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X *. SYNTHESIS OF NEW (η^2-DISULFIDO) COMPLEXES; COMPARISON OF THEIR REACTIVITY WITH THAT OF (η^2-DIOXO) DERIVATIVES

JEAN-LOUIS MIGOT, JEAN SALA-PALA and JACQUES-E. GUERCHAIS

Laboratoire de Chimie Inorganique Moléculaire, Laboratoire Associé au CNRS 322, Faculté des Sciences et Techniques, 29283 Brest-Cédex (France)

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Summary

The new compounds $[M(\eta^5\text{-}C_5H_5)_2(X\text{–}X)R]$ (with M = Nb : X = S, R = Me, Bu, η^1-C_5H_5; X = Se, R = Me; with M = Ta : X = S, R = Me) are described. The reactions of $[Nb(\eta^5\text{-}C_5H_5)_2(S\text{–}S)Me]$ (A) with some nucleophiles and electrophiles have been studied. A reacts with triphenylphosphine to give the corresponding monosulfido complex. Loss of the S_2 ligand and formation of a μ-oxoderivative $[\{Nb(\eta^5\text{-}C_5H_5)_2Me\}_2O]\ X_2 \cdot 2OH_2$ (X = I or BF_4) occurs upon treatment of A with CH_3I or Ph_3CBF_4. $[Nb(\eta^5\text{-}C_5H_5)_2Me\ I]I$, MeSSMe, have also been identified as product from the reaction with CH_3I. Reaction of A with hexafluorobutyne gives an unexpected new compound, the nature of which is discussed.

Introduction

Dioxygen-metal complexes have been widely studied, mainly as models for biological and industrial processes involving molecular oxygen [2]. The isolation and characterization of a great variety of such complexes and study of the various reactions they undergo have yielded general information about the bonding, structure and reactivity of the coordinated dioxygen moiety. In contrast, only a few studies of the synthesis and chemistry of complexes with the disulfido ligand were reported before 1976 [3], though there have been considerable developments in the past [4]. These complexes are of interest since, although S_2 is formally similar to O_2, the presence of low-lying *d* orbitals can have a pronounced effect, giving rise to an interesting and specific chemistry.

Previous work revealed the tendency of niobium to give disulfido complexes: thus $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2(OH)]$ reacts with hydrogen sulfide in methanol in presence of

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* For part IX see ref. 1.

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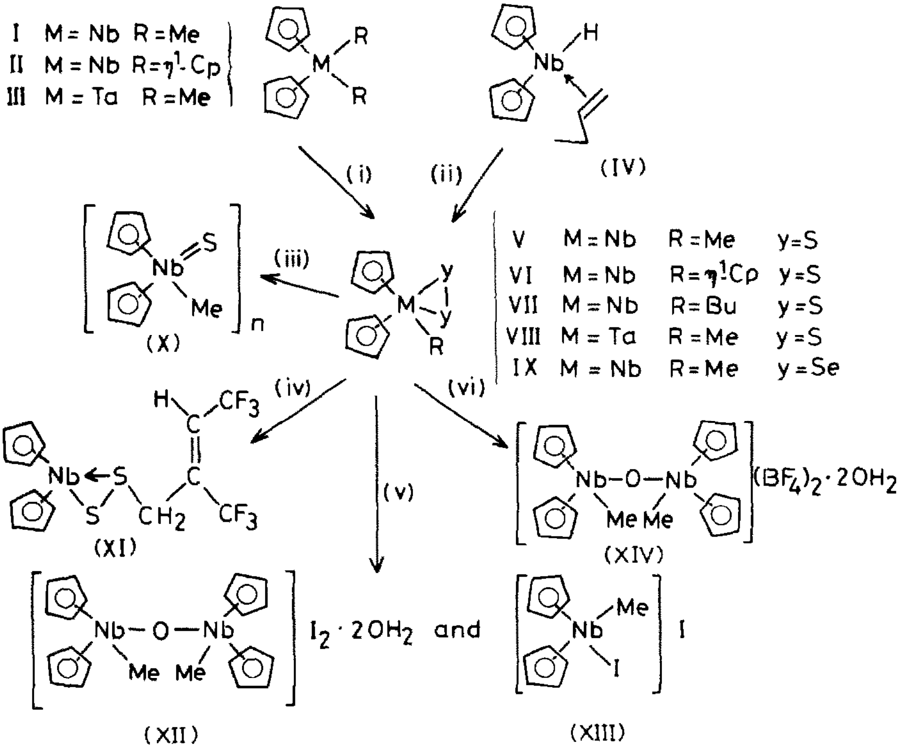
MX (M = NH_4 or K; X = Cl, Br, I, CN, SCN, N_3) to give the complexes $[Nb(\eta^5\text{-}C_5H_5)_2(S\text{-}S)X]$ [3a]. We recently described the peroxo analogues $[Nb(\eta^5\text{-}C_5H_5)_2(O\text{-}O)X]$ (X = Cl, NCO) [5], and the $\eta^2\text{-}S_2$ niobium complexes seemed worthy of further investigation in order not only to get new insights in the chemistry of $\eta^2\text{-}S_2$ derivatives but also to compare the chemistries of $\eta^2\text{-}S_2$ and $\eta^2\text{-}O_2$ complexes.

We report here the preparation of some alkyl complexes $[Nb(\eta^5\text{-}C_5H_5)_2(Y\text{-}Y)R]$ (Y = S, Se) in which cyclooctasulfur and red selenium are used to introduce Y_2 ligands. Some aspects of the reactivity of $[Nb(\eta^5\text{-}C_5H_5)_2(S\text{-}S)Me]$ are also described. Part of this work has been briefly communicated [6a].

Results and discussion

Syntheses of $[M(\eta^5\text{-}C_5H_5)_2(Y\text{-}Y)R]$ (M = Nb, Ta; Y = S, Se) complexes

In solution in benzene, cyclooctasulfur reacts thermally or photochemically with $[Nb(\eta^5\text{-}C_5H_5)_2Me_2]$ (I) to give orange-brown solutions which after work-up yield orange microcrystals of $[Nb(\eta^5\text{-}C_5H_5)_2(S\text{-}S)Me]$ (V) in moderate yield (ca. 50%). Compound V is soluble in common organic solvents except alkanes. Both the pure compound and solutions are stable in air for some hours. The IR spectrum shows a sharp and intense peak near 550 cm^{-1} which is assignable to ν(S–S) by comparison



Scheme 1. (i) and (ii) cyclooctasulfur or red selenium in benzene, reflux or $h\nu$ for 12 h. V: 50% (from I); VI: 20% (from II); VII: 50% (from IV); VIII: 15% (from III); IX: 10% (from I). (iii) PPh_3 in CH_2Cl_2, $h\nu$ for 72 h, 20%. (iv) hfb in benzene, 50°C for 7 d, 17%. (v) CH_3I in CH_2Cl_2, r.t. for 15 h. XII: 50%; XIII: 10%. (vi) Ph_3CBF_4 in CH_2Cl_2, r.t. for 72 h, 10%.

with previous works [3a]. The crystal structure, which was reported elsewhere [6b], consists of monomeric eighteen electron units involving a bent-sandwich system with a S_2 side-on ligand (S–S 2.010(5), Nb–S 2.515(3) and 2.432(3) Å) and a niobium-coordinated methyl group (Nb–C 2.327(1) Å).

Use of similar procedures with $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$ (II), $[Nb(\eta^5\text{-}C_5H_5)_2H(CH_2{=}CH{-}C_2H_5)]$ (IV) and $[Ta(\eta^5\text{-}C_5H_5)_2Me_2]$ (III) gave the new disulfido complexes VI–VIII (see Scheme 1). Quadrupole broadening by the ^{93}Nb nucleus results in a poorly resolved ^1H NMR spectrum in the butyl range for compound VII, but the ^{13}C Fourier-transform NMR spectrum shows four sharp signals consistent with the presence of a butyl ligand.

The reaction of I with red selenium affords the red-brown complex $[Nb(\eta^5\text{-}C_5H_5)_2(Se{-}Se)Me]$ (IX), the IR spectrum of which includes a peak at 370 cm^{-1} which may be assigned to the $\nu(Se{-}Se)$ vibration [7]. This reaction differs from that between selenium and $[M(\eta^5\text{-}C_5H_5)_2Me_2]$ (M = Zr, Hf), which gives $[M(\eta^5\text{-}C_5H_5)_2(Se{-}Me)_2]$ via selenium insertion into the two metal–carbon σ-bonds [8].

On the basis of the spectroscopic data given in the experimental section, the structures of complexes VI–IX are believed to be analogous to that found by an X-ray study for compound V [6b].

Since metallo-oxaziridines, i.e. compounds containing a $\overline{\mathrm{M{-}O{-}N}}\mathrm{R}$ ring have been recently reported [9], preparation of a metallo-thioaziridine from the reaction of S_7NH and compound I was attempted. The reaction does not give the expected $\overline{\mathrm{Nb{-}S{-}N}}\mathrm{H}$ derivative, but the disulfido complex V.

The syntheses of complexes V, VI, VIII and IX correspond to oxidations with sulfur or selenium of 17 electron species with cleavage of one of the two Nb–C σ-bonds and replacement of the leaving group by a two-electron ligand. Thus they may be compared with the preparations of the peroxo complexes $[Nb(\eta^5\text{-}C_5H_5)_2(O{-}O)Cl]$, i.e. oxidation of $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$ with hydrogen peroxide [5]. In both cases, formation of a 16 electron intermediate $[Nb(\eta^5\text{-}C_5H_5)_2X]$ (X = R, Cl) seems likely. In the synthesis of complex VII from IV, such a species would result from the butene insertion into the Nb–H bond. The formation of these $\eta^2\text{-}S_2$ derivatives, together with the syntheses of $[M(\eta^5\text{-}C_5H_5)_2S_4]$ (M = Mo, W) [10] and $[Ti(\eta^5\text{-}C_5H_5)_2S_5]$ [11] from reactions with S_8, confirms that cyclooctasulfur can fragment under relatively mild conditions to give products containing the MS_x ring. The factors that determine ring size remain poorly understood, but it is noteworthy that for some of the species with $x = 2$, viz. $[Nb(\eta^5\text{-}C_5H_5)_2(S{-}S)X]$ [3a and this work] and $[M(S{-}S)_2(dape)_2]$ (M = Rh, Ir, dape = bis(dialkylphosphino)ethane) [3c], the dioxygen analogues have been described [5,12]. The dioxygen analogues are not known for $x = 4$ or 5, although a poorly characterized material believed to be $[Ti(\eta^5\text{-}C_5H_5)_2(O{-}O)]_n$ has been reported [13].

Reactivity of $[Nb(\eta^5\text{-}C_5H_5)_2(S{-}S)Me]$ (V)

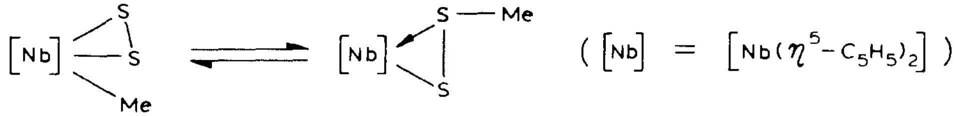
With triphenylphosphine. Treatment of V in THF with PPh_3 gives the monosulfido complex $[Nb(\eta^5\text{-}C_5H_5)_2(S)Me]$ for which the observed $\nu(Nb{-}S)$ value (435 cm^{-1}) may indicate a polymeric structure involving sulphur bridging [14], although mass spectral data correspond to monomer units. Since $SPPh_3$ was identified, this reaction apparently proceeds as in eq. 1:

$$[Nb(\eta^5\text{-}C_5H_5)_2(S{-}S)Me] + PPh_3 \rightarrow [Nb(\eta^5\text{-}C_5H_5)_2(S)Me] + SPPh_3 \qquad (1)$$

This sulfur transfer may be compared to the oxygen-transfer reaction observed in the synthesis of the oxo-product [Nb(η^5-C_5H_5)$_2$(O)Cl] from the corresponding peroxo-complex and PPh_3 [5].

With hexafluorobut-2-yne (hfb). It was of particular interest to examine this reaction since Clark et al. [15a] recently showed that dioxygen platinum complexes [Pt(O–O)L_2] (L = PR_3) react readily with hfb to give, via 1,2-addition of the dioxygen molecule across the acetylenic C≡C bond, the complex [Pt(O–CR=CR–CR=CR–O)L_2] (R = CF_3). Similarly [Ti(η^5-C_5H_5)$_2S_3$]$_2$ was shown to react with acetylenes to give the dithiolene derivatives Ti(–S–Cr=CR–CR=CR–S)(η^5-C_5H_5)$_2$ [15b]. In the light of these results we expected that reaction of hfb with V would give a dithiolene complex, but in fact a different product was obtained.

Thermal reaction of hfb with V (50°C; 7 days) give a complex XI as blue, air-sensitive microcrystals; its elemental analysis and mass spectrum are consistent with the formula $C_{15}F_6H_{13}NbS_2$, corresponding to a 1/1 complex. The ^{1}H and ^{19}F NMR spectra give important and surprising structural information. The ^{1}H NMR spectrum clearly exhibits a η^5-C_5H_5 signal (δ 5.62 ppm, relative intensity 10) and a singlet which position (δ 3.52 ppm) and intensity correspond to a CH_2 group. However, a careful examination of this spectrum reveals a further resonance near the η^5-C_5H_5 signal (δ 5.80 ppm, rel. int. 1) indicating the presence of an olefinic CH unit. The ^{19}F NMR spectrum shows the two CF_3 groups to be non-equivalent. ^{1}H decoupling experiments (selective irradiation at 5.80 ppm) shows that the lowfield signal arises from coupling with three equivalent ^{19}F nuclei and a proton. The ^{1}H and ^{19}F NMR data are consistent with the presence of a *cis*-C(CF_3)=CHCF_3 unit in XI [16]. These results show that the reaction of V with hfb is rather complex, and involves both S_2 and methyl groups. Since single crystals suitable for an X-ray study cannot be obtained we cannot be sure about the structure of XI, but the spectroscopic data suggest that it has the structure shown in Scheme 1. It is tempting to speculate that this eighteen electron structure arises from hfb insertion into a CH bond of the hypothetical intermediate [Nb(η^5-C_5H_5)$_2$(η^2-S–SMe)] formed reversibly from V:



With methyliodide and triphenylmethyl tetrafluoroborate. Treatment of complex V with CH_3I in dichloromethane at room temperature gives a precipitate of compound XII, the IR spectrum of which shows a broad and intense absorption at 780 cm^{-1} assignable to ν(Nb–O–Nb). This, together with the analytical data and conductivity measurements, suggests the compound XII to be [{Nb(η^5-C_5H_5)$_2$Me}$_2$O]$I_2 \cdot 2OH_2$. It probably has the same basic structure as [{(Nb(η^5-C_5H_5)$_2$Cl}$_2$O] (BF_4)$_2$, of which an X-ray study has been made [17]. However, coordination of the OH_2 molecules, leading to niobium atoms with 18 electron configurations, seems likely. Chromatography of the filtrate gives small amounts of the previously described [Nb(η^5-C_5H_5)$_2$MeI]I (XIII) [18], while VPC experiments indicate the formation of dimethyldisulfide.

Similarly, V reacts with Ph_3CBF_4 to give the tetrafluoroborate analogue of complex XII, $[\{Nb(\eta^5\text{-}C_5H_5)_2Me\}_2O](BF_4)_2 \cdot 2\ OH_2$ (XIV).

The formation of complexes XII–XIV, together with the VPC identification of MeSSMe during the reaction with CH_3I, suggests that the reactions of V with CH_3I and Ph_3CBF_4 proceed via electrophilic attack on the two sulfur atoms followed by decomplexation of the sulfur-containing ligand. The resulting electron-deficient niobium species then would react with traces of water to give XII or XIV, and with iodide to give XIII.

It is noteworthy that complexes $[MoO(S\text{–}S)(dtc)_2]$ (dtc = S_2CNR_2) do not react with CH_3I, but only with strong electrophilic reagents such as CH_3SO_3F, to undergo alkylation of one of the two sulfur atoms [4c].

Other reactions

Bubbling of HCl gas through a THF solution of V gives a precipitate of the well-known complex $[Nb(\eta^5\text{-}C_5H_5)_2Cl_2]$. V does not react with SO_2, either as a neat liquid or in dichloromethane. Under these conditions, the peroxo complex $[Nb(\eta^5\text{-}C_5H_5)_2(O\text{–}O)Cl]$ gave the corresponding sulfato complex $[Nb(\eta^5\text{-}C_5H_5)_2(SO_4)Cl]$ [5].

All the reactions and structures of the new compounds V–XIV are represented in Scheme 1. Some of the chemistry of $[Nb(\eta^5\text{-}C_5H_5)_2(S\text{–}S)Me]$ (V) is rather unexpected. The reaction with hfb, which involves both S_2 and methyl groups of V, was unexpected.

Experimental

All the reactions were carried out under dry dinitrogen using conventional Schlenk tube techniques. All solvents were distilled before use. Solutions were irradiated in Pyrex glass tubes using a mercury vapor lamp HANAU TQ 150. Analyses were performed by the "Service Central de microanalyse du CNRS".

Infrared spectra were recorded on a PYE-UNICAM spectrophotometer from 200 to 4000 cm^{-1} (Nujol mulls between CsI windows). ^1H, ^{13}C and ^{19}F NMR spectra were obtained on a JEOL FX 100 spectrophotometer ($SiMe_4$ as internal standard for ^1H and ^{13}C; CF_3CO_2H as external standard for ^{19}F). Mass spectra were obtained with a VARIAN MAT 311 mass spectrophotometer. Both analytical and spectroscopic data are shown in Table 1.

$[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Nb [19]; M = Ta [20]), $[M(\eta^5\text{-}C_5H_5)_2Me_2]$ (M = Nb [21]; M = Ta [21]), $[Nb(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)_2]$ [22] and $[Nb(\eta^5\text{-}C_5H_5)_2H(CH_2{=}CHC_2H_5)]$ [23] were prepared according to literature procedures.

(η^2-Disulfido)methyl-bis(η^5-cyclopentadienyl)niobium (V)

Compound I (7.6 mmol) in benzene (250 cm^3) was treated with sulfur (8.6 mmol) and the mixture was refluxed or irradiated for 12 h. The resulting orange-brown solution was concentrated, filtered and then chromatographed on an alumina column made up with dichloromethane/pentane (1/1). Elution with dichloromethane gave an orange solution from which the final product was obtained as orange crystals by slow evaporation under reduced pressure. Yield 50%.

(η^2-Disulfido)(η^1-cyclopentadienyl)-bis(η^5-cyclopentadienyl)niobium (VI)

This was prepared analogously to V starting from II instead of I. Elution of a

(Continued on p. 434)

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA

Compound		Analysis[a] (%)			Selected IR data (cm^{-1})	^{1}H and ^{13}C NMR data[b]
		C	H	S or Se		
[Nb(η^5-C$_5$H$_5$)$_2$(S–S)Me]	V	44.5 (43.7)	4.6 (4.3)	21.6[c] (21.2)	540s ν(S–S)	^{1}H[d]: 1.10, 3, s, Me; 5.60, 10, s, η^5-C$_5$H$_5$; ^{13}C[d]: 7.7, s, CH$_3$; 105.8, s, η^5-C$_5$H$_5$.
[Nb(η^5-C$_5$H$_5$)$_2$(S–S)(η^1-C$_5$H$_5$)]	VI	51.4 (51.1)	4.1 (4.3)		545m ν(S–S)	^{1}H[d]: 5.95, c, C$_5$H$_5$
[Nb(η^5-C$_5$H$_5$)$_2$(S–S)Bu]	VII	49.6 (48.8)	5.8 (5.6)	17.6 (18.6)	550s ν(S–S)	^{1}H[d,e]: 5.57, s, η^5-C$_5$H$_5$. ^{13}C[d]; 14.1, s, CH$_3$; 26.1, s, CH$_2$; 29.0, s, CH$_2$; 37.7, s, CH$_2$; 105.4, s, η^5-C$_5$H$_5$.
[Ta(η^5-C$_5$H$_5$)$_2$(S–S)Me]	VIII	33.2 (33.9)	3.1 (3.4)	16.8 (16.4)	540s ν(S–S)	^{1}H[d]: 0.95, 3, s, Me; 5.60, 10, s, η^5-C$_5$H$_5$.
[Nb(η^5-C$_5$H$_5$)$_2$(Se–Se)Me]	IX	34.1 (33.3)	3.5 (3.3)	38.0 (39.9)	370m ν(Se–Se)	
[Nb(η^5-C$_5$H$_5$)$_2$(S)Me]	X	47.3 (48.9)	4.6 (4.8)	11.0[f] (11.9)	435s ν(NbS)	^{1}H[d]: 0.78, 3, s, Me; 6.00, 10, s, η^5-C$_5$H$_5$.

$[Nb(\eta^5\text{-}C_5H_5)_2(SSCH_2(hfb)H)]$	XI	38.5 (38.8)	2.6 (2.8)	14.9 [g,h] (13.8)	1140-1270vs ν(CF)	^1H [d]: 3.52, 2, s, CH_2; 5.62, 10, s, $\eta^5\text{-}C_5H_5$; 5.80, 1, s, CH. ^{13}C [d]: 42.6, s, CH_2; 104.9, s, $\eta^5 C_5H_5$. ^{19}F [i].
$[(Nb(\eta^5\text{-}C_5H_5)_2Me)_2O]I_2 \cdot 2OH_2$	XII	34.8 (33.8)	4.2 (3.9)	0.4 [j,k] (0.0)	780vs ν(Nb–O–Nb) 1620w $\delta(OH_2)$ 3420m and 3500m ν(OH)	
$[Nb(\eta^5\text{-}C_5H_5)_2(Me)I]I$	XIII					^1H [d]: 1.17,3, s, Me; 5.21, 10, s,$\eta^5\text{-}C_5H_5$
$[(Nb(\eta^5\text{-}C_5H_5)_2Me)_2O]\ (BF_4)_2 \cdot 2OH_2$	XIV	38.0 (37.6)	3.7 [l] (4.3)		775vs ν(Nb–O–Nb) 1060 and 1080vs ν(BF) 1650w $\delta(OH_2)$ 3580m and 3650m ν(OH)	

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[a] Calculated values are given in parentheses. [b] Given as chemical shift, relative intensity (excepted for ^{13}C), multiplicity (J in Hz), assignment. c = complex multiplet, quart = quartet, quint = quintet. [c] Mass spectrum shows a highest band, parent ion (P^+) at $m/e = 302$ and peaks at 287 ($P^+ - S$), 270 ($P^+ - Me$), etc. [d] in $CDCl_3$. [e] Poorly resolved broad peaks in the butyl range 0.5–2 ppm. [f] Mass spectrum shows parent peak (P^+) at $m/e = 270$; some weak peaks appear at higher values (287, 293, 295 and 308); intense peaks at 255 ($P^+ - Me$). [g] Other analytical data: F, 24.2 (24.6); Nb, 19.4 (20.0)%. [h] Mass spectrum shows a highest band, parent ion (P^+) at $m/e = 464$; other peaks at 445 ($P^+ - F$), 255, 242, etc. [i] ^{19}F in $[(CD_3)_2\ CO]$ δ relative to CF_3CO_2H: 17.6, 3, quart, $^5J(F\text{–}F) = 11.9$, $^4J(F\text{–}H) = 0$, CF_3; 22.8, 3, quint, $^5J(F\text{–}F) = 11.9$, $^3J(F\text{–}H) = 9.5$, CF_3. Usual coupling constant values for a *cis*-$C(CF_3){=}CH(CF_3)$ unit (values given in parentheses for a *trans* unit): $^5J(F\text{–}F) = 12\text{–}15$ (2–2.5); $^4J(F\text{–}H) = 0$ (0–3); $^3J(F\text{–}H) = 9\text{–}11$ (8–9); see ref. 16. [j] Other analytical data: I, 31.6 (32.5); Nb, 22.8 (23.8)%. [k] Conductivity measurement (CH_3NO_2; 10^{-3} M; 20°C) Λ 161 Ω^{-1} cm^2 mol^{-1}, consistent with the formulation as a 2/1 electrolyte. [l] Other analytical data: F, 21.6 (21.7); Nb, 26.9 (26.5)%.

Florisil column with dichloromethane/THF (85/15) followed by concentration gave a purple solid. Yield 20%.

(η^2-Disulfido)n-butyl-bis(η^5-cyclopentadienyl)niobium (VII)

This was prepared as described for compound V but using IV instead of I. Elution of a Florisil column with dichloromethane gave an orange solution which was evaporated under reduced pressure. The residue was stirred with pentane (25 cm^3) to give VII as an orange powder. Yield 50%.

(η^2-Disulfido)methyl-bis(η^5-cyclopentadienyl)tantalum (VIII)

The reaction was carried out as described above for V but using III instead of the niobium analogue I. Elution of a Florisil column with dichloromethane/THF (90/10) gave orange crystals. Yield 15%.

(η^2-Diselenido)methyl-bis(η^5-cyclopentadienyl)niobium (IX)

This was prepared analogously to V using red selenium instead of sulfur. Elution of a Florisil column with benzene/THF (85/15) gave a brown solid, the analytical data for which always indicated a slightly low selenium content. Yield 10%.

The new complexes V–IX are stable in air, both in the solid state and in solution for periods of hours, except for complex VII which is air sensitive. Compounds V, VII, VIII are rather soluble in CH_2Cl_2, C_6H_6, and THF, but insoluble in alkanes. Complexes VI and IX have low solubilities.

Reaction of V with triphenylphosphine. Synthesis of methyl-sulfido-bis(η^5-cyclopentadienyl)niobium (X)

A dichloromethane solution of V (2.7 mmol) and PPh_3 (2.7 mmol) was irradiated for ca. 72 h, concentrated and chromatographed on a Florisil column made up with dichloromethane/hexane (1/1). Elution with pure CH_2Cl_2 gave first $SPPh_3$ (2.2 mmol) and then some starting material V. Elution with CH_2Cl_2/THF (95/5) gave a brown solution, from which X was obtained in 20% yield by concentration.

Reaction of V with hexafluorobut-2-yne. Synthesis of complex XI

A stirred solution of V (3.4 mmol) and hfb (3.7 mmol) in benzene (ca 50 cm^3) was kept for ca 7 days at 40–50°C. After concentration under vacuo and filtration, the resulting violet solution was chromatographed on a Florisil column made up with CH_2Cl_2/hexane (1/1). Elution with this solvent mixture gave a yellow band, which after concentration afforded small amounts of a yellow liquid; on the basis of spectroscopic data this could be 3,4-bis(trifluoromethyl)-1,2-dithiethene $[\overline{S{-}C(CF_3){=}C(CF_3)S}]$ [24]. Further elution with a CH_2Cl_2/THF (95/5) mixture gave a violet solution. This was reduced (20 cm^3) and pentane (15 cm^3) added. After ca. 20 h at -60°C, crystals were filtered and dried in vacuo. In some experiments, IR spectrum indicated that small amounts of the yellow product described above were still present. The violet product was then dissolved in CH_2Cl_2 (15 cm^3) and chromatographed as above. Yield of spectroscopically pure product 17%.

XI is a very air-sensitive compound which slowly decomposes in the solid state even when kept under dinitrogen or in vacuo. It is very soluble in common organic solvents except alkanes.

Reaction of V with methyliodide. Syntheses of complexes XII and XIII

Excess CH_3I (5 mmol) was added to a solution of V (2 mmol) in CH_2Cl_2 (100 cm^3). The mixture was stirred at room temperature for 15 h during which a yellow product separated. The solid (compound XII) was filtered off, washed with CH_2Cl_2 (4×20 cm^3) and dried in vacuo. Yield 50%. The orange filtrate was evaporated under reduced pressure and the solid residue extracted with CH_2Cl_2 (20 cm^3). The resulting solution was chromatographed (Florisil column made up with CH_2Cl_2). Two coloured spots developed. The first corresponded to a small amount of iodine; the second, after concentration, gave orange crystals which were identified as complex XIII by comparison of its spectroscopic data with that of an authentic sample [18]. Yield 10%. VPC analysis of the CH_2Cl_2 solution obtained in the column chromatography experiment before elution of the first coloured spot showed the presence of dimethyldisulfide MeSSMe, which was identified by comparison of its retention time with that of an authentic sample.

Reaction of complex V with triphenylmethyl tetrafluoroborate. Synthesis of complex XIV

A CH_2Cl_2 solution (100 cm^3) containing Ph_3CBF_4 (1 mmol) and V (1 mmol) was stirred at room temperature for ca. 72 h during which complex XIV precipitated. The solid was filtered off then washed with CH_2Cl_2 (3×30 cm^3) and dried in vacuo. Yield 10%.

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