Reactions of a "C_4" hydrocarbon cut containing a mixture of alkynes and olefins towards (N,N-diethyldithiocarbamato)-tungsten(II) and -molybdenum(IV) complexes. Crystal structure of [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡C-CH=CH$_2$)]

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Abstract

The reactions of a "C_4" cut of hydrocarbons containing buta-1,3-diene, buta-1,2-diene, buty-1-ne, and vinylacetylene with [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)$_3$] and [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] gives the complexes [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡C–CH=CH$_2$)] (**1a**), [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡CCH$_2$CH$_3$)] (**1b**) and [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(η^2-CH≡C–CH=CH$_2$)] (**3a**), [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$-(η^2-CH≡CCH$_2$CH$_3$)] (**3b**), respectively. In the tungsten complexes the alkynes behave as four-electron π-bonded ligands, whereas in the molybdenum complexes the bonding involves two electrons only. The crystal structure of **1a** has been determined by an X-ray diffraction study. The lability and the reversible binding of the alkynes has been demonstrated for complexes **3a** and **3b**. Monocyanoacetylene, containing the strong electron-withdrawing CN group, also acts as a four-electron π-bonded ligand in [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡CCN)] (**2**).

Introduction

An industrial mixture of hydrocarbons not easy to handle and difficult to separate contains alkynes and olefins. We thought it of interest to explore the use of

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the selective reactions of some organometallic complexes towards one unsaturated substrate relatively to that of others to separate the various constituents of a "C_4" cut of hydrocarbons. Several types of reactions of alkynes with organometallic complexes have been described: (i) those in which the nature of the alkyne is not changed fundamentally and which give complexes of the type [M]RC$_2$R' or [M]RC$_2$R'[M], ([M] = metal and other ligands); (ii) alkyne cyclisation or heterocycle formation reactions; (iii) alkyne insertion reactions in [M]–H, [M]–C, [M]–S bonds; (iv) formation of acetylides [M]–C≡CR; (v) cleavage of the C≡C bond in the presence of clusters. Some of these reactions occur with olefins. Compounds able to fix alkynes selectively in monomeric complexes in reactions of type i) seemed to offer the possibility of separating two unsaturated substrates. However, we must note that alkyne ligands in, for example, monomeric early transition-metal complexes are very sensitive to metal d_π orbital occupancies, because such ligands can also act simultaneously as excellent π-acids through π * ‖ and excellent π-bases through π ‖ bonding [1]. With this in mind we decided to examine the reactions of the "C_4" cut towards a tungsten(II) (d^4) complex, [W(CO)$_3$(dtc)$_2$] (dtc = diethyldithiocarbamato ligand) and a molybdenum(IV) (d^2) complex, [MoO(dtc)$_2$], both known to react more readily with alkynes than with olefins [1–4]. The behaviour of the cyano-substituted alkynes HC≡CCN (mca) and NCC≡CCN (dca), which contain the electron-withdrawing CN group, in the presence of the tungsten complex was also examined.

Results and discussion

Reaction of [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)$_3$] with the "C_4" cut

Bubbling of the "C_4" gaseous mixture (buta-1,3-diene: 24.4%, b.p. $-4.4\,^\circ$C; buta-1,2-diene 12.3%, b.p. 18–19$\,^\circ$C; but-1-yne 26%, b.p. 8.1$\,^\circ$C; vinylacetylene 36%, b.p. 5.1$\,^\circ$C; "C_5" cut 1.2%) into a toluene solution of [W(CO)$_3$(dtc)$_2$] resulted in an immediate and quantitative reaction, the colour of the solution turning from orange to deep green. The ^{1}H NMR data for the green solid are consistent with the presence of two compounds [W(dtc)$_2$(CO)(η^2-CH≡C–CH=CH$_2$)] (**1a**), and [W(dtc)$_2$(CO)(η^2-CH≡CCH$_2$CH$_3$)] (**1b**), in which the alkyne acts as a four-electron donor π-bonded ligand [2,5]. In addition to the two signals from very deshielded acetylenic protons (Table 1) there is an ABX pattern assignable to the vinylacetylene in **1a**. Comparison of the integrals of the various peaks allows to attribution of the most deshielded proton (12.99 ppm) to the compound **1a**. The quadruplet and the triplet expected for the CH$_2$CH$_3$ group in **1b** are obscured by the resonances of the non equivalent dtc ligands. The ratio of **1a** to **1b** is 11/4, whereas in the original gas mixture the ratio of vinylacetylene to but-1-yne is 11/8. This indicates that vinylacetylene probably has the greater affinity for the starting tungsten compound. No olefin fixation was detected. As expected [6], the ^{13}C chemical shifts for the acetylenic carbons of four electron donor alkynes are significantly shifted towards lower fields compared with those associated with donation of two electrons from the alkyne to the metal center (Table 2). Moreover the ^{13}C–^{1}H coupling constants of 208 Hz (**1a**) and 207 Hz (**1b**) indicate a degree of s character in the C–H bond intermediate between sp and sp^2 [6,7].

Attempts to separate the mixture of **1a** and **1b** by using specific reagents for olefinic bonds such as [Fe(η^5-C$_5$H$_5$)(CO)$_2$(THF)]PF$_6$ [8] or [Zr(η^5-C$_5$H$_5$)$_2$(H)Cl] [9]

Table 1

^{1}H NMR spectra (δ (ppm), J(Hz) (CDCl$_3$ solutions) (s, singlet; d, doublet; m, multiplet)

Compound	HC≡	Other alkyne protons	(dtc) protons
[W(CO)(dtc)₂(η²-CH=C—C(H_A)=C(H_B))] with H_X, H_A **(1a)**	12.99(s)	5.59–5.63(dd) H$_A$, $^3J_{AX}$ 10.2, $^2J_{AB}$ 2.2; 5.76–5.92(dd) H$_B$, $^3J_{BX}$ 17.1, $^2J_{AB}$ 2.2; 7.61–7.71(dd) H$_x$, $^3J_{AX}$ 10.2, $^3J_{BX}$ 17.1	3.89–3.48(m) CH$_2$; 1.69–0.69(m) CH$_3$
[W(CO)₂(dtc)₂(η²-CH≡CCH₂CH₃)] **(1b)**	12.59(s)	^{a}	3.89–3.48(m) CH$_2$; 1.69–0.69(m) CH$_3$
[W(CO)(dtc)₂(η²-CH≡CCN)] **(2)**	13.35(s)		3.94–3.52(m) CH$_2$; 1.44–1.19(m) CH$_3$
[MoO(dtc)₂(η²-CH=C—C(H_A)=C(H_B))] with H_X, H_A **(3a)**	8.82(s) ^{b}	7.08–7.02(dd) H$_x$; 5.85–5.57(m) H$_A$ + H$_B$ ^{c}	3.97–3.74(m) CH$_2$; 1.53–1.13(m) CH$_3$
[MoO(dtc)₂(η²-CH≡CCH₂CH₃)] **(3b)**	8.45(s)	^{a}	3.97–3.74(m) CH$_2$; 1.53–1.13(m) CH$_3$

^{a} Signals of CH$_2$ and CH$_3$ alkyne groups are obscured by the (dtc) peaks. ^{b} A signal at 2.91 ppm was attributed to the acetylenic proton of the free ligand. ^{c} The H$_A$, H$_B$ and H$_X$ peaks of 3a are partially superposed with those of the free vinylacetylene.

Table 2

^{13}C NMR spectra (δ (ppm), J (Hz), $CDCl_3$ solutions)

	C^1	C^2	C^3	C^4	CO
[W(CO)(dtc)$_2$(η^2-C^{1}H≡C^2-C^{3}H=C^{4}H$_2$)] ^{a}	204.36	212.35	131.87	124.22	236.60
	^1J(C–H) 208		^1J(C–H) 162	^1J(C–H) 159	J(W–C) 143
[W(CO)(dtc)$_2$(η^2-C^{1}H≡C^{2}C^{3}H$_2$C^{4}H$_3$)] ^{a}	200.36	203.01	30.08	15.99	236.83
	^1J(C–H) 207				J(W–C) 143

^{a} (dtc) ligands: CH_2, 45.9–44.0 ppm; CH_3, 16.0–12.2 pm

failed. These complexes were found not to react with **1a**, complexes **1a** and **1b** could also not be separated by column chromatography.

Structure of [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡C–CH=CH$_2$)] 1a

An X-ray diffraction study of **1a** revealed the presence of one organometallic molecule together with one water molecule in the asymmetric unit in the $P2_1/n$ space group. The geometry around the tungsten atoms (Fig. 1) may be regarded as pseudooctahedral with one coordination site occupied by the alkyne, or as pentago-
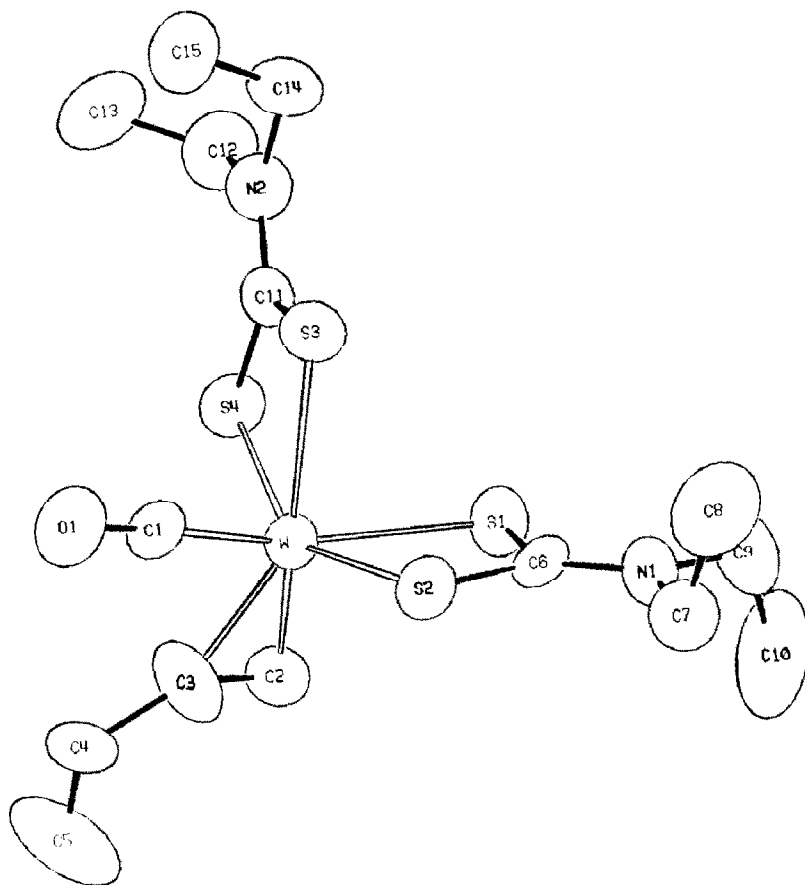

Fig. 1. ORTEP drawing of [W(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(CO)(η^2-CH≡C–CH=CH$_2$)].

Table 3

Selected bond lengths (Å) for $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-CH}{\equiv}\text{C-CH}{=}\text{CH}_2)]$ (1a) [a] and for $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-CH}{\equiv}\text{CH})]$ (A) [2]

	1a	A
W–S(1)	2.558(3)	2.557(1)
W–S(2)	2.409(3)	2.399(1)
W–S(3)	2.587(4)	2.588(9)
W–S(4)	2.493(3)	2.550(1)
W–C(1)	1.913(12)	1.936(7)
W–C(2)	1.997(13)	2.015(9)
W–C(3)	2.062(13)	2.038(8)
C(2)–C(3)	1.32(2)	1.29(1)
C(3)–C(4)	1.46(2)	
C(4)–C(5)	1.25(2)	

[a] Selected bond angles (°) for 1a: C(1)–W–C(2), 110.5(5); C(1)–W–C(3), 72.9(5); C(2)–W–C(3), 38.0(5).

nal pyramidal if two coordination sites are allocated to this ligand. The C≡O and C≡C bonds are parallel (see the values of C–W–C angles, Table 2), as in the structure of the analogous acetylene complex $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-}C_2H_2)]$ [2]. The geometrical parameters are quite similar in both structures (Table 3).

Thus, the theoretical features of bonding established for acetylene complexes [2,5] hold for 1a. The vinylacetylene ligand acts formally as a four-electron donor exclusively through its C(2)–C(3) acetylenic bond. In terms of the coordinate system used previously [2,5] the $d_{x^2-y^2}$ and d_{xy} empty orbitals of tungsten are stabilized by this donation, the filled d_{xz} orbital takes part in π back-donation into the antibonding orbitals of both the carbonyl and the alkyne, and the filled d_{yz} orbital is involved in interactions with the antibonding orbitals of the carbonyl (π-type) and of the alkyne (δ-type) ligands. The presence of the vinyl group in the ligand does not influence the nature of this bonding.

There is one water molecule for each molecule of the organometallic complex in the network. Hydrogen-bonding, probably of the bifurcated type, may involve the S(3), S(4) and O(1) (carbonyl) as acceptor atoms. The corresponding O(2)(water)–acceptor distances are 2.60, 3.13, and 2.84 Å, respectively. These interactions do not however influence the geometrical parameters in the organometallic molecule. The sole consequence of the presence of the water molecule may be the inversion of the orientation of one terminal ethyl group of the dtc ligand attached by the S(1) and S(2) atoms, with respect to the S_2CN plane. The surroundings of the tungsten atom remain the same as in the acetylene complex.

Reaction of $[W(S_2CN(C_2H_5)_2)_2(CO)_3]$ with $HC{\equiv}CCN$

A relatively unexpected result is the fixation of the electron-deficient alkyne as a four electron donor ligand, as revealed by the position of the acetylenic proton peak (δ 13.3) in $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-CH}{\equiv}\text{CCN})]$ (2). This is to our knowledge the first example of such a donation from mca to a metal. Moreover the only examples of π-bonded monocyanoacetylene are $[Pt(\eta^2\text{-CH}{\equiv}\text{CCN})(PPh_3)_2]$ [10] and $[Mo(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-CH}{\equiv}\text{CCN})]$ [11]. No reaction occurs with dicyanoacetylene in the presence of $[W(S_2CN(C_2H_5)_2)_2(CO)_3]$.
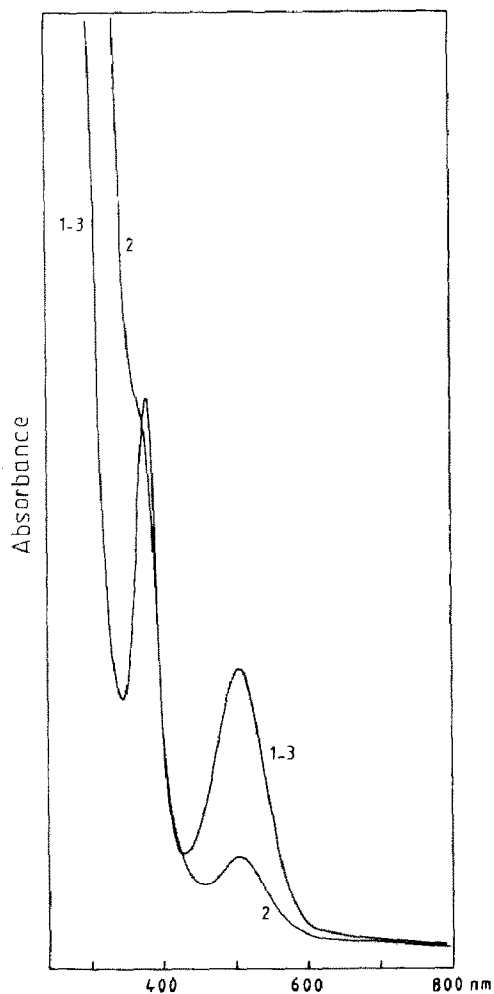
Fig. 2. UV-visible spectra of (1) [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]; (2) [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(η^2-CH≡C–CH=CH$_2$)] (3a) and [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(η^2-CH≡CCH$_2$CH$_3$)] (3b) obtained by bubbling the "C$_4$" mixture through the solution of (1); (3) [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] recovered by solvent evaporation of the 3a + 3b solution. The spectra were recorded with CH$_2$Cl$_2$ solutions (10^{-3} M). Spectra 2 and 3 are exactly superposed.

Reaction of the "C$_4$" cut with [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$]

Only the alkynes of the "C$_4$" cut bond to [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$], to give a mixture of the complexes [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(η^2-CH≡C–CH=CH$_2$)] (3a) and [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$(η^2-CH≡CCH$_2$CH$_3$)] (3b). No evidence for bonding of olefins to molybdenum was observed, although other activated olefins are known to react with [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] [12].

The position of the two acetylenic protons (8.82 and 8.45 ppm) (Table 1) is characteristic of π-bonding by two-electron donor alkynes by interaction of the π_{xz} orbital with the d_{yz} empty orbital of molybdenum The positions of the signals from the two acetylenic protons (δ8.82 and 8.45) and the C≡C carbon atoms ($\sim$ 130 ppm CH≡(^{1}J(CH) $\sim$ 160 Hz) and $\sim$ 117 ppm ≡C–) are characteristic of two-electron donor alkynes π-bonded through interaction of the π_{xz} orbital with the d_{yz} empty
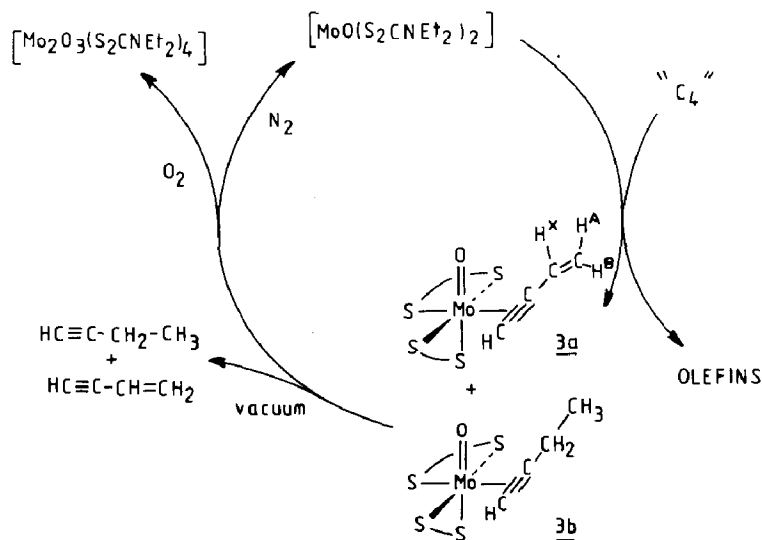
Fig. 3. Reactions of [MoO(dtc)$_2$] with the "C$_4$" cut.

orbital of molybdenum [7,13*]. The competition between the $2p_y$ oxygen and the π_{xz} alkyne orbitals to interact with the vacant metal d_{yz} lowers the Mo=O bond order compared with that in [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$], giving rise to lowering of 30 cm^{-1} in the ν(Mo=O) frequency. These spectroscopic features are consistent with *cis*-bonding of the alkyne to the oxo group, and with the C≡C bond lying perpendicular to the Mo=O direction [14]. The filled metal d_{xy} overlaps the vacant alkyne π^*_{xy} orbital.

The lability of the alkynes in solution is manifested by the presence of an acetylenic proton resonance at δ 2.91 associated with an ABX spectrum in the δ 5.57–7.08 range, assignable to free vinylacetylene. The signals of free 1-butyne are probably obscured by those from the dtc ligands.

When the solvent is evaporated off under reduced pressure the molybdenum–alkyne bonds are broken and the original [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] recovered can again fix the alkynes under the conditions used previously. The UV-visible spectra of [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] and of the 3a + 3b mixture are shown in Fig. 2. The initial [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] gives peaks at 375 and 500 nm that are not present in the spectrum of the alkyne adducts. The weak absorption at 500 nm in the spectrum of the 3a + 3b mixture may arise from the equilibrium mixture shown in eq. 1, the presence of which was indicated by the ^{1}H NMR spectrum (vide supra).

$$\left[MoO(S_2CN(C_2H_5)_2)_2(\eta^2\text{-alkyne})\right] \rightleftharpoons \left[MoO(S_2CN(C_2H_5)_2)_2\right] + \text{alkyne} \qquad (1)$$

In the presence of oxygen [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] and the compounds 3a and 3b are converted into the purple dimeric [Mo$_2$O$_3$(S$_2$CN(C$_2$H$_5$)$_2$)$_4$] (Fig. 3), which was characterized by infrared spectroscopy [15], whereas [MoO(S$_2$CN(CH$_3$)$_2$)$_2$(η-2-RC$_2$R'$)$] (R = R' = H; R = R' = CF$_3$; R = H, R' = CO$_2$CH$_3$) complexes are transformed into the yellow dinuclear [Mo$_2$O$_4$(S$_2$CN(CH$_3$)$_2$)$_2$] [4]. We note, however, that [MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$] can be oxidized to [Mo$_2$O$_3$(S$_2$CN(C$_2$H$_5$)$_2$)$_4$] and fi-

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nally to $[Mo_2O_4(S_2CN(C_2H_5)_2)_2]$ during a three-day period by use of a threefold excess of $OPPh_3$ [16].

Experimental

The reactions were performed under nitrogen by Schlenk tube techniques. Solvents were purified by standard methods and purged with nitrogen before use.

$[W(S_2CN(C_2H_5)_2)_2(CO)_3]$ [16], $[MoO(S_2CN(C_2H_5)_2)_2]$ [17] and $HC\equiv CCN$ [18] were prepared by published methods.

The "C_4" hydrocarbon cut supplied by the Institut Français du Pétrole, was contained in a metallic cylinder.

The ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer. Chemical shifts (δ values) are relative to internal TMS. The UV-visible spectra were recorded on a Varian Cary 219 spectrophotometer. Infrared spectra of samples, examined as Nujol mulls on CsI plates or as KBr pellets, were recorded on a Perkin Elmer 1430 spectrophotometer.

Microanalyses were performed at the Centre de Microanalyses of the CNRS.

Reaction of [W(S₂CN(C₂H₅)₂)₂(CO)₃] with the "C₄" cut

The "C_4" mixture was bubbled for 2 min through a toluene solution (30 ml) of $[W(S_2CN(C_2H_5)_2)_2(CO)_3]$ (575 mg, 1.01 mmol). The solution, which turned immediately from orange to deep green, was stirred for 1 h at room temperature under a "C_4" atmosphere. The solvent was then evaporated off, and the solid residue was dissolved in CH_2Cl_2 and the solution transferred to a silica gel column (hexane). A deep green fraction containing a mixture of $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-}CH\equiv C\text{-}CH=CH_2)]$ (**1a**) and of $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-}CH\equiv CCH_2CH_3)]$ (**1b**) was eluted with a hexane/CH_2Cl_2 mixture (2/1 by volume). The yield was quantitative, but compounds **1a** and **1b** could not be separated on chromatography column.

The cylinder containing the "C_4" cut was placed in a bath water (30°C) before being opened to allow bubbling of the gas. The **1a**/**1b** ratio (determined by ^1H NMR spectroscopy was ca. 11/4 (whereas the ratio of the corresponding alkynes was 11/8 in the starting gaseous mixture). Recrystallization from hexane/CH_2Cl_2 gave crystals of **1a** and **1b**.

Preparation of [W(S₂CN(C₂H₅)₂)₂(CO)(η²-CH≡CCN)] 2

Monocyanoacetylene, obtained by dehydratation of 140 mg (2.03 mmol) of $CH\equiv CCONH_2$ with P_4O_{10}, was condensed into 40 ml of a toluene solution of $[W(S_2CN(C_2H_5)_2)_2(CO)_3]$ (800 mg, 1.42 mmol). After 1 h stirring at room temperature the solution was dark-green. It was chromatographed on silica gel (hexane). Elution with hexane/CH_2Cl_2 (3/1) gave the starting tungsten compound. Complex **2** was then eluted with a mixture hexane/CH_2Cl_2 (1/1) (yield 40%).

Complex **2**: Found: C, 30.3; N, 7.5; S, 23.2; W, 32.7. $C_{14}H_{21}N_3OS_4W$ calcd.: C, 30.06; N, 7.51; S, 22.93; W, 32.86%. IR (cm^{-1}, KBr); 2200 m, $\nu(C\equiv N)$; 1945s, $\nu(C\equiv O)$. ^1H NMR (δ ppm) 13.3; $HC\equiv C$; 1.13–1.43, triplets of CH_3 (dtc) groups; 3.52–3.91, quadruplets of CH_2 (dtc) groups.

Reaction of the "C₄" cut with [MoO(S₂CN(C₂H₅)₂)₂]

As before, the gaseous "C_4" was bubbled for 2 min through an intense pink dichloromethane solution of $[MoO(S_2CN(C_2H_5)_2)_2]$. The mixture was stirred for 1

h, during which the solution became orange. Hexane (50 ml) was added. The solution was filtered and the filtrate was cooled ($-20\,^\circ$C) overnight. Yellow crystals of $[MoO(S_2CN(C_2H_5)_2)_2(\eta^2\text{-}CH{\equiv}C\text{-}CH{=}CH_2)]$ (3a) and of $[MoO(S_2CN(C_2H_5)_2)_2(\eta^2\text{-}CH{\equiv}CCH_2CH_3)]$ (3b) separated and were filtered off and dried under a nitrogen stream. Infrared (Nujol, cm^{-1}): 1765, 1785, $\nu(C{\equiv}C)$; 925, $\nu(Mo{=}O)$.

When the yellow crystals of 3a and 3b were dissolved in CH_2Cl_2, and the solvent was evaporated off under vacuum, a pink precipitate was obtained. It gave the same infrared spectrum as $[MoO(S_2CN(C_2H_5)_2)_2]$. Infrared (Nujol, cm^{-1}): $[MoO(S_2CN(C_2H_5)_2)_2]$, 955, $\nu(Mo{=}O)$.

X-ray structure analysis of $[W(S_2CN(C_2H_5)_2)_2(CO)(\eta^2\text{-}CH{\equiv}C\text{-}CH{=}CH_2)]$ (2a)

Crystals suitable for X-ray studies were grown from a hexane/CH_2Cl_2 mixture and one of them ($0.35 \times 0.25 \times 0.15$ mm), chosen at random, was mounted on an Enraf–Nonius CAD4 diffractometer. The unit cell was determined and refined by Search and Setang programs of the CAD4 routines.

Crystal data: monoclinic, $P2_1/n$, a 7.243(5), b 15.833(8), c 18.348(11) Å, β 93.51(6)°, U 2100 Å^3, $\mu(\text{Mo-}K_a)$ 60.1 cm^{-1}, $Z = 4$. The intensities of 1942 independent reflections measured in a ω–2θ scan (θ_{min} 2°, θ_{max} 25°) with $I > 3\sigma(I)$ were used in the solution and refinement of the structure. All calculations were carried out by use of the Enraf–Nonius SDP library [19], with neutral atom

Table 4

Positional parameters and their estimated standard deviations [a]

Atom	x	y	z	B (Å^2)
W	0.84683(8)	0.23992(3)	0.40995(3)	3.21(1)
S(1)	0.8096(6)	0.1119(2)	0.3253(2)	4.27(9)
S(2)	0.6445(6)	0.2758(2)	0.3054(2)	4.15(8)
S(3)	0.5552(5)	0.1846(2)	0.4691(2)	4.04(9)
S(4)	0.9272(5)	0.1382(2)	0.5106(2)	4.06(8)
O(1)	0.764(2)	0.3968(7)	0.5028(7)	6.2(3)
O(2)	0.156(2)	0.2412(9)	0.0918(8)	11.1(5)
N(1)	0.590(2)	0.1491(8)	0.2097(7)	5.0(3)
N(2)	0.637(2)	0.0717(8)	0.5720(7)	4.6(3)
C(1)	0.791(2)	0.3365(9)	0.4672(8)	3.9(3)
C(2)	1.107(2)	0.2456(9)	0.3802(8)	4.2(3)
C(3)	1.073(2)	0.3190(9)	0.411(1)	5.2(4)
C(4)	1.163(2)	0.398(1)	0.434(1)	5.1(4)
C(5)	1.322(3)	0.415(1)	0.416(2)	9.2(8)
C(6)	0.670(2)	0.175(1)	0.2715(8)	3.9(3)
C(7)	0.474(3)	0.207(1)	0.161(1)	5.9(4)
C(8)	0.274(3)	0.192(2)	0.173(1)	8.7(6)
C(9)	0.623(2)	0.063(1)	0.181(1)	7.1(5)
C(10)	0.793(4)	0.055(2)	0.140(1)	11.8(8)
C(11)	0.700(2)	0.1257(8)	0.5226(8)	3.5(3)
C(12)	0.763(3)	0.016(1)	0.620(1)	5.7(4)
C(13)	0.796(3)	0.043(2)	0.693(1)	8.0(6)
C(14)	0.435(2)	0.065(1)	0.585(1)	5.0(4)
C(15)	0.362(2)	0.126(1)	0.637(1)	6.3(5)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos\gamma)B_{1,2} + ac(\cos\beta)B_{1,3} + bc(\cos\alpha)B_{2,3}]$

scattering factors. The structure was solved and refined [218 variables) by conventional three-dimensional Patterson, difference Fourier and full-matrix least squares methods. An empirical absorption correction (DIFABS [20], abs_{min} 0.7779, abs_{max} 1.4526) applied after isotropic refinement lowered the value of R from 0.125 to 0.090. The positions of hydrogen atoms were calculated by use of the HYDRO program. They were included in the final refinement with $B_{iso}(H) = 1.2\ B_{iso}(C)$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The final residuals were $R = 0.046$, $R_w = 0.060$, GOF $= 1.37$. The weighting scheme employed was $w^{-1} = \sigma^2(F) = \frac{1}{4}[\sigma(I)I + 0.07^2(I)]$. The final atomic coordinates for non-hydrogen atoms are listed in Table 4.

A full list of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structure factors are available from the authors.

Acknowledgements

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