (97.4 ppm), was present, and this signal sharpened on warming. This phenomenon, which is concentration independent and reversible with temperature, clearly suggested a rapid unidentate-bidentate exchange of the two dithioacid ligands (eq.1) at higher temperatures.



(1)

The xanthato and thioxanthato derivatives $[Mo(\eta\text{-}C_5H_5)(NO)(S_2CX)_2]$ (**25**: X = OMe; **26**: X = OEt; **27**: X = SEt), analogous to the dithiophosphato complexes **17**–**20**, presented temperature dependent ^1H NMR spectra. In the case of the methylxanthato derivative **25**, in an acetone-d_6/CS_2 solvent mixture, the spectra were obtained over the temperature range 180 to 290 K. At 180 K, the spectrum showed two singlets in the characteristic range for S_2COMe protons (3.9–4.3 ppm). On increasing the temperature, these two signals coalesced at about 210 K, and a sharp resonance was observed at 4.10 ppm at ambient temperature. Since these NMR changes were reversible and concentration independent, these observations also indicated facile intramolecular unidentate-bidentate scrambling of the dithio ligand at ambient temperature. Approximate activation parameters for this scrambling process, obtained in the usual way [17] from plots of ln $1/\tau$ versus T^{-1} for E_A and ln (τT) versus T^{-1} for $\Delta H^\star$ and $\Delta S^\star$ (good linear plots were obtained in both instances), were as follows: $E_A = 29 \pm 8$ kJ mol^{-1}, $\Delta H^\star = 33 \pm 8$ kJ mol^{-1}, $\Delta S^\star = -29 \pm 8$ J K^{-1} mol^{-1}.

The $\Delta G^\star$ value (42 ± 16 kJ mol^{-1}) was deduced from $\Delta H^\star$ and $\Delta S^\star$ at coalescence temperature (210 K).

In contrast, up to 330 K, ^{31}P NMR spectra of the mixed complexes $[M(\eta\text{-}C_5H_5)(NO)\{PS_2(OR)_2\}(S_2CNR_2)]$ only showed a sharp singlet in the characteristic range of monodentate $PS_2(OR)_2$ groups, indicating stereochemical rigidity. The absence of scrambling of the unidentate $PS_2(OR)_2$ ligand with the bidentate S_2CNR_2 ligand may be attributed to the stronger tendency of the dithiocarbamate than of a dithiophosphate group to act as a bidentate ligand (which is a reflection of the high nucleophilicity of S_2CNR_2 compared to $S_2P(OR)_2$). Consistent with this difference is the fact that in $[M(NO)(S_2CNR_2)_3]$ complexes (M = Mo, W) the three dithiocarbamate groups act as bidentate ligands [11,13], while for the corresponding tungsten dithiophosphato derivatives **28**–**29** an octahedral structure with one monodentate $PS_2(OR)_2$ ligand seems likely.

(Continued on p. 324)

TABLE 2

^{31}P NMR DATA FOR VARIOUS MOLYBDENUM AND TUNGSTEN *O,O'*-DIALKYLDITHIOPHOSPHATE COMPLEXES IN $(CD_3)_2CO$

Complex	*T*(K)	δ [a] (ppm)		
		dtp bidentate		dtp monodentate
Molybdenum complexes				
$[Mo(\eta\text{-}C_5H_5)(CO)_2\{PS_2(OMe)_2\}]$ **(1)**	298	103.7 sept (^3J(PH 14)		
$[Mo(\eta\text{-}C_5H_5)(CO)_2\{PS_2(OEt)_2\}]$ **(2)**	298	100.3 quint (^3J(PH) 9)		
$[Mo(\eta\text{-}C_5H_5)(CO)_2\{PS_2(O\text{-}i\text{-}Pr)_2\}]$ **(3)**	298	98.4 t (^3J(PH) 12)		
$[Mo(\eta\text{-}C_5H_5)(CO)_3\{S_2\overline{POCH_2CH_2O}\}]$ **(6)**	298			111.4 quint (^3J(PH) 13)
cis-$[Mo(NO)_2\{PS_2(OEt)_2\}_2]$ **(8)**	298	100.0 quint (^3J(PH) 10)		
cis-$[Mo(NO)_2\{PS_2(O\text{-}i\text{-}Pr)_2\}_2]$ **(9)**	298 [b]	97.0 s		
$[Mo(\eta\text{-}C_5H_5)(NO)(I)\{PS_2(OEt)_2\}]$ **(12)**	298	104.1 quint (^3J(PH) 10)		
$[Mo(\eta\text{-}C_5H_5)(NO)(I)\{PS_2(Oi\text{-}Pr)_2\}]$ **(13)**	298	101.1 t (^3J(PH) 12)		
$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(OEt)_2\}_2]$ **(17)**	298 [b]		100.4 br	
	203	92.9 quint (^3J(PH) 8)		105.9 quint (^3J(PH) 8)
$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}_2]$ **(18)**	328 [b]		97.2 s	
	298 [b]		97.4 br	
	195	90.9 t (^3J(PH) 14)		103.4 t (^3J(PH) 14)
$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(OEt)_2\}(S_2CNMe_2)]$ **(21)**	227 [b]			107.3 s

$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(OEt)_2\}(S_2CNEt_2)]$ **(22)**	227 [b]			107.4 s
$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}(S_2CNMe_2)]$ **(23)**	227 [b]			105.4 s
$[Mo(\eta\text{-}C_5H_5)(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}(S_2CNEt_2)]$ **(24)**	227 [b]			105.4 s
Tungsten complexes				
$[W(\eta\text{-}C_5H_5)(CO)_2\{PS_2(OEt)_2\}]$ **(4)**	298	111.3 quint (^3J(PH) 9)		
$[W(\eta\text{-}C_5H_5)(CO)_2\{PS_2(Oi\text{-}Pr)_2\}]$ **(5)**	298	109.3 t (^3J(PH) 12)		
$[W(\eta\text{-}C_5H_5)(CO)_3\{S_2\overline{POCH_2CH_2O}\}]$ **(7)**	298			127.4 quint (^3J(PH) 12)
cis-$[W(NO)_2\{PS_2(OEt)_2\}_2]$ **(10)**	298	100.0 quint (^3J(PH) 10)		
cis-$[W(NO)_2\{PS_2(O\text{-}i\text{-}Pr)_2\}_2]$ **(11)**	298	97.0 t (^3J(PH) 12)		
$[W(\eta\text{-}C_5H_5)(NO)(I)\{PS_2(O\text{-}i\text{-}Pr)_2\}]$ **(14)**	191 [b]	107.1 s		
$[W(\eta\text{-}C_5H_5)(NO)\{PS_2(OEt)_2\}_2]$ **(19)**	328 [b]		100.9 s	
	191 [b]	95.6 d (J(PP) 3)		104.7 d (J(PP) 3)
$[W(\eta\text{-}C_5H_5)(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}_2]$ **(20)**	328 [b]		98.9 s	
	191 [b]	93.3 d (J(PP) 4)		102.4 d (J(PP) 4)
$[W(NO)\{PS_2(OEt)_2\}_3]$ **(28)**	298 [b]	77.8 d [c] (J(PP) 3)		105.2 t (J(PP) 3)
$[W(NO)\{PS_2(O\text{-}i\text{-}Pr)_2\}_3]$ **(29)**	191 [b]	74.7 d [c] (J(PP) 3)		103.2 t (J(PP) 3)

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[a] Chemical shifts reported to 85% H_3PO_4 with J in Hz. [b] Decoupled spectrum. [c] Coupling with ^{183}W ($I = 1/2$; natural abundance = 14.2%) J(P–W) 15 Hz.

Experimental

General procedures

All operations were performed under pure nitrogen. Elemental analyses were performed by the "Service Central de Microanalyse du CNRS, Vernaison".

Physical measurements

Infrared spectra were recorded on a Pye-Unicam spectrophotometer from 200 to 4000 cm^{-1}, using dichloromethane solutions or Nujol mulls between caesium iodide windows or samples in caesium bromide pellets. ^1H, ^{13}C and ^{31}P NMR spectra were obtained in $CDCl_3$ or in $(CD_3)_2CO$ on a JEOL FX 100 spectrometer using TMS or H_3PO_4 85% as reference. Mass spectra were obtained with a Varian MAT 311 spectrophotometer (Centre de Mesures Physiques, Rennes, France). Conductivity measurements were made with a Tacussel CD 6N apparatus.

Material

All solvents were dried by standard techniques and thoroughly deoxygenated before use. P_4S_{10} (Prolabo), $M(CO)_6$ (M = Mo, W) (Ventron), diazald p-$CH_3C_6H_4SO_2N(Me)(NO)$ (Aldrich) and sodium dialkyldithiocarbamates (Merck) were used without further purification. Sodium *O,O'*-dialkyldithiophosphates [19], potassium alkylxanthates [20], sodium ethylthioxanthate [21], $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ [22], $[M(\eta\text{-}C_5H_5)(NO)I_2]_2$ [22–23], $[Mo(\eta\text{-}C_5H_5)(NO)I_2(py)]$ (py = pyridine) [23], $[M(\eta\text{-}C_5H_5)(CO)_2(NO)]PF_6$ (or BF_4) [24] were prepared for M = Mo, W as described in the literature.

Syntheses

$[M(\eta\text{-}C_5H_5)(CO)_2\{PS_2(OR)_2\}]$ *(1–5)*. P_4S_{10} (1.8 mmol) was dissolved in the corresponding alcohol ROH (100 cm^3) with gentle warming, and $[M(\eta\text{-}C_5H_5)(CO)_3Cl]$ (1.7 mmol) was then added. The suspension was refluxed with stirring for ca 15 h and then evaporated to dryness. After extraction with CH_2Cl_2 (ca. 15 cm^3), the solution was chromatographed on a Florisil column made up with CH_2Cl_2/hexane (1/1). Elution with this mixture gave a purple solution which afforded, after concentration to dryness and stirring with hexane, a purple microcrystalline product (**1**–**5**) (analytical and spectroscopic data are given in Table 1). Yield: **1**: 7%; **2**: 20%; **3**: 65%; **4**: 40%; **5**: 30%.

$[M(\eta\text{-}C_5H_5)(CO)_3\{S_2\overline{POCH_2CH_2O}\}]$ *(6–7)*. These complexes were prepared as described above for **1**–**5** using an ethylene glycol/toluene mixture (1/9; 100 cm^3) as solvent (reflux ca. 6 d). Yield: **6**: 22%; **7**: 5%.

cis-$[M(NO)_2\{PS_2(OR)_2\}_2]$ *(8–11)*. These were prepared analogously to **1**–**5**; a solution of $[M(\eta\text{-}C_5H_5)(CO)(NO)_2]Y$ (Y = PF_6, BF_4) (4 mmol) and $NaPS_2(OR)_2$ (8 mmol) in the corresponding alcohol ROH was heated at reflux for ca 1–2 h. Yield: **8**: 37%; **9**: 36%; **10**: 27%; **11**: 25%.

$[M(\eta\text{-}C_5H_5)(NO)I(S\text{–}S)]$ *(12–16)*. These syntheses were carried out at room temperature as described above for compounds **1**–**5** using alcoholic solutions of $[M(\eta\text{-}C_5H_5)(NO)I_2]_2$ with 2 molar equiv. $M^I(S\text{–}S)$. (Stirring at room temperature for ca. 15 h; concentration to dryness; extraction with CH_2Cl_2; chromatography on a silica gel column; elution with CH_2Cl_2/hexane 2/1]. Yield: **12**: 80%; **13**: 60%; **14**: 50%; **15**: 50%; **16**: 55%.

In many experiments, further elution with CH_2Cl_2/THF 19/1 gave variable amounts of the corresponding disubstituted derivative $[M(\eta\text{-}C_5H_5)(NO)(S\text{-}S)_2]$.

The molybdenum complexes **12–13** were also prepared by reactions between the monomeric derivative $[Mo(\eta\text{-}C_5H_5)(NO)I_2(C_5H_5N)]$ (4 mmol in 100 cm^3 CH_2Cl_2) and Na(S–S) (4 mmol in 100 cm^3 THF) (elution with CH_2Cl_2).

$[M(\eta\text{-}C_5H_5)(NO)(S\text{-}S)_2]$ (17–27). The reactions were carried out as described above for compounds **12–16** using equimolar quantities of $[M(\eta\text{-}C_5H_5)(NO)I(S\text{-}S)]$ and M^I(S–S) or starting from $[M(\eta\text{-}C_5H_5)(NO)I_2]_2$ with 4 molar equiv. of M^I(S–S) in alcohol (Mo complexes: reflux for ca. 15 h; elution with CH_2Cl_2/THF 19/1 after elution with CH_2Cl_2/hexane 2/1 of variable amounts of $[Mo(\eta\text{-}C_5H_5)(NO)I(S\text{-}S)]$. W complexes: stirring at r.t. for ca. 15 h; elution with CH_2Cl_2/hexane 2/1 gave $[W(\eta\text{-}C_5H_5)(NO)I(S\text{-}S)]$ and $[W(NO)(S\text{-}S)_3]$, then elution with CH_2Cl_2 gave the expected $[M(\eta\text{-}C_5H_5)(NO)(S\text{-}S)_2]$ complex. The molybdenum mixed complexes **21–24** were made by reactions between $[Mo(\eta\text{-}C_5H_5)(NO)I(S_2CNR_2)]$ and $NaPS_2(OR)_2$. Yield: **17**: 40%; **18**: 39%; **19**: 35%; **20**: 35%; **21**: 40%; **22**: 53%; **23**: 37%; **24**: 41%; **25**: 55%; **26**: 50%; **27**: 48%.

$[W(NO)\{PS_2(OR)_2\}_3]$ (28–29). These tungsten complexes were prepared as described above for the corresponding $[W(\eta\text{-}C_5H_5)(NO)\{PS_2(OR)_2\}_2]$ derivatives **19–20** but at reflux instead of room temperature and an excess of $NaPS_2(OR)_2$ was used. Elution with CH_2Cl_2. Yield: **28**: 40%; **29**: 35%.

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