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IX *. CS_2 COMPLEXES: SYNTHESIS, REACTIVITY AND THEIR USE AS LIGAND; CRYSTAL STRUCTURE OF $(n\text{-}C_4H_9)(\eta^5\text{-}C_5H_5)_2Nb(\mu\text{-}CS_2)W(CO)_5$

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Summary

Carbon disulphide reacts with niobium complexes $[Nb(\eta\text{-}C_5H_5)_2(Me)_2]$ and $[Nb(\eta\text{-}C_5H_5)_2H\ (CH_2{=}CHC_2H_5)]$ to produce the new η^2-CS_2 derivatives $[Nb(\eta\text{-}C_5H_5)_2(Me)(\eta^2\text{-}CS_2)]$ (1) and $[Nb(\eta\text{-}C_5H_5)_2(Bu)(\eta^2\text{-}CS_2)]$ (2) respectively. Treatment of 1 and 2 with methyl iodide affords the respective cationic η^2-dithioalkyl ester complexes $[Nb(\eta\text{-}C_5H_5)_2(Me)\{\eta^2\text{-}C(S)SMe\}]\ I$ (3) and $[Nb(\eta\text{-}C_5H_5)_2(Bu)\{\eta^2\text{-}C(S)SMe\}]\ I$ (4). Hetero-dinuclear complexes $[(Bu)(\eta\text{-}C_5H_5)_2Nb(\eta\text{-}CS_2)M(CO)_n]$ (M = Cr, Mo, W; $n = 5$. M = Fe; $n = 4$) and $[(Bu)(\eta\text{-}C_5H_5)_2Nb(\mu\text{-}CS_2)Mn(CO)_2(\eta\text{-}CH_3C_5H_4)]$ and an homodinuclear complex $[(Bu)(\eta\text{-}C_5H_5)_2Nb(\mu\text{-}CS_2)Nb(\eta\text{-}C_5H_5)_2(Bu)]$ have been synthesized. The structure of the niobium—tungsten derivative has been determined by single-crystal X-ray diffraction. Crystal data are space group $P2_1/c$, a 12.935(4), b 12.742(4), c 14.565(4) Å, β 103.27(3)°, $Z = 4$. The $Nb(\mu\text{-}CS_2)$—W unit is planar within ±0.06 Å. The CS_2 group is η^2-bonded to niobium through a C=S linkage and σ-bonded to manganese through the other sulfur atom. The ^{13}C NMR spectra indicate that 2 has a larger σ-donor/π-acceptor ratio than CO.

Introduction

The chemistry of heteroallenes—metal complexes has recently been recognized as a novel and exciting area for synthetic and theoretical studies. In par-

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ticular attempts have been made to develop the highly promising carbon disulphide chemistry [1]. The main interest in these complexes arises from the expectation that they will provide insight into the intermediates and reaction mechanisms involved in catalytic reactions of carbon dioxide. In addition, there is great interest in such derivatives since a wide range of coordination modes have already been identified for the CS_2 ligand [1,12] and since η^2-CS_2 complexes are precursors for thiocarbonyl compounds [13,15]. However, the factors that determine the mode of bonding of the CS_2 moiety are poorly understood, and it therefore seemed of interest to study the chemistry of the CS_2—metal complexes further in order to unravel these factors.

We describe below the synthesis of some carbon disulphide bis(cyclo-pentadienyl)niobium complexes $[Nb(\eta^5\text{-}C_5H_5)_2(R)(\eta^2\text{-}CS_2)]$ (1 R = Me; 2 R = Bu), and examination of the nucleophilic character of the uncoordinated sulphur atom. In particular we have investigated (i) the reactions of 1 and 2 with nucleophilic reagents such as alkyl halides and (ii) the possibility that 1 and 2 might act as weakly-bonded two electron ligands. These reactions have been found to give, respectively, dithioalkylester derivatives and a series of hetero dinuclear complexes $[Bu(\eta^5\text{-}C_5H_5)_2Nb(CS_2)ML_n]$ (M = Cr, Mo, W; L_n = $(CO)_5$. M = Fe, L_n = $(CO)_4$. M = Mn; L_n = $[\eta^5\text{-}CH_3C_5H_4(CO)_2]$). The structure of the niobium—tungsten derivative has been determined by X-ray diffraction. Some of the results have been described in a preliminary communication [16].

Results and discussion

η^2-CS_2 niobium complexes

Irradiation of a benzene solution of $[Nb(\eta\text{-}C_5H_5)_2(Me)_2]$ containing an excess of carbon disulphide affords, after further work-up, microcrystals of the pink complex $[Nb(\eta\text{-}C_5H_5)_2(Me)(CS_2)]$ (1). This complex is quite air stable in the solid state but air sensitive in solution. It is very soluble in common organic solvents except alkanes. The most pertinent features of its proton-decoupled ^{13}C NMR spectrum is the peak due to the carbon atom of the CS_2 group, 317 ppm downfield of Me_4Si. This position indicates carbenoid character for this carbon atom, and supports the formation of a η^2-CS_2 complex rather than a dithioacetato derivative.

The crystal structure of 1, which has been reported elsewhere [17], does consist of discrete $[Nb(\eta\text{-}C_5H_5)_2(Me)(\eta^2\text{-}CS_2)]$ units. The niobium atom is coordinated by a CS_2 molecule through a C=S linkage, the Nb—CS_2 unit being nearly planar. The carbon atom of the CS_2 group presents a carbenoid character (Nb—C(CS_2) 2.206(8); Nb—C(CH_3) 2.346(8) Å).

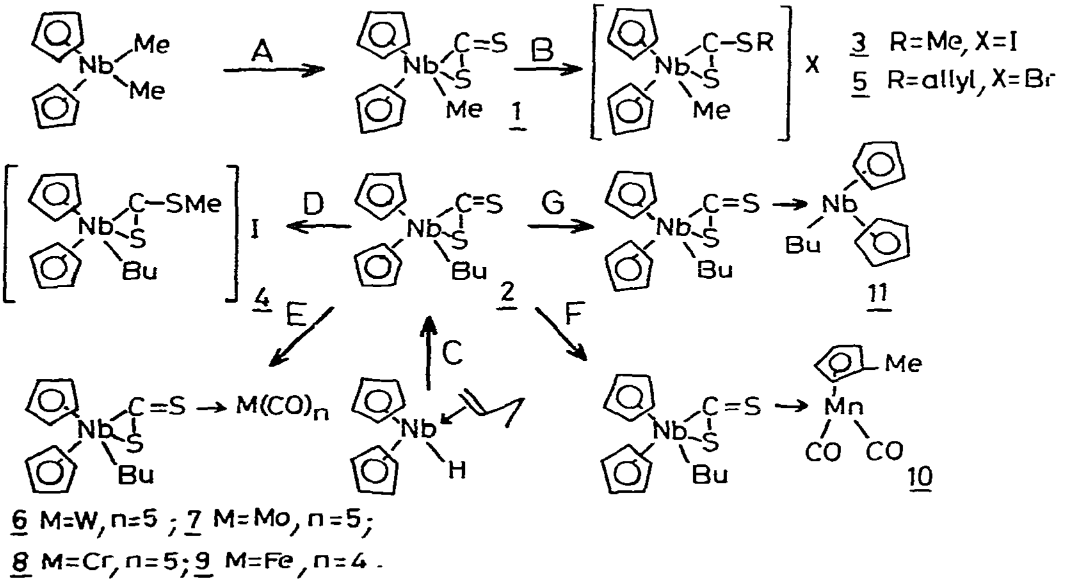
The synthesis of 1 corresponds to the transformation of the 17 electron species $[Nb(\eta\text{-}C_5H_5)_2(Me)_2]$ into a 18 electron species with substitution of one alkyl group by CS_2 acting as a two electron ligand. From this point of view, it can be compared with the synthesis of $[Nb(\eta\text{-}C_5H_5)_2(Me)(S_2)]$ from $[Nb(\eta\text{-}C_5H_5)_2(Me)_2]$ and S_8 which we previously reported [16]. In contrast, the previously reported reactions between CS_2 and metal—alkyl (or aryl) derivatives involve CS_2 insertion into metal—carbon σ bonds: $[Re(CO)_5(Ph)]$ affords the complex $[Re(CO)_4(SSCPh)]$, the structure of which has been determined by

X-ray methods [18,19] while [$TaMe_3Cl_2$] gives the corresponding tris(dithioacetato) derivative [20].

Carbon disulphide also reacts with a benzene solution of [$Nb(\eta\text{-}C_5H_5)_2(H)(CH_2{=}CHC_2H_5)$] to give the butyl derivative [$Nb(\eta\text{-}C_5H_5)_2(Bu)(CS_2)$] (2). For complex 2, as for all the butyl derivatives presented below, the signals from the ^1H NMR spectrum, cannot be resolved and this can be attributed to unfavourable relaxation times and possibly to quadrupole broadening by the niobium nucleus. However, in all the complexes, the butyl moiety was clearly characterized by four peaks in ^{13}C NMR spectra. On the basis of the spectroscopic data given in the experimental part ($\nu(C{=}S)$ 1132 for 1; 1135 for 2), we assume that compound 2 has a structure similar to that of the related methyl derivative 1. As in formation of complex 1, the existence of a 16 electron species as an intermediate ([$Nb(\eta\text{-}C_5H_5)_2(Bu)$] resulting from the insertion of the butene group in the Nb—H bond) seems likely.

Alkylation of the η^2-CS_2 ligand

Treatment of the compounds [$Nb(\eta\text{-}C_5H_5)_2(R)(CS_2)$] (1 R = Me; 2 R = Bu) in benzene with either an equimolar quantity or excess of methyl iodide at ca. 40°C caused precipitation of yellow powders. Theses complexes, 3 and 4, are sparingly soluble in organic solvents. They have been characterized by analysis and molar conductivity measurement. Their formulation as [$Nb(\eta\text{-}C_5H_5)_2(R)\{\eta^2\text{-}C(S)SMe\}$] I (3 R = Me; 4 R = Bu), i.e. 18 electron cationic complexes containing a dithiomethylester group acting as a bidentate ligand via carbon and



SCHEME 1: Carbon disulphide-bis(cyclopentadienyl)niobium derivatives. A: irradiation with CS_2 in benzene (55%); B:3: MeI in toluene; 5 $CH_2{=}CHCH_2Br$ in benzene (almost quantitative); C: CS_2 in diethyl ether (60—70%); D: MeI in toluene (almost quantitative). E: 6 photochemical reaction with $W(CO)_6$ in toluene (5 h, 20—30%). 7 $Mo(CO)_6$ in toluene, 24 h at 80°C or irradiation (6 h, 30—40%). 8 photochemical reaction with $Cr(CO)_6$ in toluene (12 h, 20—30%). 9 photochemical reaction with $Fe(CO)_5$ in benzene (16 h, 20%). F: photochemical reaction with [$Mn(\eta\text{-}CH_3C_5H_4)(CO)_3$] in THF (6 h, 10%). G: [$Nb(\eta\text{-}C_5H_5)_2(H)(CH_2{=}CHC_2H_5)$] in diethyl ether (20%).

sulphur atoms (see Scheme 1) was deduced from IR spectroscopy. The observed ν(CS) values (3 1115; 4 1130, 1145 cm^{-1}) were similar to that previously reported for [Ru(CO)$_2$(PPh$_3$)$_2$(SCSMe)]$^+$ [21], the structure of which was confirmed by X-ray analysis [22]; monodentate coordination of the dithiomethylester group via its central carbon atom caused a significant shift of the ν(CS) frequency (1005 cm^{-1} for [Os(H)(CO)$_2$(PPh$_3$)$_2$(CS$_2$Me)]) [23]. Allylbromide reacts similarly with 2 producing the compound {Nb(η-C$_5$H$_5$)$_2$(Me){η^2-C(S)-SCH$_2$=CHCH$_2$}] Br (5).

It is noteworthy that in the reactions with 1 and 2, an excess of the alkylating reagent does not afford dithiocarbene complexes by alkylation of the two sulphur atoms. Such formation of dithiocarbene derivatives has been reported previously [14,24].

Dinuclear complexes with a CS_2 bridge

In an attempt to test the ability of compounds 1 and 2 to act as ligands through the uncoordinated sulphur atom, irradiation of a toluene solution of 2 in presence of hexacarbonyl tungsten was carried out. After alumina column chromatography, an orange microcrystalline powder of the compound [(Bu)-(η-C$_5$H$_5$)$_2$Nb(CS$_2$)W(CO)$_5$] (6) was isolated. This complex is fairly air stable in the solid state, while solutions in dichloromethane decompose only slowly, allowing suitable crystals to be obtained for crystallographic examination. The structure (see below) confirms that a W(CO)$_5$ fragment is coordinated by a molecule of 2 through the uncoordinated sulphur atom. Two carbonyl resonances of relative intensity 4/1, corresponding to the *cis*- and *trans*-CO ligands in respect to the sulphur atom, are observed on the ^{13}C NMR spectrum of 6. The *cis*-carbonyl resonance (198.8 ppm) is shielded relative to the *trans*-carbonyl (203.5 ppm). They both appear at lower field than the CO resonance of W(CO)$_6$ (191.4 ppm); this deshielding is indicative of an increase in electron density at the tungsten atom [25—27] and shows that 2 as ligand has a larger σ-donor/π-acceptor ration than carbon monoxide.

Surprisingly the chemical shift of the carbon atom of the CS$_2$ group (δ 317.0 ppm for 2) and the carbon—sulfur stretching vibration (1120—1135 for 6; 1135 cm^{-1} for 2) are not significantly affected by coordination to the tungsten atom. In the light of the ability of 2 to coordinate readily to the Lewis acid W(CO)$_5$ other carbonyl complexes were investigated. In similar experiments, 2 reacted with Mo(CO)$_6$, Cr(CO)$_6$, Fe(CO)$_5$ and [Mn(η-MeCp)(CO)$_3$] to give the new heterodinuclear complexes [(Bu)(η-C$_5$H$_5$)$_2$Nb(CS$_2$)Mo(CO)$_5$] (7), [(Bu)(η-C$_5$H$_5$)$_2$Nb(CS$_2$)Cr(CO)$_5$] (8) [(Bu)(η-C$_5$H$_5$)$_2$Nb(CS$_2$)Fe(CO)$_4$] (9) and [(Bu)-(η-C$_5$H$_5$)$_2$Nb(CS$_2$)Mn(η-MeCp)(CO)$_2$] (10) respectively. For complexes 7 and 8, infrared spectra of dichloromethane solutions exhibit four bands in the ν(CO) region (2065m, 1975sh, 1940vs, 1895m cm^{-1} for 7; 2060s, 1975sh, 1935vs, 1900sh cm^{-1} for 8). The observed values agree well with those found in the niobium—tungsten derivative 6 described above (2060m, 1980s, 1930vs, 1895sh) and in the complex [(triphos)Co(CS$_2$)Cr(CO)$_5$] (2055, 1982, 1930 and 1887 cm^{-1}) [28]. They indicate a distorted C_{4v} symmetry around the Group VI metal since for pure C_{4v}-LM(CO)$_5$ derivatives only three bands ($2a_1 + e$) are expected.

It is noteworthy that upon the replacement of W by Mo and Cr, while the

CS_2 ^{13}C resonance does not shift significantly, deshielding of the carbonyl resonance by ca. 10 and 20 ppm is observed in the ^{13}C NMR spectra. The diamagnetic shielding influence of the metal itself has been reported to be an important factor in producing such a shift, which also occurs with the hexacarbonyl derivatives and in isostructural carbonyl complexes of these methals [25—27].

For the niobium—manganese complex **10**, two absorptions due to the CO stretching vibrations are evident at 1915 and 1850 cm^{-1}, in agreement with the results previously reported by Dixneuf et al. [11] for the compound $[(PhMe_2P)_2(CO)_2Fe(CS_2)Mn(CO)_2(\eta\text{-}C_5H_5)]$ (1914 and 1853 cm^{-1}). The other data characterising the new complexes **6—10** are listed in Table 1 and do not require further discussion. The similarity between the infrared and NMR spectra of **6** and derivatives **7—10** supports the idea that in the latter the molecule **2** acts as a two-electron ligand via one of the lone-pairs of the uncoordinated sulphur, just as in **6**.

In order to obtain homodinuclear complexes, the compound $[Nb(\eta\text{-}C_5H_5)_2(H)(CH_2{=}CHC_2H_5)]$ (as possible precursor of the Lewis acid $[Nb(\eta\text{-}C_5H_5)_2(C_4H_9)]$) was treated with **2**, to give the unstable compound $[Nb(\eta\text{-}C_5H_5)_2(Bu)]_2(CS_2)$ (**11**).

Crystal structure of the niobium—tungsten complex 8

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2, interatomic distances and angles with estimated standard deviations in Table 3 and details of important molecular planes in Table 4. It is noteworthy that due to the low number of independent reflections significantly above background (582) in respect to the number of refined parameters (262), the estimated standard deviations are large (although the final R_w value is 0.052) and comparison of distances and angles with those of other molecules is not easy. Despite this low accuracy the X-ray analysis unequivocally confirms the proposed structure, the $[Nb(\eta\text{-}C_5H_5)_2(Bu)(\eta^2\text{-}CS_2)]$ molecule acting as a monodentate two-electron ligand through the uncoordinated sulphur atom. The following are the principal structural features of the structure:

(1) The overall geometry of the Nb—CS_2 moiety resembles that found in other metal complexes containing η^2-CS_2 ligand and particularly in **1** [17]. The Nb—CS_2 fragment is planar within ±0.02 Å while the tungsten atom and the carbon and oxygen atoms of the apical carbonyl group lies ca. 0.06 Å out of this plane. It is noteworthy that this plane is not very different from the plane which bisects the $(\eta\text{-}C_5H_5)_2Nb$ bent sandwich fragment. The Nb—S(1) bond length (2.52(3) Å) and the Nb—C(6) distance (2.11(6) Å) do not appear significantly different from the values observed in complex **1** (2.503(4) and 2.206(8) Å respectively) [17]. In contrast the C(6)—S(1) bond length (1.52(8) Å) appears to be shorter than the corresponding distance in $[(triphos)Co(CS_2)Cr(CO)_5]$ (1.66(3) Å; triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) [10] and $[(PhMe_2P)(CO)_2Fe(CS_2)Mn(CO)_2(\eta\text{-}C_5H_5)]$ (1.642(6) Å) [11].

(2) The geometry of the bis(η-cyclopentadienyl)niobium moiety is that commonly found in bent bis(η-cyclopentadienyl) systems. The two cyclopentadienyl rings, which are almost planar, are twisted away from the eclipsed configuration with respect to one another by a 10(2)° angle.

The Nb—C distances are in the range 2.19—2.46 Å (mean 2.36 Å) and the C—C distances within the rings are in the range 1.24—1.52 Å (mean 1.40 Å) and do not vary in any systematic manner.

(3) The niobium atom is σ-bonded to a butyl group with a Nb—C(7) bond length of 2.38(10) Å not significantly different from other Nb—C alkyl bonds previously reported (2.346(8) in $[Nb(\eta\text{-}C_5H_5)_2(CH_3)(CS_2)]$ [17]; 2.309(31) in $[Nb(\eta\text{-}C_5H_5)_2(C_3H_5)(CS_2)]$ [5]; 2.316(8) Å in $[Nb(\eta^5\text{-}C_5H_5)_2(C_2H_4)(C_2H_5)]$ [29]). The four carbon atoms of the η-C_4H_9 group are close to the plane which contains the Nb—CS_2 fragment.

(4) The coordination core of the tungsten atom is a distorted octahedral. The deviation from planarity in the $W(CO)_4$ fragment is ±0.12 Å. The W—S bond (2.56(3) Å) is nearly perpendicular to the $W(CO)_4$ equatorial plane. The four W—C equatorial bonds average (2.04(10) Å) are significantly longer than the W—C apical distance (1.75(7) Å).

All the reactions and structures of the new compounds **1**—**11** are shown in Scheme 1. These results and studies in progress clearly show η^2-CS_2 derivatives 1 and 2 have a rich chemistry, and can be the precursors for a wide range of new compounds.

Experimental section

Preparative studies

All operations were performed under pure dinitrogen. Solvents were purified by standard methods and degassed before use.

IR spectra were measured with a Perkin—Elmer 557 spectrometer. ^1H and ^{13}C NMR spectra were recorded at 100 MHz on a JEOL FX 100 spectrometer operating in the F.T. model (Me_4Si as internal standard). Mass spectra were obtained with a Varian Mat 311 spectrophotometer (Centre de Mesures Physiques, Rennes, France). Solutions were irradiated in Pyrex glass tubes using a mercury vapor lamp Hanau TQ 150. All chemical analyses were performed by Centre de Microanalyses du C.N.R.S., France.

Bis(cyclopentadienyl)niobium dichloride was prepared as in the literature [30].

$[Nb(\eta\text{-}C_5H_5)_2(Me)(CS_2)]$ (1). A benzene solution containing $[Nb(\eta\text{-}C_5H_5)_2Me_2]$ (ca. 1 g prepared from $[Nb(\eta\text{-}C_5H_5)_2Cl_2]$ and MeLi as described in the literature [31]) and carbon disulphide (ca. 15 cm^3) was irradiated for several days and then concentrated to dryness. After extraction with dichloromethane, the solution was chromatographed on an alumina column made up with CH_2Cl_2. Elution with CH_2Cl_2 gave a pink band from which was obtained a pink product 1 (analytical and spectroscopic data are given in Table 1). Yield ca. 55%. Further elution with THF gave a violet-brown product, which was very air-sensitive and was not identified.

$[Nb(\eta\text{-}C_5H_5)_2(Bu)(CS_2)]$ (2). An excess of CS_2 was added at 0°C to a diethyl ether solution of $[Nb(\eta\text{-}C_5H_5)_2H(CH_2{=}CHC_2H_5)[$ [32]. The mixture was allowed to warm slowly to room temperature and then kept at 35°C for 12 h. The solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2. Alumina column chromatography as described for 1 afforded 2 as pink microcrystals. Yield 60—70%.

[Nb(η-C_5H_5)$_2$(Me){η^2-C(S)SMe}] I (3). To a stirred toluene solution of 1 (1 mmol) at 35—40°C a toluene solution of methyl iodide (3 mmol) was added dropwise. A yellow product separated quickly. It was filtered off, washed twice with toluene, and dried under vacuo. Yield almost quantitative.

[Nb(η-C_5H_5)$_2$(Bu){η^2-C(S)SMe}] I (4) *and [Nb(η-C_5H_5)$_2$(Me){η^2-C(S)-$SCH_2CH{=}CH_2$}] Br* (5). These were prepared analogously to 3 using a slight excess of MeI or $CH_2{=}CHCH_2Br$. They were isolated as white powders in almost quantitative yields.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)W(CO)$_5$] (6). A toluene solution of 2 (1 mmol) and $W(CO)_6$ (1.5 mmol) was irradiated for 5 h and then chromatographed on an alumina column. Elution with benzene/THF (19/1) gave a small amount of the starting material 2 and an orange band was separated using CH_2Cl_2 as eluant. The solvent was removed in vacuo. Crystallisation from a CH_2Cl_2/pentane mixture gave an orange microcrystalline product. Yield 20—30%.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)Mo(CO)$_5$] (7). This was prepared analogously to 6 when a toluene solution containing 2 (1 mmol) and $Mo(CO)_6$ (1.2 mmol) was heated at 80°C for 24 h (or irradiated for 6 h). (Elution with benzene; crystallisation from a benzene/pentane mixture). Yield 30—40%.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)Cr(CO)$_5$] (8). The reaction was carried out as described above for compound 6 using $Cr(CO)_6$ (1.2 mmol) (irradiation for 12 h). An orange band was separated using CH_2Cl_2 as eluant. The solvent was removed in vacuo. Stirring the residue with pentane affords a microcrystalline orange product. Yield 20—30%.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)Fe(CO)$_4$] (9). This was prepared as described above for compound 6 using $Fe(CO)_5$ (3 mmol) instead of $W(CO)_6$ and benzene as solvent (irradiation for ca. 16 h). 9 was isolated as an orange solid after elution with benzene, concentration in vacuo and stirring with pentane. Yield 20%.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)Mn(CO)$_2$(η-$CH_3C_5H_4$)] (10). A mixture of 2 (1 mmol) and [Mn(η-$CH_3C_5H_4$)$(CO)_3$] (3 mmol) in THF (50 cm^3) was irradiated for 6 h. The complex **10** was separated from the starting materials by alumina column chromatography (elution with benzene). The solvent was removed under reduced pressure and the residue stirred with pentane and crystallised at —60°C. Yield 10%. A similar reaction in benzene did not give **10**, suggesting that [Mn(η-MeCp)$(CO)_2$(THF)] is an intermediate in the reported reaction.

[(Bu)(η-C_5H_5)$_2$Nb(μ-CS_2)Nb(η-C_5H_5)$_2$(Bu)] (11). To a diethyl ether solution of 2 at 0°C was added a large excess of a diethyl ether solution of [Nb(η-C_5H_5)$_2$(H)($CH_2{=}CHC_2H_5$)] (prepared as above). The yellow precipitate which rapidly appeared was filtered off, washed with pentane, and dried under vacuo. Yield 20%.

Crystallographic studies of [(Bu)(η^5-C_5H_5)$_2$Nb(μ-CS_2)W(CO)$_5$] (6)

X-ray data collection. Orange crystals, slightly air unstable, were obtained by recrystallization from a dichloromethane/pentane mixture.

Crystal data. $C_{20}H_{19}O_5NbS_2W$ (M = 680.25), monoclinic; a 12.935(4), b 12.742(4), c 14.565(4) Å, β 103.27(3)°, V 2334 Å^3, D_m 1.97(5), $Z = 4$, D_c 1.94, Mo-K_α radiation, λ 0.7107 Å, μ(Mo-K_α) 5.85 mm^{-1}. Systematic absences: $h0l$: $l = 2n + 1$ and $0k0$: $k = 2n + 1$; space group : $P2_1/c$ (density measured by pycnometry in n-tetradecane).

TABLE 1

ANALYTICAL AND SPECTROSCOPIC RESULTS

Compound	Colour	Analysis [a] (%)	
		C	H
1 $[Nb(\eta\text{-}Cp)_2(Me)(\eta^2\text{-}CS_2)]$	pink	44.9 (45.9)	4.1 (4.1)
2 $[Nb(\eta\text{-}Cp)_2(Bu)(\eta^2\text{-}CS_2)]$	pink	50.5 (50.6)	5.4 (5.3)
3 $[Nb(\eta\text{-}Cp)_2(Me)[\eta^2\text{-}C(S)SMe]\,I$	yellow	34.5 (34.2)	3.7 (3.5)
4 $[Nb(\eta\text{-}Cp)_2(Bu)[\eta^2\text{-}C(S)SMe]\,I,0.5C_6H_6$	yellow	42.0 (42.5)	4.7 (4.7)
5 $[Nb(\eta\text{-}Cp)_2(Me)[\eta^2\text{-}C(S)SCH_2CH{=}CH_2]\,Br$	yellow	42.6 (41.4)	4.3 (4.1)
6 $[(Bu)(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)W(CO)_5]$	orange	35.2 (35.3)	2.8 (2.8)
7 $[(Bu)(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)Mo(CO)_5]$	orange	40.2 (40.6)	3.3 (3.2)
8 $[(Bu)(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)Cr(CO)_5]$	orange	43.7 (43.8)	3.6 (3.5)
9 $[(Bu)(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)Fe(CO)_4]$	orange	43.3 (43.5)	3.8 (3.6)
10 $[(Bu)(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)Mn(CO)_2(\eta\text{-}MeCp)]$	purple	50.7 (50.6)	4.8 (4.8)
11 $[Bu(\eta\text{-}Cp)_2Nb(\mu\text{-}CS_2)Nb(\eta\text{-}Cp)_2(Bu)]$	yellow	52.3 (54.7)	5.9 (6.0)

[a] Calculated values are given in parentheses. [b] Given as: chemical shift (τ), multiplicity (J in Hz), assignment. solvent $CDCl_3$ unless otherwise stated. [c] Given as: chemical shift (δ), multiplicity (J in Hz), assignment. solvent $CDCl_3$ unless otherwise stated. [d] Nujol mulls. [e] CH_2Cl_2 solutions. [f] Mass spectrum shows parent ion P^+ at $m/e = 314$; other selected peaks at 299 ($P^+ - Me$), 270 ($P^+ - CS$), 238 ($P^+ - CS_2$) and 223 ($P^+ - Me - CS_2$). [g] High-resolution mass spectrum shows parent ion P^+ at $m/e = 355.9998$ (calcd.: 355.9992); other

Preliminary cell dimensions and the space group were determined from Weissenberg and precession photographs.

The crystal selected for X-ray analysis, of approximate dimensions 0.25 × 0.15 × 0.025 mm, was sealed in a Lindemann tube. Data were collected on a Enraf-Nonius CAD-4 automatic four circle diffractometer (Centre de diffractométrie automatique de Lyon-France). Unit cell dimensions given above were determined from a least-squares treatment of 25 independent reflections by using Mo-K_α radiation with a graphite monochromator. Intensity data for

			^{1}H [b] and ^{13}C [c] NMR data	Selected Ie data (cm^{-1})	
S	Nb	Other element		ν(CS) [d]	ν(CO) [e]
19.7 (20.4)	28.7 [f] (29.6)		^{1}H: 4.56, s, Cp; 8.90, s, Me. ^{13}C: 5.6, s, Me; 106.8, s, Cp; 318.0, s, CS_2	1132vs	
16.8 (18.0)	26.2 [g] (26.1)		^{1}H [h]: 4.55, s, Cp; ^{13}C [i]: 14.0, s, CH_3; 24.7, s, $C^{\alpha}H_2$; 29.2, s, $C^{\beta}H_2$; 38.6, s, $C^{\delta}H_2$; 106.6, s, Cp; 317.0, s, CS_2	1135vs	
13.9 (14.0)	18.7 (20.4)	26.2 [j] (27.9)	k	1115s	
11.0 (11.9)	17.6 (17.3)	24.0 [l] (23.6)	k	1130s 1145sh	
12.4 (14.7)	19.8 (21.4)	18.0 [m] (18.4)	k	1125m 1135m	
9.2 (9.4)		27.3 [n] (27.0)	^{1}H [h]: 4.49, s, Cp. ^{13}C: 14.0, s, CH_3; 25.6, s, $C^{\alpha}H_2$; 29.1, s, $C^{\beta}H_2$; 38.9, s, $C^{\gamma}H_2$, 106.7, s, Cp; 198.8, s, CO; 203.5, s, CO; 315.2, s, CS_2	1120s 1135m	1895sh 1930vs 1980s 2060m
10.1 (10.8)		16.2 [p] (16.2)	^{1}H [h]: 4.50, s, Cp. ^{13}C: 14.0, s, CH_3; 25.5, s, $C^{\alpha}H_2$; 29.1, s, $C^{\beta}H_2$; 38.9, s, $C^{\gamma}H_2$; 106.7, s, Cp; 205.6, s, CO; 215.2, s, CO; 316.0, s, CS_2	1120s 1130sh	1895m 1940vs 1975sh 2065m
11.6 (11.7)		9.9 [q] (9.5)	^{1}H [h]: 4.50, s, Cp. ^{13}C: 14.0, s, CH_3; 25.6, s, $C^{\alpha}H_2$; 29.1, s, $C^{\beta}H_2$; 38.9, s, $C^{\gamma}H_2$; 106.7, s, Cp; 216.2, s, CO; 224.3, s, CO; 314.4, s, CS_2	1125sh 1135vs	1900sh 1935vs 1975sh 2060s
11.8 (12.2)		10.3 [r] (10.7)	^{1}H [h]:4.50, s, Cp. ^{13}C: 14.0, s, CH_3; 29.1, s, $C^{\beta}H_2$; 38.8, s, $C^{\gamma}H_2$; 106.7, s, Cp; 215.6, s, CO	1125vs	1932vs 1960sh 2020s
12.0 (11.7)		9.2 [s] (10.1)	^{1}H [h,t]: 5.20, s, Cp; 5.55, s, Cp(Me); 8.10, s, Me(Cp); ^{13}C [t]: 14.7, s, CH_3 (Bu); 25.7, s, $C^{\alpha}H_2$; 30.4, s, $C^{\beta}H_2$; 30.9, s, CH_3(MeCp); 39.6, s, $C^{\gamma}H_2$; 82.7, d, Cp(MeCp); 106.8, s, Cp; 235.5, s, CO	1135s	1850vs 1915vs
9.4 (10.1)	29.6 (29.2)		^{1}H [h]: 4.55, s, Cp	1133s	

selected peaks at 312 ($P^+ - CS_2$) and 280 ($P^+ - CS_2$). [h] Butyl resonances appear as a poorly resolved signal at τ 7.5—9.5. [i] Carbon atoms of the butyl group given as $Nb—C^{\alpha}H_2—C^{\beta}H_2—C^{\gamma}H_2—CH_3$. [j] I; molar conductivity (10^{-3} *M*, nitromethane, 20° C) 93 $\Omega^{-1} cm^2 mole^{-1}$. [k] Low solubility. [l] I; molar conductivity (10^{-3} *M*, nitromethane, 20°C) 87 $\Omega^{-1} cm^2 mol^{-1}$. [m] Br. [n] W. [p] Mo. [q] Cr. [r] Fe. [s] Mn. [t] Solvent: C_6D_6.

reflections with $\theta < 30°$ were collected using the w-2θ scan method. Two standard reflections, scanned every 100 reflections, were used to place the intensity data on a common scale; systematic variations in these standards was not observed. Of 5962 reflections originally scanned, 582 unique ones with $I > 2.5\sigma(I)$ were used in subsequent calculations. The intensities and $\sigma(I)$ values were corrected for Lorentz and polarization effects but no absorption corrections were applied. The scattering factors were taken from International Tables for X-ray crystallography [33].

TABLE 2

ATOMIC FRACTIONAL CELL COORDINATES [a] (X10^3) AND THERMAL PARAMETERS (Å)^2 FOR [(Bu)(η-C_5H_5)$_2$Nb(CS_2)W(CO)$_5$]

Atom	x	y	z	B_{eq}
W	830.0(0.2)	298.1(0.3)	471.0(0.2)	3.65
Nb	391.0(0.5)	294.4(0.8)	298.2(0.4)	4.85
S(1)	535(2)	195(2)	411(2)	7.15
S(2)	660(2)	374(2)	366(2)	7.78
C(11)	289(5)	255(6)	150(5)	4.95
C(12)	357(5)	338(6)	130(4)	5.70
C(13)	462(7)	303(9)	166(5)	9.01
C(14)	467(6)	204(9)	185(5)	7.47
C(15)	371(7)	172(6)	164(5)	7.37
C(21)	344(6)	472(5)	296(5)	4.79
C(22)	250(5)	402(7)	300(6)	6.41
C(23)	292(7)	349(7)	294(6)	7.10
C(24)	374(5)	392(6)	439(5)	4.87
C(25)	421(8)	459(7)	382(6)	8.90
C(6)	554(5)	297(6)	362(4)	5.11
C(7)	313(8)	137(8)	339(8)	8.51
C(8)	206(8)	141(6)	305(6)	5.89
C(9)	156(7)	051(8)	345(9)	9.47
C(10)	035(9)	048(7)	309(7)	8.73
C(1)	953(6)	261(5)	542(5)	5.66
C(2)	779(6)	158(8)	434(6)	8.11
C(3)	887(9)	449(8)	509(7)	9.45
C(4)	902(7)	311(8)	357(6)	9.27
C(5)	763(5)	287(7)	585(6)	7.64
O(1)	1042(4)	228(4)	597(3)	7.62
O(2)	767(5)	061(5)	423(4)	8.61
O(3)	892(6)	538(5)	521(5)	9.45
O(4)	850(4)	316(5)	307(4)	9.16
O(5)	723(4)	282(5)	650(4)	8.88

[a] Least-squares estimated standard deviations are given in parentheses. The atoms are numbered as shown in Fig. 1.

Structure solution and refinement. The structure was solved by heavy-atom techniques. Tungsten atom positions were determined from a three-dimensional Patterson function (R = 0.29). A first Fourier synthesis using the coordinates of these atoms revealed the niobium atoms (R = 0.21) while a second Fourier synthesis gave the positions of the two sulphur atoms of the asymetric unit. Refinement continued with isotropic thermal parameters for these four atoms (R = 0.17). The remaining non-hydrogen atoms were located by successive Fourier difference syntheses and the least-squares refinement was carried out isotropically down to $R_w = 0.072$ with $R_w = w^{1/2}\ (F_o - |F_c|)/w^{1/2}F_o[w^{1/2} = 1$ if $F_o < P1$; $w^{1/2} = P1/F_o$ if $F_o \geqslant P1$ with $P1 = (F^2_{o_{max.}}(10)^{1/2}]$. Anisotropic refinement of these 29 atoms resulted in a final R_w value of 0.052. During the final stage of refinement, no parameter shifted by more than 0.25σ.

Final positional and thermal parameters are listed in Table 2. Interatomic distances and angles with estimated standard deviations are given in Table 3. Relevant least squares plane data for selected atomic groups are listed in Table 4. Tables of observed and calculated structure factors are available on request from the authors.

TABLE 3

INTERATOMIC DISTANCES (Å) AND ANGLES (deg) IN [(Bu)(η-C_5H_5)$_2$Nb(CS_2)W(CO)$_5$]

Interatomic distances				Angles			
W—C(1)	1,75(7)	W—O(1)	3,06(5)	C(6)—Nb—S(1)	37(3)	S(1)—C(6)—S(2)	135(5)
W—C(2)	1,94(10)	W—O(2)	3,17(6)	S(1)—Nb—C(7)	73(4)	S(1)—C(6)—Nb	87(4)
W—C(3)	2,09(10)	W—O(3)	3,20(6)	Nb—C(6)—S(2)	139(4)	C(6)—S(2)—W	112(5)
W—C(4)	2,08(10)	W—O(4)	3,13(6)				
W—C(5)	2,04(9)	W—O(5)	3,22(6)				
W—S(2)	2,56(3)	C(1)—O(1)	1,31(9)	W—C(1)—O(1)	177(6)	S(2)—W—C(1)	173(5)
Nb—C(6)	2,11(8)	C(2)—O(2)	1,24(11)	W—C(2)—O(2)	166(7)	S(2)—W—C(2)	89(4)
Nb—S(1)	2,52(3)	C(3)—O(3)	1,14(11)	W—C(3)—O(3)	163(8)	S(2)—W—C(3)	91(4)
S(1)—S(2)	2,94(8)	C(4)—O(4)	1,06(12)	W—C(4)—O(4)	171(9)	S(2)—W—C(4)	89(4)
C(6)—S(1)	1,52(8)	C(5)—O(5)	1,18(11)	W—C(5)—O(5)	179(7)	S(2)—W—C(5)	92(4)
C(6)—S(2)	1,67(8)						
Nb—C(11)	2,31(8)	Nb—C(21)	2,34(7)	C(11)—C(12)—C(13)	106(11)	C(21)—C(22)—C(23)	100(9)
Nb—C(12)	2,45(8)	Nb—C(22)	2,29(9)	C(12)—C(13)—C(14)	113(11)	C(22)—C(23)—C(24)	111(11)
Nb—C(13)	2,31(11)	Nb—C(23)	2,21(9)	C(13)—C(14)—C(15)	106(12)	C(23)—C(24)—C(25)	113(11)
Nb—C(14)	2,39(11)	Nb—C(24)	2,46(8)	C(14)—C(15)—C(11)	115(10)	C(24)—C(25)—C(21)	107(9)
Nb—C(15)	2,47(7)	Nb—C(25)	2,41(9)	C(15)—C(11)—C(12)	96(10)	C(25)—C(21)—C(22)	108(10)
Nb—C_{av}	2,39	Nb—C_{av}	2,34	C—C—C_{av}	107	C—C—C_{av}	108
C(11)—C(12)	1,45(11)	C(21)—C(22)	1,52(11)	Nb—C(7)—C(8)	110(8)		
C(12)—C(13)	1,41(13)	C(22)—C(23)	1,52(12)	C(7)—C(8)—C(9)	109(11)		
C(13)—C(14)	1,28(15)	C(23)—C(24)	1,24(12)	C(8)—C(9)—C(10)	113(10)		
C(14)—C(15)	1,28(13)	C(24)—C(25)	1,41(11)				
C(15)—C(11)	1,48(10)	C(25)—C(21)	1,42(11)				
C—C_{av}	1,38	C—C_{av}	1,42				
Nb—C(7)	2,38(10)	C(8)—C(9)	1,49(13)				
C(7)—C(8)	1,36(13)	C(9)—C(10)	1,54(13)				

TABLE 4

EQUATIONS OF AND DISTANCES FROM SELECTED LEAST-SQUARES BEST PLANES AND INTERPLANAR ANGLES IN $[(Bu)(\eta\text{-}C_5H_5)_2Nb(CS_2)W(CO)_5]$

Equations of least-squares planes

The equations are of the form $Ax + By + Cz + D = 0$ where x, y, z (in Å) refer to the orthogonal system a,b,c^*.

Plane	Atoms in plane	*A*	*B*	*C*	*D*
P(1)	five atoms C(11) to C(15)	0.1949	−0.2133	−0.9573	−1.9743
P(2)	five atoms C(21) to C(25)	0.5510	−0.7409	−0.3839	−4.1589
P(3)	Nb, S(1), S(2), C(6)	0.3870	−0.5118	−0.7670	−3.5861
P(4)	W, C(2) to C(5), O(2) to O(5)	−0.7441	0.3228	−0.5849	−9.5246

Distances (Å) from the least-squares planes

from P(1): C(11) −0.12; C(12) 0.10; C(13) −0.05; C(14) −0.04; C(15) 0.11

from P(2): C(21): 0.00; C(22): −0.04; C(23): 0.08; C(24): −0.08; C(25) 0.04

from P(3): Nb 0.00; C(6) 0.02; S(1) −0.01 S(2) −0.01; W 0.07; C(1) 0.05; O(1) 0.05; C(7) 0.14; C(8) −0.02; C(9) −0.16; C(10) −0.31

from P(4): W 0.03; C(2) 0.16; O(2) −0.06; C(3) −0.12; O(3) 0.12; C(4) 0.05; O(4) −0.10; C(5) −0.03; O(5) −0.05

Interplanar angles (deg)

P(1)—P(2) 56.4; P(1)—P(3) 25.8; P(3)—P(4) 90.3; P(2)—P(3) 30.6

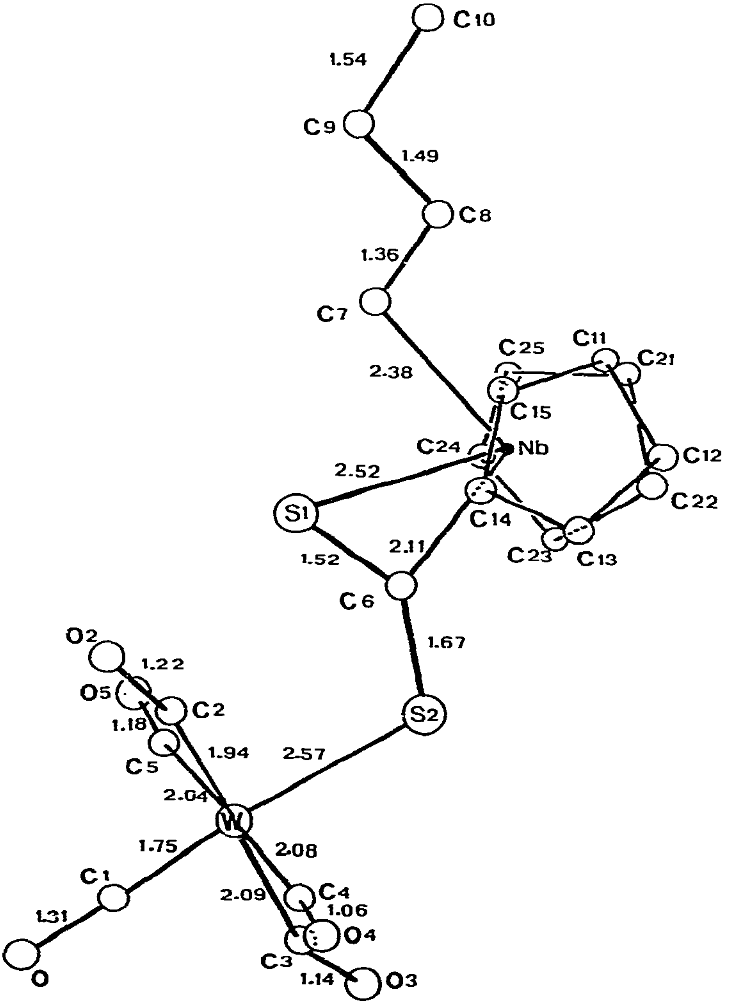


Fig. 1. View of the molecular structure of $[(Bu)(\eta\text{-}C_5H_5)_2Nb(CS_2)W(CO)_5]$.

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