Articles

Chemistry of η^2-CS₂ Niobocene Complexes: Synthesis and Characterization of New 1,3-Dithiol-2-ylidene Complexes via Reactions with Activated Alkynes

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The reaction of CS₂ with Cp′₂Nb(H)(η^2-CH₂=CH₂) or Cp′₂Nb(H)(η^2-CH₂=CHPh) (Cp′ = η^5-C₅H₄SiMe₃) affords the alkylniobocene complexes Cp′₂Nb(Et)(η^2-CS₂-*C,S*) (**2**) and Cp′₂-Nb(CH₂CH₂Ph)(η^2-CS₂-*C,S*) (**3**), respectively. The interaction of η^2-CS₂-containing complexes Cp′₂NbCl(η^2-CS₂-*C,S*) with alkynes bearing electron-withdrawing groups gives rise to a new family of 1,3-dithiol-2-ylidene niobocene species, Cp′₂NbX($=\overline{CS(R)C=C(R)S}$) (**6**, X = Cl, R = CF₃; **7**, X = Cl, R = COOMe; **8**, X = Cl, R = COOᵗBu; **9**, X = Et, R = COOMe; **10**, X = Et, R = COOᵗBu; **11**, X = CH₂CH₂Ph, R = COOMe; **12**, X = CH₂CH₂Ph, R = COOᵗBu). In a similar way, with the carboxylate complexes Cp′₂Nb(OC(O)H-*O*)(η^2-CS₂-*C,S*) (**4**) and Cp′₂-Nb(OC(O)CH₃-*O*)(η^2-CS₂-*C,S*) (**5**) as starting materials, other 1,3-dithiol-2-ylidene species have been isolated Cp′₂Nb(OC(O)Y−O)($=\overline{CS(R)C=C(R)S}$) (**13**, Y = H, R = COOMe; **14**, Y = H, R = COOᵗBu; **15**, Y = CH₃, R = COOMe; **16**, Y = CH₃, R = COOᵗBu). The structures of all complexes have been determined by spectroscopic methods. The structure of **2** was established by single-crystal diffractometry studies. The molecular structure shows a typical bent-sandwich geometry around the niobium atom with the ethyl and carbon disulfide ligands arrayed in the plane between the two cyclopentadienyl rings.

Introduction

The chemistry of carbon disulfide with transition-metal substrates has become the focus of increased attention. As a result, the η^2-CS₂-*C,S* group has been found to have a wide range of reactivity, taking part in such reactions as sulfur abstraction to give thiocarbonyl−metal species, alkylations at nucleophilic exo sulfur atoms, and formation of polynuclear complexes via utilization of one or both sulfur atoms coordinated to other metals.[1] However, the range of chemistry for metallocenes of the early transition metals[2] is less developed than that of complexes of the later group metals.

The cycloaddition of alkynes bearing electron-withdrawing substituents to a η^2-CS₂-*C,S* moiety, which exhibits 1,3-dipolar character, has been widely employed in the preparation of the 1,3-dithiolium carbene struc-

ture[3] and has proven to be a useful method for preparing carbene complexes of both early and late transition metals. Some of the latter type have been useful in providing interesting organic molecules, such as tetra-thiafulvalenes.[3b,c]

Recently, as a continuation of our studies on the use of unsaturated molecules in the synthesis of niobium organometallic complexes, the reactivity of carbon disulfide containing niobocene species toward several electrophilic synthons was examined.[4] The results

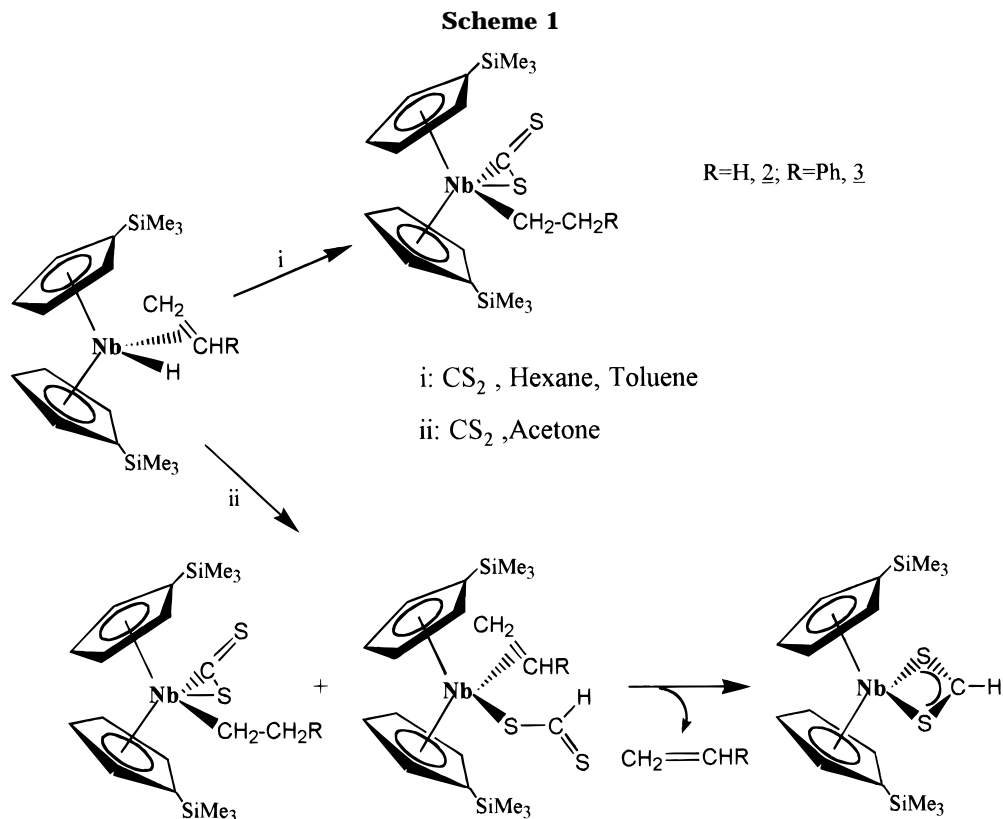[†] Universidad de Castilla-La Mancha.
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[§] Faculté de Sciences Gabriel.
[∥] Faculté des Sciences et des Techniques.
⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.
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(2) Some representative examples: (a) Fachinetti, G.; Del Nero, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1976**, 1046. (b) Fachinetti, G.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1612. (c) Moise, C.; Tirouflet, J. *J. Organomet. Chem.* **1980**, *197*, C23. (d) Okuda, J.; Herberich, G. E. *J. Organomet. Chem.* **1987**, *320*, C35. (e) Conan, F.; Sala-Pala, J.; Guerchais, J. E.; Li, J.; Hoffmann, R.; Mealli, C.; Mercier, R.; Toupet, L. *Organometallics* **1989**, *8*, 1929. (f) Conan, F.; Sala-Pala, J.; Guerchais, J. E.; Toupet, L. *Organometallics* **1990**, *9*, 59.
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Scheme 1

R=H, **2**; R=Ph, **3**

i: CS$_2$, Hexane, Toluene

ii: CS$_2$,Acetone

encouraged us to try other reactivity ways with the aim of collecting new data on the interactions of niobocene species with unsaturated molecules.[5] This paper will focus on the synthesis of new η^2-CS_2-*C,S*-containing alkylniobocene complexes, as well as the preparation of an extensive family of new (1,3-dithiol-2-ylidene)niobocene complexes via reactions with activated alkynes.

Results and Discussion

We have previously reported the preparation of a niobocene−hydride−styrene complex, Cp′$_2$Nb(H)(η^2-CH$_2$=CHPh), as well as an extensive study on the kinetics of the hydride−olefin insertion to give the alkyl derivative.[6] Pursuing this work, we recently prepared the analogous niobocene−hydride−ethylene species Cp′$_2$-Nb(H)(η^2-CH$_2$=CH$_2$) from the reaction of Cp′$_2$NbCl with 1 equiv of EtMgBr, and an exhaustive variable-temperature NMR study of the hydride−olefin insertion ⇌ β-elimination equilibrium was performed.[7]

We are now interested in studying the behavior of both of these hydride−olefin niobocene derivatives toward carbon disulfide. The reactions of Cp′$_2$Nb(H)-(η^2-CH$_2$=CH$_2$) and *endo*-Cp′$_2$Nb(H)(η^2-CH$_2$=CHPh), which were prepared in high yields from the interaction of Cp′$_2$NbCl with the appropriate Grignard reagents in
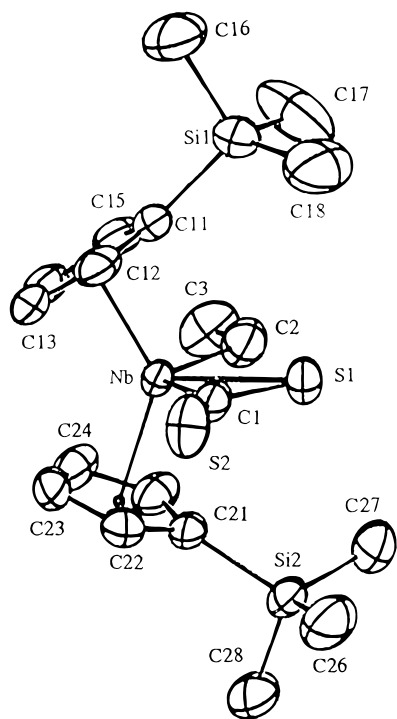
Scheme 2
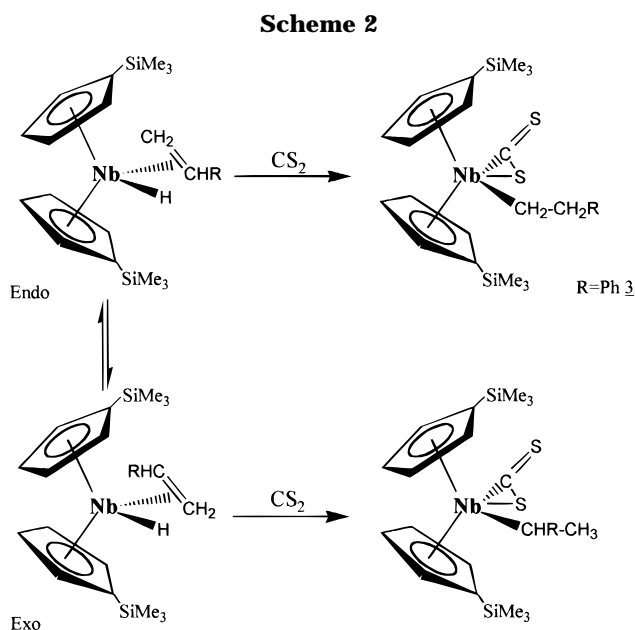
a 1:1 molar ratio, with CS$_2$ were shown to be dependent on the experimental reaction conditions. In fact, in an apolar solvent such as hexane or toluene, the alkyl−carbon disulfide complexes Cp′$_2$Nb(Et)(η^2-CS_2-*C,S*) (**2**) and Cp′$_2$Nb(CH$_2$CH$_2$Ph)(η^2-CS_2-*C,S*) (**3**) were exclusively formed (Scheme 1, route i).

The carbon disulfide promoted hydride−olefin insertion is the only process that occurs, and it gives rise exclusively to complexes **2** and **3**. However, in polar solvents such as acetone, the dithioformato derivative Cp′$_2$Nb(η^2-SC(H)S-*S,S*)[4] and free olefin are generated along with **2** and **3** (monitored by ^{1}H NMR) (Scheme 1, route ii). The (dithioformato)niobocene species results from the insertion of CS$_2$ into the Nb−H bond in the starting product to produce an η^1-dithioformato−olefin

(5) Some recent results: (a) Antiñolo, A.; Fajardo, M.; López-Mardomingo, C.; Martin-Villa, P.; Otero, A.; Kubicki, M. M.; Mourad, Y.; Mugnier, Y. *Organometallics* **1991**, *10*, 3435. (b) Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Martin-Villa, P.; Otero, A.; Kubicki, M. M.; Mugnier, Y.; El Krami, S.; Mourad, Y. *Organometallics* **1993**, *12*, 381. (c) Antiñolo, A.; Fajardo, M.; Gil-Sanz, R.; López-Mardomingo, C.; Otero, A.; Atmani, A.; Kubicki, M. M.; El Krami, S.; Mugnier, Y.; Mourad, Y. *Organometallics* **1994**, *13*, 1200. (d) Antiñolo, A.; Otero, A.; Fajardo, M.; Garcia-Yebra, C.; Gil-Sanz, R.; López-Mardomingo, C.; Martín, A.; Gómez-Sal, P. *Organometallics* **1994**, *13*, 4679.
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Figure 1. ORTEP view of **2**.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $(C_5H_4SiMe_3)_2Nb(Et)(\eta^2\text{-}CS_2)$

Nb−CP1[a]	2.126	Nb−C2	2.314(4)
Nb−CP2	2.112	C2−C3	1.518(6)
Nb−S1	2.520(1)	S1−C1	1.662(4)
Nb−C1	2.205(3)	S2−C1	1.632(3)
CP1−Nb−CP2	131.8	S1−C1−S2	136.7(2)
S1−Nb−C1	40.5(1)	Nb−C1−S2	143.3(2)
S1−Nb−C2	78.7(1)	Nb−C2−C3	121.3(3)
C1−Nb−C2	119.2(1)		

[a] CP denotes the geometrical centers of the C11−C15 and C21−C25 rings.

Scheme 3

intermediate, which was detected by ^{1}H NMR, followed by an elimination of olefin to give rise to a η^2-dithioformato ligand. This latter behavior has previously been found in the reaction of Cp′$_2$NbHL with CS$_2$.[4]

Interestingly, the addition of CS$_2$ to a mixture of both the endo and exo styrene isomers, generated by heating a solution of the pure endo isomer for several days, resulted in only complex **3** being isolated, a surprising result, since we would expect a mixture of two alkyl isomers to be formed. The CS$_2$-promoted insertion probably favors the transformation of the exo to the endo isomer because the primary alkyl-containing complex **3** would be the expected kinetic product on the basis of steric arguments.[8]

The structural characterization of the new alkyl−carbon disulfide derivatives was carried out by IR and NMR spectroscopy.

The IR spectra of complexes **2** and **3** show two characteristic bands at ca. 1130 and 630 cm^{-1}, which correspond to ν(C=S) and ν(C−S), respectively (see Experimental Section). In the ^{13}C NMR spectra there is a noteworthy resonance at ca. 310 ppm, which corresponds to the carbon atom of η^2-CS_2-C,S (see Experimental Section).

In order to gain more insight into the structure of carbon disulfide containing niobocenes, an X-ray crystal structure study of **2** was carried out. Its molecular structure is shown in Figure 1, and selected bond lengths and angles are set out in Table 1.
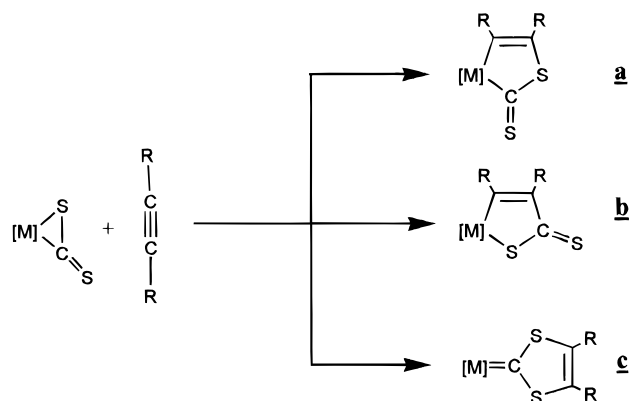
The molecule has a distorted-tetrahedral geometry characteristic of bent metallocenes.[9] The complex consists of a carbon disulfide ligand, η^2-CS_2-C,S, bonded to the Cp′$_2$NbEt unit in an exo configuration; the ethyl and carbon disulfide ligands occupy three coordination sites in the plane that bisects the Cp′ rings, as is generally observed in Cp$_2$NbX(η^2-L) complexes. The Nb, S1, C1,

C2, and C3 atoms are coplanar, all being within 0.02 Å of each other, while the S2 atom exhibits a slightly higher deviation (0.05 Å) from the best plane defined by the atoms mentioned above. The Nb−C2 bond length of 2.314(A) Å is essentially the same as the Nb−C distances observed in other niobocenes with ethyl (Cp$_2$-Nb(Et)(η^2-C$_2$H$_4$), 2.316(8) Å;[10] (Cp$_2$Nb(Et)(η^2-MeC≡CMe), 2.311(11) Å[11]) or allyl groups (Cp$_2$Nb(allyl)(η^2-CS$_2$-C,S), 2.316(8) Å[12]). It is, however, slightly shorter than the Nb−C(Me) distance of 2.234(8) Å found in the closely related Cp$_2$NbMe(η^2-CS$_2$-C,S) complex.[13] The Nb−H21 (2.66(4) Å) and Nb−H22 (2.69(4) Å) distances exclude any agostic Nb···H$_\alpha$ intramolecular interaction, observed by Nakamura et al. in the structure of Cp$_2$Nb(Et)(η^2-MeC≡CMe). Other metric parameters involving the Cp rings and the η^2-CS$_2$-C,S ligand are normal.

As was previously pointed out,[3] there has been extensive research on the interaction of coordinated carbon disulfide with activated alkynes and several studies have been published on this topic, which have indicated that the nature of the metal center and of the ancillary ligands determines whether 1,3-dithiol-2-ylidene or five-membered heterometallacyclic derivatives are formed (Scheme 3).

In order to extend the scope of this reactivity for carbon disulfide containing complexes of early transition metals,[3e] we have considered it appropriate to study the behavior of several niobocene complexes, namely Cp′$_2$-

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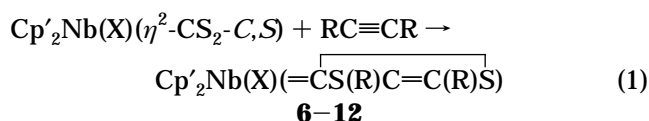
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NbCl($η^2$-CS$_2$-*C,S*) (**1**),[14] **2**, **3**, Cp$'_2$Nb(OC(O)H-*O*)($η^2$-CS$_2$-*C,S*) (**4**), and Cp$'_2$Nb(OC(O)CH$_3$-*O*)($η^2$-CS$_2$-*C,S*) (**5**),[15] toward activated alkynes.

Reactions of **1**−**3** with the activated alkynes hexafluorobut-2-yne ((F$_3$C)C≡C(CF$_3$)) and dimethyl and di(*tert*-butyl acetylene dicarboxylates ((MeOOC)C≡C(COOMe) and (ᵗBuOOC)C≡C(COOᵗBu)) under the appropriate reaction conditions, give rise to the corresponding 1,3-dithiacarbene derivatives (eq 1).

$$Cp'_2Nb(X)(η^2\text{-}CS_2\text{-}C,S) + RC≡CR \rightarrow$$

$$Cp'_2Nb(X)(=\overline{CS(R)C=C(R)S}) \qquad (1)$$
$$\textbf{6-12}$$

6, X = Cl, R = CF$_3$; **7**, X = Cl, R = COOMe; **8**, X = Cl, R = COOᵗBu; **9**, X = Et, R = COOMe; **10**, X = Et, R = COOᵗBu; **11**, X = CH$_2$CH$_2$Ph, R = COOMe; **12**, X = CH$_2$CH$_2$Ph, R = COOᵗBu

The carboxylate-containing niobocenes **4** and **5** react similarly with the activated acetylenes, giving rise to analogous 1,3-dithiocarbenes, namely Cp$'_2$Nb(OC(O)CY-*O*)($\overline{CS(R)C=C(R)S}$) (Y = H, R = COOMe (**13**), COOᵗBu (**14**); Y = CH$_3$, R = COOMe (**15**), COOᵗBu (**16**)). Attempts to reacts complexes **1**−**5** with various nonactivated alkynes were unsuccessful, indicating that the reaction is effective only with alkynes bearing electron-withdrawing groups.

A variable-temperature study of the reaction (monitored by ^{1}H NMR) did not result in the detection of any possible intermediates.

The various isolated 1,3-dithiol-2-ylidenes are quite stable, and no insertion products were observed upon treatment with an excess of activated alkynes, nor was any rearrangement to other species such as heterometallacyclics (see Scheme 3) detected upon heating. This is in contrast to previous work[3a] described for (1,3-dithiol-2-ylidene)iron complexes, Fe(=$\overline{CS(R)C=C(R)S}$)-(CO)$_2$L$_2$, where thermal isomerization to heterometallacyclics was observed.

Although we have not been able to detect intermediate species, the formation of the 1,3-dithiacarbenes may be explained by a rationale similar to that previously described for various vinyl-containing 1,3-dithiacarbene niobocenes[3e] (see Scheme 4, route *a*). The first step could correspond to an electrophilic attack of the acetylenic carbon atom on the S(exo) atom of CS$_2$ followed by nucleophilic attack of the other acetylenic carbon atom on the S bonded to the niobium atom, with attendant rupture of the Nb−S bond and the subsequent formation of a carbene function.

This proposal rules out the alternative formation of a heterometallacyclic derivative (Scheme 3, reaction *a*), since this would involve nucleophilic attack of the second acetylenic carbon atom on the niobium center (Scheme 4, route *b*) with the subsequent breaking of the

Scheme 4
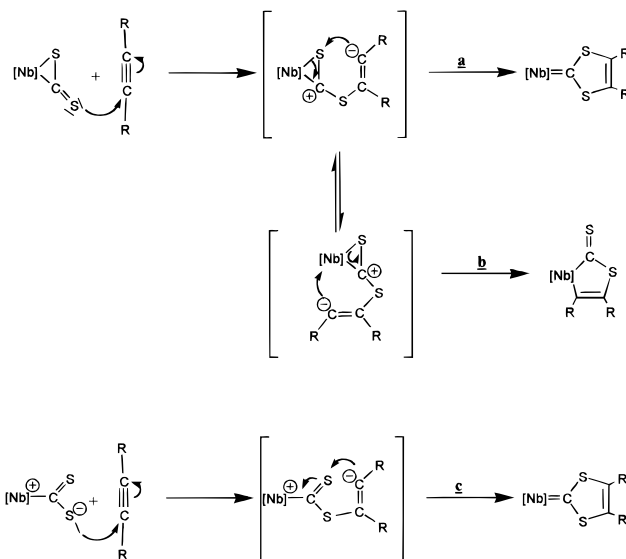
Nb−S bond, which is not a feasible step, as there is no available empty orbital in the niobium center.

We could alternatively consider an energetically more accessible reaction pathway starting from an end-on approach[16] of the (Nb−$η^2$-CS$_2$-*C,S*) resonance structure Nb$^+$−C(=S)S$^-$. Reaction with an activated alkyne would then proceed via a conventional 1,3-dipolar cycloaddition mechanism, [$_π$4s + $_π$2s] (see Scheme 4, route *c*).

The structural characterization of the various isolated 1,3-dithiocarbenes was determined from spectroscopic data. ^{13}C NMR was useful in the detection of the carbene function as the ^{13}C nucleus originating from the CS$_2$ ligand could be observed at low field (ca. 230 ppm), approximately corresponding to the ^{13}C chemical shift reported for a deshielded coordinated carbene carbon bonded to a metal.[17] Similar values were reported for related 1,3-dithiocarbenes.[3]

In addition, in all complexes the two groups of the olefinic carbons are equivalent (see Experimental Section), indicating that the 1,3-dithiocarbene is situated in a plane orthogonal to that containing the niobium atom and the chloride, alkyl, or carboxylate ligands and bisecting the Cp$'_2$Nb moiety. This structural situation was previously confirmed from a X-ray crystal structure obtained for the complex Cp$_2$Nb((CF$_3$)=CH(CF$_3$))(=$\overline{CS}$-$\overline{(CF_3)C=(CF_3)S}$).[3e] ^{13}C resonances for the olefinic carbon atoms appear at ca. 140 ppm, together with those corresponding to the different coligands, namely alkyl or carboxylate (see Experimental Section).

Experimental Section

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300 and Varian Gemini FT-200 spectrometers and referenced to the residual deuterated solvent or CFCl$_3$. The following compounds were prepared as described earlier: Cp'$_2$NbCl(η^2-CS$_2$-*C,S*),[14] Cp'$_2$Nb(H)(η^2-PhCH=CH$_2$),[7] Cp'$_2$Nb(OC(O)H-*O*)(η^2-CS$_2$-*C,S*) and Cp'$_2$Nb(OC(O)CH$_3$-*O*)(η^2-CS$_2$-*C,S*).[15] (MeOOC)C≡C(COOMe), ('BuOOC)C≡C(COO'Bu), (CF$_3$)C≡C(CF$_3$), and CS$_2$ were used as purchased.

[Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$X(η^2-CS$_2$-*C,S*)] (X = CH$_2$CH$_3$, 2; X = CH$_2$CH$_2$Ph, 3). To a solution of Cp'$_2$NbH(η^2-CH$_2$CH$_2$) (150 mg, 0.44 mmol) in hexane was added CS$_2$ (0.03 mL, 0.44 mmol), and the reaction mixture was heated at 60 °C for 1 h, forming a pink precipitate, which was filtered off and washed with cold hexane. The resulting solid was recrystallized from a mixture of dichloromethane (CH$_2$Cl$_2$) and hexane to give compound **2**. Complex **3** was prepared in a similar way.

2: IR (Nujol) ν(C=S) 1133, ν(C–S) 633 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.11 (s, 18H, SiMe$_3$), 1.66 (t, 3H, J = 7.5 Hz, CH$_2$CH$_3$), 2.25 (q, 2H, J = 7.5 Hz, CH$_2$CH$_3$), 5.32 (2H), 5.90 (2H), 6.56 (4H) (each a complex signal, C$_5$H$_4$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ −1.20 (SiMe$_3$), 14.83 (CH$_2$CH$_3$), 20.00 (CH$_2$CH$_3$), 99.98, 102.84, 115.80, 120.85 (C$^{2-5}$, exact assignment not possible), 117.42 (C^1), 317.43 (C=S). Anal. Found (calcd) for C$_{19}$H$_{31}$NbSi$_2$S$_2$: C, 48.69 (48.28); H, 6.56 (6.61). Yield: 90%.

3: IR (Nujol) ν(C=S) 1133, ν(C–S) 632 cm^{-1}; ^{1}H NMR (CD$_3$-COCD$_3$) δ 0.06 (s, 18H, SiMe$_3$), 2.55 (m, 2H, CH$_2$CH$_2$Ph), 3.10 (m, 2H, CH$_2$CH$_2$Ph), 5.76 (2H), 5.83 (2H), 6.16 (4H), 6.27 (2H), (each a complex signal, C$_5$H$_4$), 7.2–7.4 (m, 5H, Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ −1.03 (SiMe$_3$), 24.78 (CH$_2$CH$_2$Ph), 42.28 (CH$_2$CH$_2$Ph) 100.94, 103.61, 116.16, 120.25 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 116.96 (C^1, C$_5$H$_4$), 125.28, 127.66, 128.45 (C, Ph), 147.56 (C$_{ipso}$ of phenyl group), 315.33 (C=S). Anal. Found (calcd) for C$_{19}$H$_{31}$NbSi$_2$S$_2$: C, 48.69 (48.28); H, 6.56 (6.61). Yield: 90%.

[Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$X(=CS(R)C=C(R)S) (X = Cl, R = CF$_3$ (6), COOMe (7), COO'Bu (8); X = CH$_2$CH$_3$, R = COOMe (9), COO'Bu (10); X = CH$_2$CH$_2$Ph, R = COOMe (11), COO'Bu (12)) and [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(OC(O)CY-*O*)-(=CS(R)C=C(R)S) (Y = H, R = COOMe (13), COO'Bu (14); Y = CH$_3$, R = COOMe (15), COO'Bu (16)). To a solution of Cp'$_2$NbCl(η^2-CS$_2$-*C,S*) (**1**; 200 mg, 0.46 mmol) in THF (50 mL) was added 0.06 mL (0.46 mmol) of MeOOCC≡CCOOMe at room temperature. The initially orange solution slowly become brown. After 30 min the solvent was removed under vacuum and the resulting oily product was washed with hexane (20 mL) to give a red-brown oily material of complex **7**.

All the 1,3-dithiacarbene compounds were synthesized in a similar way and were isolated as oily materials, except in the case of the addition of hexafluorobut-2-yne, which was condensed over the frozen solution initially at −170 °C and the reaction mixture warmed to room temperature.

6: ^{1}H NMR (C$_6$D$_6$) δ 0.07 (s, 18H, SiMe$_3$), 5.57 (2H), 4.45 (4H), 5.02 (each a complex signal, C$_5$H$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.02 (SiMe$_3$), 108.75, 109.33, 110.81, 113.07 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 115.75 (C^1, C$_5$H$_4$), 120.00 (q, J_{CF} = 271.5 Hz, CF$_3$), C=C not observed, 228 (C=Nb); ^{19}F NMR (C$_6$D$_6$) δ −56.84 (CF$_3$).

7: ^{1}H NMR (C$_6$D$_6$) δ 0.28 (s, 18H, SiMe$_3$), 3.27 (s, 6H, COOMe), 5.55 (2H), 5.66 (2H), 6.14 (2H), 6.38 (2H) (each a complex signal, C$_5$H$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ −0.42 (SiMe$_3$), 51.89 (COOMe), 107.55, 108.83, 109.41, 112.57 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 113.33 (C^1, C$_5$H$_4$), 143.88 (C=C), 159.14 (COOMe), 238.66 (C=Nb).

8: ^{1}H NMR (C$_6$D$_6$) δ 0.09 (s, 18H, SiMe$_3$), 5.16 (2H), 5.50 (2H), 5.64 (4H) (each a complex signal, C$_5$H$_4$), 1.36 (s, 18H, COO'Bu); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.32 (SiMe$_3$), 27.99 (COOC-(CH$_3$)$_3$), 84.05 (COOC(CH$_3$)$_3$), 108.26, 109.65, 109.85, 112.95 (C$^{2-5}$; exact assignment not possible, C$_5$H$_4$), 113.35 (C^1, C$_5$H$_4$), 143.53 (C=C), 158.59 (COOC(CH$_3$)$_3$), 241.56 (C=Nb).

9: ^{1}H NMR (C$_6$D$_6$) δ 0.04 (s, 18H, SiMe$_3$), 0.81 (q, 2H, J = 7.5 Hz, CH$_2$CH$_3$), 1.48 (t, 3H, J = 10 Hz, CH$_2$CH$_3$), 3.27 (s,

mol formula	C$_{19}$H$_{31}$NbS$_2$Si$_2$
fw	472.66
cryst syst	triclinic
space group	P$\bar{1}$ (No. 2)
cell dimens	
a, Å	7.990(1)
b, Å	10.610(1)
c, Å	15.266(2)
α, deg	77.07(1)
β, deg	79.59(1)
γ, deg	66.93(1)
V, Å^3	1154.2
Z	2
ρ_{calc}, g cm^{-3}	1.360
F(000)	492
radiation, Å	λ(Mo Kα) = 0.710 73
scan type	ω−2θ
scan speed, deg min^{-1}	1.5−8.3
scan width, deg	$\Delta\omega$ = 0.8 + 0.347 tan θ
rflns measd	h, 0−9, k, −13 to +13, l, −19 to +19
θ range, deg	2−25
linear abs, μ, cm^{-1}	7.752
no. of rflns measd	5006
temp, K	296(1)
decay, %	−2.8, cor
cutoff for obsd data	$I \geq 3\sigma(I)$
no. of unique obsd data (NO)	3160
no. of variables (NV)	217
R(F)	0.028
R$_w$(F)	0.030
p in $w^{-1} = [\sigma^2(I) + (pF_o^2)^2]^{1/2}$	0.04
GOF	0.581
ρ_{max}/ρ_{min} (DF)	+0.28/−0.14

6H, COOMe), 5.07 (2H), 5.26 (4H), 5.53 (2H) (each a complex signal, C$_5$H$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.39 (SiMe$_3$), 21.86 (CH$_2$-CH$_3$), 14.98 (CH$_2$CH$_3$), 52.23 (COOCH$_3$), 104.78, 107.20, 109.48, 111.92 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 110.35 (C^1, C$_5$H$_4$), 143.53 (C=C), 159.59 (COOCH$_3$), 225.56 (C=Nb).

10: ^{1}H NMR (C$_6$D$_6$) δ 0.04 (s, 18H, SiMe$_3$), 1.48 (t, 3H, J = 7.6 Hz, CH$_2$CH$_3$), 0.81 (q, 2H, J = 10 Hz, CH$_2$CH$_3$), 1.35 (s, 18H, COOC(CH$_3$)$_3$), 5.05 (2H), 5.26 (4H), 5.52 (2H) (each a complex signal, C$_5$H$_4$); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.47 (SiMe$_3$), 27.94 (COOC(CH$_3$)$_3$), 21.13 (CH$_2$CH$_3$), 15.04 (CH$_2$CH$_3$), 82.56 (COOC(CH$_3$)$_3$), 104.77, 107.32, 109.35, 111.65 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 102.82 (C^1, C$_5$H$_4$), 143.24 (C=C), 151.09 (COOC(CH$_3$)$_3$), 227.38 (C=Nb).

11: ^{1}H NMR (C$_6$D$_6$) δ 0.23 (s, 18H, SiMe$_3$), 0.81 (m, 2H, CH$_2$CH$_2$Ph), 2.61 (m, 2H, CH$_2$CH$_2$Ph), 3.80 (s, 6H, COOMe), 5.41 (2H), 5.47 (4H), 5.75 (2H) (each a complex signal, C$_5$H$_4$), 7.09−7.33 (m, 5H, Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 0.18 (SiMe$_3$), 25.34 (CH$_2$CH$_2$Ph), 42.57 (CH$_2$CH$_2$Ph), 52.61 (COOCH$_3$), 104.61, 107.58, 108.89, 110.58 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 104.61 (C^1, C$_5$H$_4$), 142.28 (C=C), 151.89 (COOCH$_3$), 225.06 (C=Nb).

12: ^{1}H NMR (C$_6$D$_6$) δ 0.04 (s, 18H, SiMe$_3$), 1.01 (m, 2H, CH$_2$CH$_2$Ph), 1.35 (s, 18H, COOC(CH$_3$)$_3$), 2.72 (m, 2H, CH$_2$CH$_2$-Ph), 5.12 (2H), 5.30 (4H), 5.54 (2H) (each a complex signal, C$_5$H$_4$), 7.29−7.43 (m, 5H, Ph); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ 0.46 (SiMe$_3$), 25.64 (CH$_2$CH$_2$Ph), 27.66 (COOC(CH$_{33}$), 43.62 (CH$_2$CCH$_2$Ph), 82.68 (COOC(CH$_3$)$_3$), 104.67, 107.41, 109.53, 111.55 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 103.71 (C^1), 143.36 (C=C), 151.07 (COOC(CH$_3$)$_3$), 228.84 (C=Nb).

13: ^{1}H NMR (C$_6$D$_6$) δ 0.06 (s, 18H, SiMe$_3$), 3.29 (s, 6H, COOMe), 5.16 (2H), 5.67 (2H), 5.70 (2H), 5.84 (2H) (each a complex signal, C$_5$H$_4$), 8.66 (s, 1H, OOC-H); ^{13}C{^{1}H} NMR (C$_6$D$_6$) δ −0.02 (SiMe$_3$), 52.57 (COOCH$_3$), 109.57, 110.91, 111.63, 111.75 (C$^{2-5}$, exact assignment not possible, C$_5$H$_4$), 118.01 (C^1, C$_5$H$_4$), 143.53 (C=C), 159.77 (COOCH$_3$), 168.59 (OOC−H), 237.5 (C=Nb).

Table 3. Positional Parameters for
$(C_5H_4SiMe_3)_2Nb(Et)(\eta^2\text{-}CS_2)^a$

atom	x	y	z	B (Å²)
Nb	0.3337(4)	0.09257(3)	0.71191(2)	2.970(5)
CP1	0.3669	−0.1199	0.7279	
CP2	0.1821	0.2710	0.6252	
S1	0.5817(1)	0.13039(8)	0.77115(6)	3.90(2)
S2	0.7833(1)	0.0499(1)	0.58954(7)	4.80(2)
Si1	0.6164(1)	−0.2445(1)	0.88106(7)	4.20(2)
Si2	0.3035(1)	0.48717(9)	0.67264(7)	3.94(2)
C1	0.6166(4)	0.0831(3)	0.6707(2)	3.39(6)
C2	0.1941(5)	0.1465(4)	0.8524(3)	4.87(9)
C3	−0.0005(6)	0.1539(5)	0.8840(3)	6.7(1)
C11	0.4664(4)	−0.1538(4)	0.7871(2)	3.30(7)
C12	0.5194(5)	−0.1472(3)	0.6934(2)	4.48(9)
C13	0.3620(6)	−0.1030(3)	0.6486(3)	6.19(9)
C14	0.2130(5)	−0.0825(3)	0.7129(3)	5.96(9)
C15	0.2737(4)	−0.1132(3)	0.7973(3)	4.55(9)
C16	0.6869(7)	−0.4321(4)	0.8785(4)	8.4(2)
C17	0.4850(8)	−0.2061(7)	0.9895(4)	9.9(2)
C18	0.8245(5)	−0.2032(5)	0.8670(4)	8.1(1)
C21	0.2441(4)	0.3432(3)	0.6499(2)	3.31(7)
C22	0.3181(5)	0.2676(3)	0.5775(2)	4.10(8)
C23	0.2052(5)	0.1981(3)	0.5717(3)	5.38(8)
C24	0.0597(5)	0.2282(4)	0.6399(3)	5.63(9)
C25	0.0833(4)	0.3181(3)	0.6869(3)	4.43(9)
C26	0.5429(5)	0.4682(4)	0.6297(3)	6.1(1)
C27	0.2676(5)	0.4975(4)	0.7943(3)	5.6(1)
C28	0.1391(5)	0.6466(4)	0.6111(3)	6.1(1)

^{a} CP denotes the geometrical centers of the C11−C15 and C21−C25 rings. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter, defined as $^4/_3$ $[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\,(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

14: ¹H (C₆D₆) δ 0.05 (s, 18H, Si**Me₃**), 1.36 (s, 18H, COOC(**CH₃**)₃), 5.24 (2H), 5.68 (2H), 5.77 (2H), 5.89 (2H) (each a complex signal, C₅**H₄**), 8.57 (s, 1H, OOC−**H**); ¹³C{¹H} NMR (C₆D₆) δ 0.20 (Si**Me₃**), 27.63 (COOC(**CH₃**)₃), 84.56 (COO**C**(CH₃)₃), 109.57, 110.91, 111.13, 111.95 (**C²⁻⁵**, exact assignment not possible, C₅H₄), 117.36 (**C¹**), 144.23 (**C=C**), 159.20 (**C**OOC(CH₃)₃), 168.50 (OO**C**−H); 238.5 (**C=Nb**).

15: ¹H NMR (CDCl₃) δ 0.15 (s, 18H, Si**Me₃**), 1.77 (s, 3H, **CH₃**COO), 3.79 (s, 6H, COO**Me**), 5.60 (2H), 5.81 (2H), 6.07 (2H), 6.20 (2H) (each a complex signal, C₅**H₄**); ¹³C{¹H} NMR (CDCl₃) δ 0.04 (Si**Me₃**), 23.59 (**CH₃**COO), 52.85 (COO**C**H₃), 109.37, 111.41, 111.73, 112.95 (**C²⁻⁵**, exact assignment not

possible, C₅H₄), 111.79 (**C¹**, C₅H₄), 143.18 (**C=C**), 159.76 (**C**OOCH₃), 178.05 (OO**C**−CH₃), 237.5 (**C=Nb**).

16: ¹H NMR (CDCl₃) δ 0.14 (s, 18H, Si**Me₃**), 1.47 (s, 18H, COOC(**CH₃**)₃), 1.77 (s, 3H, **CH₃**COO), 5.56 (2H), 5.74 (2H), 6.04 (2H), 6.19 (2H) (each a complex signal, C₅**H₄**); ¹³C{¹H} NMR (CDCl₃) δ −0.14 (Si**Me₃**), 25.22 (**CH₃**COO), 27.70 (COOC-(**CH₃**)₃), 82.85 (COO**C**(CH₃)₃), 109.03, 110.94, 111.82, 112.09 (**C²⁻⁵**, exact assignment not possible, C₅H₄), 111.64 (**C¹**, C₅H₄), 143.97 (**C=C**), 158.07 (**C**OOC(CH₃)₃), 177.85 (OO**C**CH₃), 240.0 (**C=Nb**).

Crystal Structure Analysis of 2. An irregularly shaped red crystal having the approximate dimensions 0.15 × 0.10 × 0.10 mm was used for the unit cell determination and data collection carried out at 296(1) K on an Enraf-Nonius CAD4 diffractometer with Mo Kα radiation (λ = 0.711 073 Å). The pertinent crystallographic data are given in Table 2. All calculations were carried out by use of the Molen package with neutral-atom scattering factors taken from the usual source.[18]

Intensities were corrected for Lorentz and polarization effects. Because of the low value of the linear absorption coefficient, no absorption correction was made. All non-hydrogen atoms could be easily located from three-dimensional Patterson and subsequent difference Fourier maps. These atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the ethyl ligand bound to the niobium atom were localized on the difference Fourier map and refined in an isotropic model. Other hydrogen atoms were placed in calculated positions and included in the structure in a riding model with B_{iso} fixed at $1.3B_{eq}$ for the carbon atoms bearing them. Final positional parameters of non-hydrogen atoms are given in Table 3.

Supporting Information Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates, bond distances and angles, and least-squares planes (4 pages). Ordering information is given on any current masthead page.

OM950916S

(18) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974.