Inorganica Chimica Acta, 43 (1980) 5–10

Reactivity of Transition Metal Hydrides and Thiolates. Reaction of Trihydridobis(π-cyclopentadienyl)niobium with Dimethyldisulphide and Reactions of Niobium, Molybdenum and Tungsten Thiolates with Alkynes

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Received March 5, 1980

The reactivity of niobium, molybdenum or tungsten thiolates towards alkynes is sensitive to acetylenic substituent effects. The photolysis of [(η^5-C_5H_5)$_2$$NbH_3$] *with dimethyldisulphide gives a thiolate derivative which reacts with alkynes affording mostly the diamagnetic niobium(III) compounds* [(η^5-C_5H_5)$_2$Nb(SMe) (R^1–C≡C–R^2)] *when* R^1 *and* R^2 *are both electron-withdrawing groups; when one of the substituents* R^1 *or* R^2 *is non electron-attracting group neither acetylene nor σ-alkenyl compounds are formed. The reaction of niobium, molybdenum or tungsten thiolates prepared* in situ, *with the fluoroalkynes* R_F–C≡C–H (R_F = n-C_6F_{13},n-C_8F_{17}) *gives rise to substituted vinyl sulphides. For synthesised compounds, IR and* ^1H, ^{13}C, ^{19}F *NMR data are given.*

Introduction

The reaction of [CpMH(CO)$_3$] (Cp = η^5-C_5H_5; M = Mo, W) with an alkyl disulphide is well known [1] and gave the substituted compounds [CpM(SR)-(CO)$_3$], but to our knowledge the corresponding study with the hydrido-niobium complex [Cp_2NbH_3] has not yet been investigated. The reported niobium thiolates [2] [$Cp_2Nb(SR)_2$] (R = Me, Pr, α-thienyl) were synthetised from [Cp_2NbCl_2] treated with a thiol; oxidation of these neutral paramagnetic niobium(IV) compounds with iodine formed the diamagnetic complex cation [$Cp_2Nb(SR)_2$]$^+$. The preparation of stable tricyclopentadienyl niobium(V) dithiolates [$Cp_3Nb(SR)_2$] from [$NbCl_3(SR)_2$] and sodium cyclopentadienide has also been reported [3]. It has been shown [4, 5, 1b] that alkynes can react with the related ligands of molybdenum or tungsten thiolates to give compounds with new sulphur-containing ligands; in these reactions the products depend largely upon the acetylene and SR substituents, substituted complexes [4] and a range of types of products including many examples of insertion [5, 1b] have been prepared. However no reaction between niobium thiolates and alkynes has been studied up to now.

We, therefore report, in the present paper on the products of the reactions between several acetylenes R^1–C≡C–R^2 (R^1=R^2=CF_3, CO_2Me, Me; R^1=CF_3, n-C_8F_{17} and R^2=H) and a very unstable diamagnetic niobium thiolate obtained from irradiation of [Cp_2NbH_3] with dimethyldisulphide. The result observed with the fluoroalkyne n-C_8F_{17}–C≡C–H being odd we extended the study to the reaction of fluoroalkynes R_F–C≡C–H (R_F = n-C_6F_{13}, n-C_8F_{17}) with molybdenum and tungsten thiolates which are more available than the niobium thiolate.

Experimental

General Procedures

A nitrogen atmosphere was employed routinely for all the reactions reported herein. Chromatographic separations and purifications were effected using Florisil. Elemental analyses were performed by the Service Central de Microanalyses du C.N.R.S. (Lyon).

Physical Measurements

Infrared spectra were recorded on a Pye-Unicam spectrophotometer (Nujol mulls). ^1H, ^{13}C and ^{19}F NMR spectra were obtained in $CDCl_3$ on a Jeol FX 100 spectrometer using Me_4Si or CF_3CO_2H as references. Molecular weight measurements were made on *ca.* 10^{-2} *M* $CHCl_3$ solutions at 26 °C with a Knauer osmometer. Mass spectra were determined at 70 eV on a Varian Mat 311 spectrometer of the 'Groupement Régional des Mesures Physiques de l'Ouest'. The irradiation of the products was made using a Hanau TQ 150 mercury vapor lamp placed approximately 10 cm from the vessel. Melting points were taken in sealed capillaries immersed in a mineral oil bath and are uncorrected.

Materials

The reagents were commercial products (excepted the fluoroalkynes R_F–C≡C–H (R_F=n-C_6F_{13} and n-C_8F_{17}) and used without further purification. All solvents were distilled by standard techniques and thoroughly deoxygenated before use.

The trihydridobis(π-cyclopentadienyl)niobium and the hydrido(π-cyclopentadienyl)tricarbonyl molybdenum or tungsten were prepared by published procedure [6].

Reaction of [Cp_2NbH_3] with Dimethylsulphide

A large excess of dimethyldisulphide was added to a solution of trihydrido-niobium complex (*ca.* 1 g) dissolved in THF. The mixture was stirred and irradiated (10–12 hours) at room temperature. The resulting solution was filtered and the solvent was evaporated giving rise to a purple microcrystalline powder. That compound (I) was purified by several extractions with THF and then recrystallised in CH_2Cl_2, *ca.* 0.8 g of (I) was isolated. *Analysis*: the compound being unstable to air and warmth, no reproducible result was obtained. *IR*: 285 m, 815s and 840w, 850w, 860sh (γC–H), 940w, 945w, 1010w and 1020w (δC–H), 1305 w, 3055m and 3075w (νC–H). *^1H NMR**: 6.25,s, (Cp); 2.65,s, (SCH_3); 2.45,s, (SCH_3) respectively in the 10/3/3 ratio. *Physical properties*: the red complex(I) is very sensitive to air, warmth and moisture. It is stable for only a few hours in an inert and dry atmosphere at 25 °C. It is very soluble in tetrahydrofuran and quite soluble in methylene chloride and chloroform.

Reaction of Niobium Thiolate(I) with Alkyne R^1–C≡C–R^2 (R^1=R^2=CF_3 or CO_2Me). Preparation and Study of Alkyne Bis(η^5-cyclopentadienyl)methylthioniobium(III) complexes [(η^5-C_5H_5)$_2$Nb(SMe)($R^1C_2R^2$)] (II)

Complex (I) being unstable was used *in situ* for the reaction with the alkynes R^1–C≡C–R^2 (R^1=R^2= CF_3 or CO_2Me). The same species were obtained in the reaction of the isolated complex(I) with alkyne. In a typical reaction *ca.* 1.2 g of [Cp_2NbH_3] (5 mmol) was transferred to a thick glass reaction vessel fitted with a Teflon stopcock. This was evacuated and an oxygen-free solution of an excess of dimethyldisulphide in tetrahydrofuran was added. The solution was irradiated for a few hours and then the vessel was cooled to 77 K and the alkyne (*ca.* 12 mmol) condensed in . The reaction mixture was then allowed to warm slowly to room temperature and irradiated for 24 h. The reaction stopped the solvent was removed *in vacuo* and the residue dissolved in methylene chloride was chromatographed.

R^1=R^2=CF_3

A yellow oil was eluted off first with CH_2Cl_2 in a very low yield, followed by a band (eluant: CH_2Cl_2–THF in the 20/1 ratio) which gave the main product (IIa) [$Cp_2Nb(SMe)(CF_3C_2CF_3)$] and the third band yielded *ca.* 50 mg of a pale-yellow powder (IIIa). (IIa) was recrystallised in a methylene chloride-hexane (1/1) mixture, yield: *ca.* 35%.

(IIa). *Anal.* Calcd.: C, 41.7; H, 3.0; S, 7.4; F, 26.4; Nb, 21.5%. Found: C, 41.6; H, 3.0. S, 7.5; F, 26.1; Nb, 21.0%. *IR*: 315 w, 370w, 500vw, 610vw, 650w, 670w, 815sh and 830s, 840sh, 850sh (γC–H), 1020m (δC–H), 1115vs br and 1230s (νC–F), 1260m, 1790s (νC≡C), 3100w and 3120vw (νC–H). *^1H NMR*: 5.73,s, (C_5H_5); 2.25,s, (SCH_3), in the 10/3 ratio. ^{13}C NMR: 106.5,s, (C_5H_5); 19.5,s, (SCH_3). *^{19}F NMR*: 52.8, qu, J_{F-F} = 4.9; 55.1, qu, J_{F-F} = 4.9, in the 3/3 ratio. *Melting point*: 175 °C (dec.). *Molecular weight* (osmometry): M = 401; M_{calc} = 432.

(IIIa). That complex was only characterised by its IR and NMR spectra. *IR*: 360 m, 620w, 640w, 825s and 865m (γC–H), 1010w, 1030w, 1040w, 1120vs br and 1230m (νC–F), 1260m, 1290m, 1330w, 1345w, 2990w and 3010vw (νC–H). ^1H NMR: 6.20,s, (C_5H_5); 2.80,m, (H), in the 5/1 ratio. *^{19}F NMR*: 50.5, qu, J_{F-F} = 3.5; 66.2,qu, J_{F-F} = 3.5 in the 3/3 ratio.

Physical properties. (IIa) is a yellow compound slightly air-sensitive, it is soluble in common organic solvents. (IIIa) is a pale yellow complex.

R^1=R^2=CO_2Me

The product mixture from the reaction with the dimethyl acetylenedicarboxylate was chromatographed. Elution with CH_2Cl_2 gave a yellow band from which an oily compound was obtained by concentration; a distillation and a fractional crystallisation allowed the separation of three organic compounds (IV), (Va) and (Vb). (IV) is obtained in a negligible yield, the white (V) crystals are isolated in *ca.* 5–7% yield. A second band was collected with the CH_2Cl_2–THF (5/1 ratio) eluant affording the required product (IIb) by concentration in 40% yield.

(IIb). *Anal.* Calcd.: C, 49.5; H, 4.6; S, 7.8; Nb, 22.5%. Found: C, 49.3; H, 4.6; S, 7.8; Nb, 21.1%. *IR*: 360 m br, 830s and 850sh (γC–H), 900 w, 1020 m and 1040m (δC–H), 1060w, 1170m, 1220s and 1240s (νC–O), 1300m, 1705s and 1750s, (νC=O), 1800m (νC≡C), 3130 (νC–H). *^1H NMR* 5.75,s, (C_5H_5); 3.90,s, (CO_2CH_3); 3.83,s, (CO_2CH_3); 2.25,s, (SCH_3), in the 10/3/3/3 ratio. *Molecular weight* (osmometry): M = 371; M_{calc} = 412. *Physical properties*: (IIb) is a yellow compound slightly air-sensitive and soluble in common organic solvents.

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* ^1H, ^{19}F and ^{13}C NMR data are given as: δ(ppm/TMS) or δ(ppm/CCl_3F), nature of the signal, assignment, coupling constant (Hz); s = singlet, d = doublet, qu = quartet.

(IV). That pale-yellow oil was obtained in too low a yield for a complete analysis, it is only characterised by its IR and NMR spectra. *IR*: 360 m br, 740 m, 790 w, 850w, 920w, 1020m, 1060w, 1170s, 1210s, 1270s, 1650m (νC=C), 1750vs (νC=O). *^1H NMR*: 3.70,s, (CO_2CH_3); 2.67,s, (SCH_3) in the 6/3 ratio.

(V). (V) is a mixture of isomeric dimethyl-2-methylthiobut-2-enedioates in 1/1 ratio. Fractional crystallisation gave the pure isomers (Va) (*trans*) and (Vb) (*cis*).

(Va). *Anal.* Calcd.: C, 44.2; H, 5.3; S, 16.8%. Found: C, 44.2; H, 5.3; S, 16.8%. *IR*: 375m, 560w, 650m, 700m, 780m, 810w, 850sh, 870m, 900m, 950w, 990m, 1025m, 1060m, 1100w, 1190s br, 1200s, 1250s br, 1600 m (νC=C), 1715s and 1730s (νC=O), 3020w and 3080 (νC–H). *^1H NMR*: 6.32,s, (H); 3.92,s, (CO_2CH_3); 3.82,s, (CO_2CH_3); 2.40,s, (SMe), in the 1/3/3/3 ratio. *Melting point*: 55 °C. *Mass spectrum* m/e: $[M]^+$ = 190 (parent: 190); $[M–CH_3]^+$ = 175; $[M–OCH_3]^+$ = 159; $[M–SCH_3]^+$ = 143; $[M–CO_2CH_3]^+$ = 131; $[CO_2CH_3]^+$ = 59; $[SCH_3]^+$ = 47.

(Vb). *^1H NMR*: 5.65,s, (H); 3.90,s, (CO_2CH_3); 3.72,s, (CO_2CH_3); 2.42,s, (SCH_3), in the 1/3/3/3 ratio.

The thermal reaction (*ca.* 40 °C) of $[Cp_2NbH_3]$ with dimethyldisulphide and dimethyl acetylenedicarboxylate gave quite the same product than the photolytic reaction but the yields were much more lower, above all for complex (IIb).

Reaction of Niobium Thiolate(I) with the Acetylenes $R^1–C{\equiv}C–H$ (R^1=CF_3, n-C_8F_{17}) or $CH_3–C{\equiv}C–CH_3$

In the same way as described above, the reactants niobium thiolate(I), prepared *in situ*, and alkyne were irradiated and after work-up on the mixture no complex well-defined containing the alkyne was isolated. With the trifluoropropyne and the but-2-yne only complex(I) was isolated. The fluoroalkyne n-$C_8F_{17}–C{\equiv}C–H$ gave mostly an organic product(VII) which will be described below.

Reaction of $[CpM(SMe)(CO)_3]$ (M = Mo or W) with Fluoroalkynes $R^1–C{\equiv}C–H$ (R^1=n-C_6F_{13}, n-C_8F_{17})

The alkynes n-$R_F–C{\equiv}C–H$ were added to the thiometallates prepared *in situ*, but, such as mentioned above for niobium, identical results were obtained when isolated thio-metallates were used. In a typical reaction, to a solution of *ca.* 5.7 mmol of $[CpMH(CO)_3]$ in tetrahydrofuran, dimethyldisulphide in excess was added. The mixture was stirred (1–2 h; *ca.* 30 °C), and to the resulting solution were added 12 mmol of n-$R_F–C{\equiv}C–H$. It was irradiated at room temperature for *ca.* 30 h. The tetrahydrofuran was then evaporated to dryness, and the residue was dissolved in methylene chloride and chromatographed. Three types of compounds were separated. The first component (eluant: methylene chloride–hexane in the 1/3 ratio) obtained in too low a yield was not identified, but its infrared spectrum showed the presence of fluorine and carbonyl groups. The second components identified to a mixture of *cis* + *trans* vinylic sulphides (VI) and (VII) were purified by distillation *in vacuo* (yields *ca.* 20–30% for Mo and 5–10% for W). The third components were non-fluorinated complexes ($[CpW(CO)_3SMe]$ or $[\{CpMo(CO)_2SMe\}_2]$).

The same products were obtained by the thermal reactions but the yields were lower than those of the photolytic reactions.

(VI). $n\text{-}\underset{i}{C}F_3\underset{j}{C}F_2(\underset{k}{C}F_2)_3\underset{l}{C}F_2\underset{A}{C}H{=}CH\underset{B}{S}\underset{C}{C}H_3$: 3,4,5,6,7,8-tridecafluoro-2-methylthio-1-decene.

Anal.: Calcd.: C, 27.6; H, 1.3; S, 8.2; F, 63.0%. Found: C, 27.8; H, 1.5; S, 8.1; F, 62.6%. *IR*: 500w, 535w, 560w, 610w, 650w, 670w, 720m, 745m, 805m, 850m, 920w, 940m, 970w, 1060m, 1150s and 1210vs, 1250vs (νC–F), 1600 m (νC=C). *^1H NMR*: Isomer *cis* (40%); 6.80, d of tr, (H_B), $J_{B–A}$ = 10.5, $J_{B–l}$ = 3; 5.42, d of tr, (H_A), $J_{A–B}$ = 10.5, $J_{A–l}$ = 15.75; 2.45,s, (H_C). Isomer *trans* (60%): 7.15, d of tr, (H_B), $J_{B–A}$ = 15, $J_{B–l}$ = 2; 5.28, d of tr, (H_A), $J_{A–B}$ = 15, $J_{A–l}$ = 12. *^{19}F NMR*: 80.8, *i*; 126.5, *j*; 123.3 and 122, *k*; 109.2, *l*. *Boiling point: ca.* 30 °C/1 mmHg. *Mass spectrum* m/e: $[M]^+$ = 392 (parent: 392); $[M–CH_3]^+$ = 377; $[M–F]^+$ = 373; $[M–CF_3]^+$ = 323; $[C_3F_7]^+$ = 169; $[C_3F_5]^+$ = 131; $[–CF_2–CH{=}CHSCH_3]^+$ = 123; $[C_2F_5]^+$ = 119; $[C_2F_4]^+$ = 100; $[CF_3]^+$ = 69; $[SCH_3]^+$ = 47.

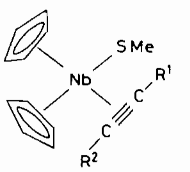
(VII). $n\text{-}\underset{i}{C}F_3\underset{j}{C}F_2(\underset{k}{C}F_2)_5\underset{l}{C}F_2\underset{A}{C}H{=}CH\underset{B}{S}\underset{C}{C}H_3$: 3,4,5,6,7,8,9,10-heptadecafluoro-1-methylthio-1-decene.

Anal. Calcd.: C, 26.8; H, 1.0; S, 6.5; F, 65.6%. Found: C, 26.8; H, 1.1; S, 6.5; F, 65.2%. *IR*: 530w, 560w, 655m, 710w, 730w, 740w, 750w, 850w, 940m, 990m, 1120m and 1135m, 1150s, 1210vs, 1245vs (νC–F), 1330w, 1620m (νC=C). *^1H NMR*: Isomer *cis* (40%): 6.68, d of tr, (H_B), $J_{B–A}$ = 10.5, $J_{B–l}$ = 3; 5.38, d of tr, (H_A), $J_{A–B}$ = 10.5, $J_{A–l}$ = 15; 2.40,s, (H_C). Isomer *trans* (60%): 7.05, d of tr, (H_B), $J_{B–A}$ = 15, $J_{B–l}$ = 2.25; 5.25, d. of tr., (H_A), $J_{A–B}$ = 15, $J_{A–l}$ = 11.25; 2.36,s, (H_C). *^{19}F NMR*: 80.4, *i*; 125.8, *j*; 121.2, *k*; 108.4, *l*. *Mass spectra* m/e: $[M^+]$ = 492 (parent: 492).

Results

Irradiation of $[Cp_2NbH_3]$ with dimethylsulphide in tetrahydrofuran afforded an unstable purple complex(I). Owing to its unstability, good elemental analysis were not obtained, however the diamagnetism of the compound, obvious from the sharpness of NMR peaks, indicates that niobium probably exists in its +5 formal oxidation state. (I) is therefore different from the known neutral paramagnetic compound $[Cp_2Nb(SR)_2]$ [2]. The data presently available do not allow us to formulate precisely that complex which contains two cyclopentadienyl and two SMe groups per niobium.

Photochemical treatment of (I) with alkynes gave the complexes (II) $[Cp_2Nb(SMe)(R^1C_2R^2)]$ when the alkynes used are electronegative (R^1=R^2=CF_3 or CO_2Me). From their spectroscopic properties the complexes (IIa) and (IIb) have similar structures. Elemental analysis, molecular weight and spectroscopic data on (II) are in accord with a structure in which the alkyne, acting as a two-electron donor, has substituted at least one SMe group of (I). The lack of strong F–F coupling on the ^{19}F NMR spectrum of (IIa) is in accord with a *trans* derivative [7].

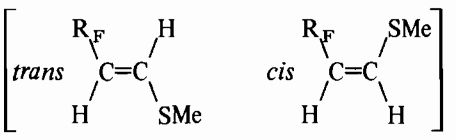


$R^1 = R^2 = CF_3$ (IIa)

$R^1 = R^2 = CO_2Me$ (IIb)

Compounds (II) showed in their IR spectra the expected features for an alkyne complex; thus the medium band near 1790 cm^{-1} is assigned to a ν(C≡C), bands arising from the CF_3 or CO_2Me groups occur in the respective regions: 1110–1240 cm^{-1} (νC–F) and 1700–1750 cm^{-1} (νC=O), 1210–1250 cm^{-1} (νC–O). Some by-products were also formed in a low yield in the reaction of (I) with the dimethyl acetylenedicarboxylate. An oily compound(IV) and a mixture of *trans* (Va) (50%) and *cis* (Vb) (50%) dimethyl-2 methylthiobut-2-enedioates, $MeCO_2CH$=$C(SMe)CO_2Me$, were separated off by distillation. The two components (Va) and (Vb) were obtained pure by fractional crystallisation and their stereochemistry were readily deduced from their elemental analysis, mass spectra and spectroscopic data. The mass spectrum of isomer (Va) showed a molecular ion M^+ and characteristic ions $[M–SCH_3]^+$ and $[M–CO_2CH_3]^+$. The NMR resonances of (Va) and (Vb) components were assigned by comparison with those of analogous compounds [8]. Owing to its very low yield, the elemental analysis of (IV) was not determined; however, the IR and ^{1}H NMR spectra suggested for (IV) a formulation such as $(CO_2Me)_2C$=$C(SMe)_2C$=$C(CO_2Me)_2$. When complex (I) reacted, in the same way, with the acetylenes R–C≡C–H (R = CF_3, n-C_8F_{17}) or the but-2-yne, which are less electronegative alkynes than those (hexafluorobut-2-yne and dimethyl acetylenedicarboxylate) used above, no complex of type (II) or else organometallic compound containing the coordinated alkyne was characterised; however with the fluoroalkyne n-C_8F_{17}–C≡C–H some organometallic compound containing fluorine was detected by IR and NMR. The reaction of $[Cp_2NbH_3]$ with dimethyldisulphide and but-2-yne or trifluoropropyne gave only compound (I) whereas with the fluoro-alkyne n-C_8F_{17}–C≡C–H some vinylic sulphide (VIb) was obtained.

The reaction of fluoroalkynes R_F–C≡C–H (R_F = n-C_6F_{13}, n-C_8F_{17}) with $[CpMH(CO)_3]$ (M = Mo, W) and dimethyldisulphide was also investigated in view of the similarity in reactivity towards R_F–C≡C–H of these hydridocomplexes to hydrido-niobium compound. Indeed the main features of the reactions appear the same for these two kinds of complexes; irradiation of a tetrahydrofuran solution of $[CpMH(CO)_3]$ (M = Mo, W) in the presence of dimethyldisulphide and fluoroalkynes afforded mainly a mixture of *cis* (40%)–*trans* (60%) vinylic sulphides(VI) and (VII)



and thiolates $[CpW(SMe)(CO)_3]$ (VIII) or $[\{CpMo(SMe)(CO)_2\}_2]$ (IX). However, such as above mentioned for niobium, trace amount of carbonyl fluorinated organotungsten or molybdenum complexes have been detected by IR and NMR techniques, but these species were not identified. When the acetylenes reacted with the thiolates $[CpM(SMe)(CO)_3]$, the substituted vinylic sulphides yields were quite similar to those obtained according to the method described above. Complexes (VIII) and (IX) were identified by comparison of their spectroscopic data with those of samples prepared according to methods described elsewhere [1, 9]. The mixture of isomeric olefins (VI) or (VII) was not separated. The stereochemistry of isomers (VI) or (VII) was deduced from elemental analysis, IR and mass spectra [18], and from the characteristic coupling constants of vicinal vinylic protons [10] (J = 10.5 Hz for the *cis* and 15 Hz for the *trans* protons) and vinylic protons and α or β fluorine in the ^{1}H NMR. The ratios of the two isomers were determined from the integration of the easily identifiable SMe peaks on the ^{1}H NMR spectra. The IR spectra show bands characteristic of CF_3 and CF_2 groups in the 1100–1250 cm^{-1} range and exhibit the νC=C peak near 1600 cm^{-1}.

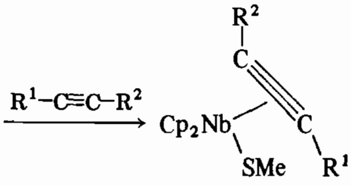
Discussion

Complex (I) has not been fully characterised, however two structures could be suggested for that diamagnetic compound from its ^{1}H NMR spectra: a dimeric structure $[\{Cp_2Nb(SMe)_2\}_2]$ (Nb–Nb)

(Ia) or a monomeric structure such as [$Cp_2NbH(SMe)_2$] (Ib). Although no obvious hydrogen peak (Nb–H) was detected on the NMR spectrum, the monomeric stoichiometry (Ib) seems more likely. The geometry of the [Cp_2MX_3] compounds has been discussed by Lauher and Hoffmann [11]; the three X ligands lie in the bisector plane of the [Cp_2M] moiety. Our ^1H NMR results agree with such a geometry, the H ligand occupying one of the extreme positions.

The reactivity of acetylenic compounds towards (I) was sensitive to substituent effects. While alkynes having two electron-withdrawing groups (CF_3–C≡C–CF_3 and $MeCO_2$–C≡C–CO_2Me) gave rise to a substitution reaction, trifluoropropyne, but-2-yne and the fluoroalkyne n-C_8F_{17}–C≡CH afforded neither acetylene nor σ-alkenyl complexes. Alkynes having electron-attracting groups gave stable σ-alkenyl derivatives with dihydrido-molybdenum or -tungsten complexes [12], whereas with niobium thiolate acetylene species were obtained. Usually the stability of alkenyl complexes increases with the increase of electron-withdrawing properties of the substituents of the alkyne [12, 13, 1b]. The absence of σ-alkenyl niobium species, even when (I) reacted with electronegative alkynes, could be accounted for in terms of lack of an electron-donating nature of the niobium(V) [$Cp_2Nb(SMe)$–] moiety. The formation of *cis* and *trans* $MeCO_2CH{=}C(SMe)CO_2Me$ in the reaction of (I) with dimethyl acetylenedicarboxylate is in agreement with the following mechanism:

(I) + R^1–C≡C–R^2 → [σ-alkenyl complex]



+ *cis–trans*-R^1–CH=C(SMe)R^2 (1)

$R^1 = R^2 = CF_3, CO_2Me$

The hydrogenation was not stereoselective. Such a mechanism was suggested previously by Nakamura and Otsuka [12] for the reaction of dihydrido-molybdenum complex with diphenylacetylene.

The reactivity of niobium thiolate (I) and of [Cp_2NbH_3] towards alkynes are quite different. The reaction of trihydrido-niobium complex with CF_3–C≡C–CF_3 is mostly characterised by the cleavage of C–F bond in hexafluorobut-2-yne giving σ paramagnetic fluorine compounds [Cp_2NbFX] (X = F, –$C(CF_3){=}CHCF_3$) and also a cyclometallic complex [$Cp_2Nb\{(CF_3)C{=}C(CF_3)\}_2$], the alkyne compound [$Cp_2NbH(CF_3$–C≡C–$CF_3)$] was only formed in a very low yield [14]. Now the use of alkynes having non electron-attracting substituents gave rise to the acetylene complex [6a]. Reaction of hexafluorobut-2-yne with the sixteen-electron compound [Cp_2NbCl], formed *in situ* from [Cp_2NbCl_2] by amalgam reduction, afforded also an acetylene derivative [15], (I) and [Cp_2NbCl] have therefore a closely reactivity towards alkynes.

As in the reactions of niobium thiolate (I) with non electron-attractive alkynes no well-defined σ-alkyl, σ-alkenyl or acetylene complex was obtained when molybdenum or tungsten thiolates reacted with fluoroacetylenes R_F–C≡C–H (R_F = n-C_6F_{13}, n-C_8F_{17}). For explaining the formation of *cis* and *trans* substituted vinyl sulphides (VI), a reaction path where a σ-alkenyl intermediary derivative is formed as in reaction (1) could be suggested. The alkenyl sulphide R^1–CH=CHSR^2 are well known [16], but the fluoroalkenyl sulphides are less numerous [CF_3-$CH{=}C(SR^1)R$ with R = CF_3 or H and R^1 = H, Et, t-Bu, Ph; $(CF_3)_2C{=}C(SR)_2$ with R = Et, t-Bu] [17], and those described here [R_F–CH=CH(SMe) with R_F = n-C_6F_{13}, n-C_8F_{17}] are new.

Acknowledgement

The authors wish to thank Professor A. Cambon and Dr. M. Le Blanc, (University of Nice) for the gift of samples of R_F–C≡C–H, and Mr. J. Y. Le Gall, (University of Brest) for experimental assistance in the NMR study.

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