Studies of the reactivity towards insertion and electrophilic processes of Nb–H and Nb(η^2-CS$_2$) moieties of bis(trimethylsilylcyclopentadienyl)niobium complexes

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Abstract

The interaction of MeI with the complexes [Nb(η^5-C$_5$H$_4$SiMe$_3$)XCS$_2$–C,S] (X = Cl **1**, X = Br **2**) affords the cationic complexes containing a methyldithiocarboxylate group, [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$XC(S)SMe–C,S)]I (X = Cl **3**, X = Br **4**) as the result of the electrophilic attack of MeI in the sulfur (*exo*) atom of the coordinated CS$_2$. In contrast, the trihydride [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$H$_3$] **5** interact under mild conditions in THF, with phosphites giving rise to new hydrideniobium(III) complexes, [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$HL] (L = P(OMe)$_3$ **6**, P(OEt)$_3$, **7**, P(OPh)$_3$ **8**). Complexes Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$HL undergo an insertion of CS$_2$ into the niobium–hydrogen bond to give products, the nature of which are highly dependent on L. With L = CO [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$S(S)CH–S)(CO)] **10** is obtained, whereas [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$(SCHSSS)] **11** with an η^2-dithioformate is the product of similar reactions for **6**, **7** and **8**. Finally, using several electrophile synthons of Group 11 metals, we have prepared two families of early-late heterobimetallic complexes. Compound **1** reacts, through the sulfur (*exo*) atom of the CS$_2$, with [MPPh$_3$]PF$_6$ to give cationic heterobimetallic complexes [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl(μ-CS$_2$)(C(S)S-M(PPh$_3$))][PF$_6$] (M = Cu **12**, M = Ag **13**, M = Au **14**). In a similar way, **6–8** react with [AuPPh$_3$][PF$_6$] to give the species containing a hydride bridge [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$L(μ-H)(AuPPh$_3$)][PF$_6$] (L = P(OMe)$_3$ **15**, L = P(OEt)$_3$ **16**, L = P(OPh)$_3$ **17**). All the complexes described have been characterized using IR and NMR techniques.

Key words: Niobium; Cyclopentadienyl complexes; CS$_2$ complexes; Insertion; Hydrides

1. Introduction

After the preparation of the first carbon disulfide transition metal complex [1], an extensive chemistry of the interaction of CS$_2$ with several transition metal substrates was discovered [2]. However, the scope of this chemistry for metallocene of early group metals [3] is less developed than for complexes of late group metals. In recent years we have focused our attention on the preparation and reactivity of niobocene complexes containing heterocumulenes, such as ketene and ketenimine [4]. Following this, we are now interested in exploring the reactivity of carbon disulfide niobocene complexes, because these and related species may be models for the metal-promoted activation of carbon dioxide, a matter of a great interest [5].

A rich chemistry of hydride complexes has developed however, because of their role in several stoichiometric and catalytic processes [6]. We have previously studied the behaviour of non-classical trihydrides [Nb(η^5-C$_5$H$_{5-n}$(SiMe$_3$)$_n$)$_2$H$_3$] towards π-acids and Lewis acids [7].

Here we describe the reactivity of hydride and carbon disulfide niobocene complexes towards insertion and electrophilic processes.

2. Results and discussion

First we studied the reactivity of **1** and **2** towards alkylation with several RX reagents. The reaction of **1**

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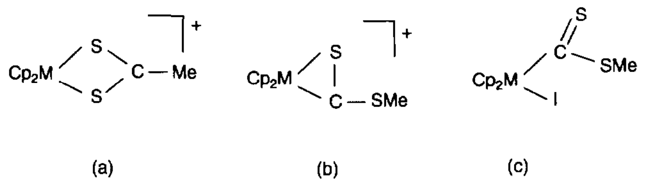


Scheme 1.

and **2** with MeI gives the corresponding methyldithiocarboxylate in accordance with eq. 1:

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{X(CS_2}\text{-}C,S)] + \mathrm{MeI(excess)} \longrightarrow [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{XC(S)SMe}\text{-}C,S]^+\mathrm{I}^- \quad (1)$$

X = Cl **3**
X = Br **4**

The complexes have been isolated as yellow air-stable crystalline solids, and they were characterized by analysis (see Experimental details).

The formation of these complexes must be considered as the result of electrophilic attack of MeI on the nucleophilic S(*exo*) atom of the coordinated CS$_2$ (see Scheme I), as has been previously published for vanadocene and other niobocene derivatives [3b,8].

A similar reaction using benzyl bromide (BzBr) or isopropyl bromide (i-PrBr) with **1** gives a mixture (1 : 1) of [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Cl$_2$] and [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$Br$_2$]. In our experimental conditions the species resulting from electrophilic attack decomposes, probably through disproportionation and rearrangement, to give a mixture of both dihalides.

Compounds **3** and **4** have been characterized spectroscopically. Their IR spectra show two characteristic bands at ca. 1130 and 630 cm^{-1} which correspond to the ν(C=S) and ν(C-S), respectively of a bidentate dithiocarboxylate [3b]. The NMR data (^{1}H and ^{13}C) (see Experimental detail) are consistent with this structure (b) (see Scheme 1). ^{13}C NMR spectra show resonances at δ 304 ppm (complex **3**) and δ 286 ppm (complex **4**) which correspond to the carbon atom of the *C*(S)SMe moiety.

In order to study these insertion processes of CS$_2$ into a Nb-H bond, we synthesised new hybride niobocene complexes, [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$HL] by using [Nb(η^5C$_5$H$_4$SiMe$_3$)$_2$H$_3$] **5**, as starting material [9].

The syntheses of several families of hydride niobocene, [Nb(η^5-C$_5$H$_5$)$_2$HL] (L = π-acid ligand) by the treatment of [Nb(η^5-C$_5$H$_5$)$_2$H$_3$] with the corresponding π-acid have been described [10]. However, these processes are not facile because drastic conditions (reflux in toluene during several days) for the elimination of H$_2$ are necessary. Moreover, frequently the substitution is not complete so that the [Nb(η^5-C$_5$H$_5$)$_2$HL] is impure. However, our trihydride complex **5** reacts easily with π-acids giving rise quantitatively to several hydride complexes. The interaction of **5** with several phosphites has allowed us to prepare three new 18-electron species [Nb(η^5-C$_5$H$_4$SiMe$_3$)$_2$-HL] in accordance with eqn. 2.

$$[\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{H_3}] + \mathrm{L} \xrightarrow{\mathrm{THF}} [\mathrm{Nb}(\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{HL}] + \mathrm{H_2} \quad (2)$$

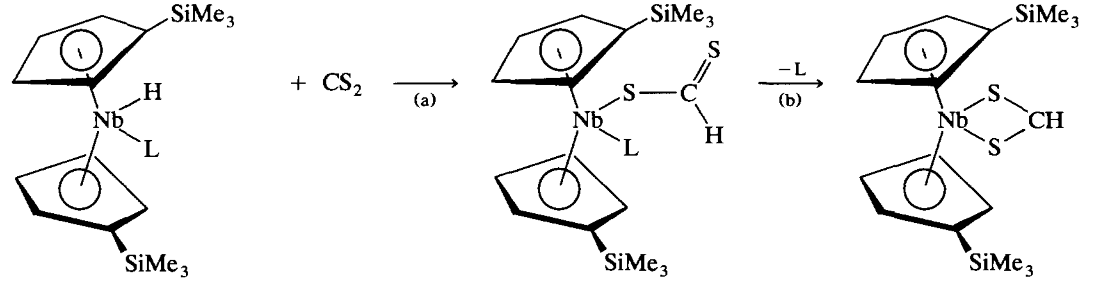
L = P(OMe)$_3$ **6**; L = P(OEt)$_3$ **7**; L = P(OPh)$_3$ **8**

These have been isolated as air-sensitive oily materials, and characterized spectroscopically (see Experimental details).

The IR spectra of **6**–**8** display a characteristic band at *ca.* 1700 cm^{-1} that corresponds to the ν(Nb–H). The presence of a terminal hydride is confirmed by a resonance in the ^{1}H NMR spectra at high-field shift values, δ −7.61 (J_{PH} = 33.6 Hz), δ −8.39 (J_{PH} = 33.6 Hz) and δ −7.17 (J_{PH} = 35.2 Hz) ppm, for complexes **6**, **7** and **8**, respectively.

The reactions with CS$_2$ evolves at room temperature with the expected insertion to give a dithioformate S(S)CH ligand, in accordance with eqn. 3.

We observed different behaviour for **9**, which reacts with carbon disulfide to give complex **10** (step (a)) containing both a η^1-dithioformate and a carbonyl [11]. All attempts to remove the CO, for instance by heating in toluene under reflux for several hours, were unsuccessful. The hydride phosphite complexes react, step (a) and (b), with carbon disulfide to yield complex **11**,

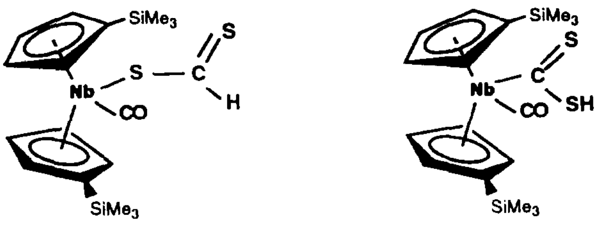


(3)

L = P(OMe)$_3$ **6**; P(OEt)$_3$ **7**
P(OPh)$_3$ **8**; CO **9**

L = CO **10**

11



(A) (B)

Scheme 2.

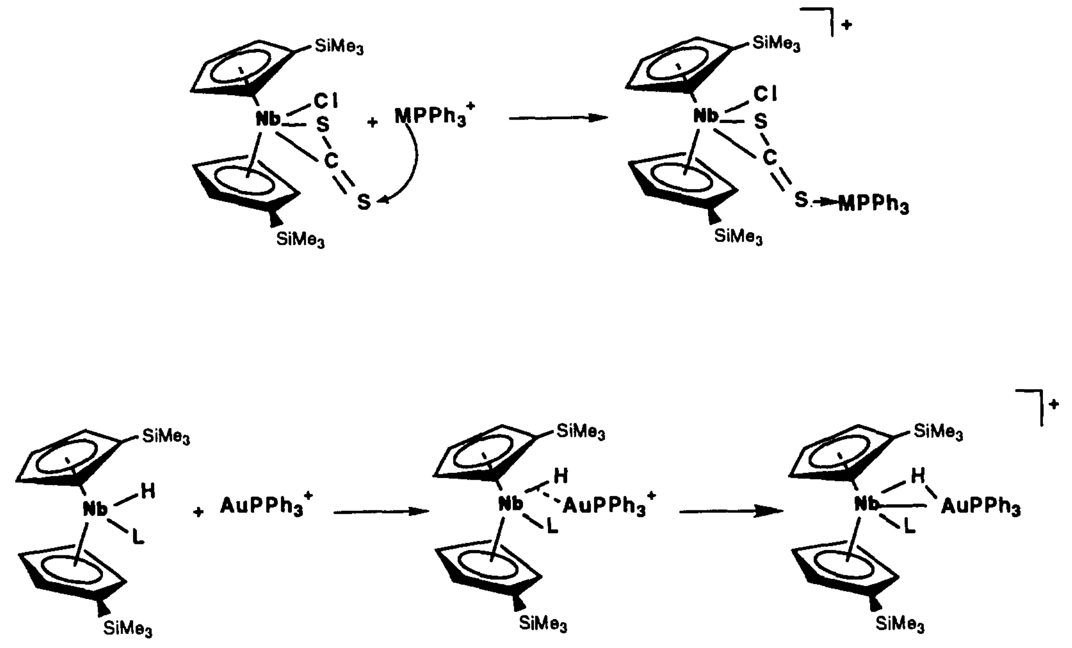
which contains an η^2-dithioformate. In the last case, an initial η^1-dithioformate complex probably forms, with loss of phosphite (step (b)), then giving the final η^2-dithioformate complex **11**. We have been unable to stop this reaction at step (a). The second step (b) corresponds to a substitution reaction of the π-acid ligand by the non-coordinated sulfur atom. The differences of behaviour in our reactions can be ascribed to the different strengths of the niobium–carbonyl and niobium–phosphite bonds. A strong interaction, Nb–CO in several carbonyl niobocene complexes has been described [12] and could explain the non-replacement of CO.

The elimination of phosphites (step (b)) to give the η^2-dithioformate ligand is, however, unusual in this type of insertion process. Similar processes with cumulenes such as isocyanate, ketene, and ketenimine have been described [13], but never the elimination a π-acid ligand. The new dithioformate niobocene derivatives have been isolated as air-sensitive solids and were characterized both by analysis and spectroscopically (see Experimental details).

The IR spectrum of **10** shows two bands at 1000 cm^{-1} and 1927 cm^{-1}, which correspond to ν(C=S) and ν(CO), respectively (see Scheme 2). IR data as well as NMR data (*vide infra*) support the (A) structure. There is no band assignable to the ν(S–H) in the IR spectrum. The most significant NMR data for **10** are the resonances at δ 11.67 ppm for the dithioformate in the ^{1}H spectrum and the resonances for the carbon atoms of carbonyl and dithioformate, which appear at δ 240.2 and δ 148.6 ppm, respectively.

^{1}H NMR spectrum of **11** shows a resonance at δ 4.17 ppm which has been assigned to the hydrogen atom of an η^2-dithioformate. In addition, the ^{13}C NMR spectrum displays the resonance of the dithioformate carbon atom at δ 120 ppm, characteristic of a tertiary carbon (attached to a hydrogen atom), and confirmed by a DEPT experiment and a ^{1}H–^{13}C heteronuclear correlation study. However, the chemical shift value in the ^{1}H NMR spectrum is very unusual, because values for other dithioformate complexes are higher [14] although some cases have been reported [15] showing them much lower. We have no explanation for this surprising value, and studies on the reactivity of the complex are in progress.

Considerable interest has been shown in early-late heterobimetallic [16] compounds. We have explored



Scheme 3.

the reactivity of **1**, **6**, **7** and **8** toward Lewis acid fragments of the Group 11 metals, $MPPh_3^+$ (M = Cu, Ag, or Au) giving several new heterobimetallic complexes, in accordance with eqns. 4 and 5.

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2Cl(CS_2)] + [MPPh_3][PF_6] \longrightarrow$$

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2(\mu\text{-}CS_2)(C(S)S\text{-}MPPh_3)][PF_6] \quad (4)$$

M = Cu **12**; M = Ag **13**; M = Au **14**

$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2HL] + [AuPPh_3][PF_6] \longrightarrow$$

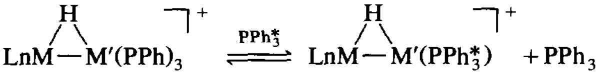
$$[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2L(\mu\text{-}H)(AuPPh_3)][PF_6] \quad (5)$$

L = P(OMe)₃ **15**; L = P(OEt)₃ **16**; L = P(OPh)₃ **17**

All complexes have been isolated as moderately air-stable, crystalline solids and they have been characterized by analysis (see Experimental details). The formation of these complexes can be considered as the result of electrophilic attack of the Lewis acid either on the sulfur (*exo*) atom of **1** of the niobium–hydrogen bond of **6–8** (see Scheme 3).

Similar behaviour of coordinated CS_2 in related complexes has been described previously [8a]. The niobium–hydrogen–gold interaction in **15–17** can be considered as a three-centre two-electron bond [17]. We have also proposed an additional niobium–gold interaction in these complexes. Related heterobimetallics are known [18]. The isolated heterobimetallic complexes have been characterized spectroscopically. Complexes **12–14** show ν(C–S) at *ca.* 600 cm^{-1} in IR spectra and a resonance at *ca.* δ 300 ppm in the ^{13}C NMR spectra for *C*(S)S.

The resonance of hydride in the ^1H NMR spectra for **15–17** appears at *ca.* −6.0 ppm as doublet duets with a phosphorus atom. The coupling is with the phosphine, because a small amount of free phosphine removes it, probably as a consequence of the following fast interchange process. The values found for J_{PH}



$$\left[LnM(\mu\text{-}H)M'(PPh_3)\right]^+ \underset{}{\overset{PPh_3^*}{\rightleftharpoons}} \left[LnM(\mu\text{-}H)M'(PPh_3^*)\right]^+ + PPh_3 \quad (6)$$

(around 60 Hz) are also consistent with data previously described [19] in complexes where a hydride acts as bridge to the M–$AuPPh_3$ bond, and consequently support the proposal of an additional Nb–Au bond in our complexes. We have previously observed similar electron donation from niobium to gold to form the metal–metal bond [18e,f].

3. Experimental details

All reactions were performed using standard Schlenk techniques under dry, oxygen-free dinitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Elemental analyses were performed with a Perkin-Elmer CHN 2400 microanalyser. NMR spectra were recorded on an Unity Varian FT 300 spectrometer, and referenced to the residual deuteriated solvent. The two-dimensional NMR spectrum and the DEPT experiment were carried out using standard Varian FT software, and processed using an IPC-Sun computer. IR spectra were recorded as Nujol mulls between CsI plates in the region 4000–200 cm^{-1} with a Perkin-Elmer PE 882 IR spectrometer.

Complexes $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2X(CS_2)]$ (X = Cl or Br), $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H_3]$ and $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2H(CO)]$ were prepared as reported previously [9,20].

3.1. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2XC(S)SMe]I$ (X = Cl 3; X = Br 4)

To a solution of **1** (300 mg, 0.63 mmol) in 40 ml of toluene was added MeI (3.15 mmol). The mixture was stirred for 0.5 h at 40°C and a yellow precipitate was formed. The suspension was filtered and the remaining solid was recrystallized by dissolving it in dichloromethane and placing a layer of diethylether above it in Schlenk tube. Yellow crystals began to grow within a few days. Complex **4** was prepared similarly. **3**: IR (Nujol) ν(C=S) 1130 cm^{-1}. ν(C,S) 628 cm^{-1} Λ_M = 130.6 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 0.13 (s, 18H, Si*Me*₃); 3.29 (s, 3H, C(S)S*Me*); 6.18 (2H); 6.66 (2H); 6.77 (2H); 6.86 (2H) (each a complex signal, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.68 (Si*Me*₃); 32.6 (C(S)S*Me*); 125.3 (C^1); 107.1, 121.3, 124.2, 127.2 (C^2, C^3, C^4, C^5; exact assignment not possible); 304.0 (*C*(S)SMe). Anal. Found (Calc. for $C_{18}H_{29}ClINbS_2Si_2$): C, 34.68(34.70); H, 4.60(4.66)%. Yield: 95%. **4**: IR (Nujol) ν(C=S) 1133 cm^{-1}; ν(C–S) 630 cm^{-1}. Λ_M = 102.9 Ω^{-1} cm^2 mol^{-1}. ^1H NMR ($CDCl_3$): δ 0.19 (s, 18H, Si*Me*₃); 3.26 (s, 3H, C(S)S*Me*); 6.30 (2H); 6.67 (2H); 6.88 (4H) (each a complex signal C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.88 (Si*Me*₃); 30.5 (C(S)S*Me*); 121.1 (C^1); 105.6, 110.9, 132.2, 127.2 (C^2, C^3, C^4, C^5; exact assignment not possible); 285.7 (*C*(S)SMe). Anal. Found (Calc. for $C_{18}H_{29}BrINbS_2Si_2$): C, 32.41(32.39), H, 4.30(4.34)%. Yield: 85%.

3.2. $[Nb(\eta^5\text{-}C_5H_4SiMe_3)_2HL]$ [L = P(OMe)₃ 6; L = P(OEt)₃ 7; L = P(OPh)₃ 8]

To a colourless solution of **5** (300 mg, 0.80 mmol) in 40 ml of THF was added P(OMe)₃ (0.80 mmol). The mixture was stirred for 2 h at 70°C and the solution became increasingly brown. The brown solution was evaporated to dryness and the residue extracted with hexane. Complex **6** was obtained as an oily material after evaporation of the solvent an a large exposition under vacuum. Complexes **7** and **8** were obtained by identical procedures. **6**: IR (Nujol) ν(Nb–H) 1682 cm^{-1}. ^{1}H NMR (C_6H_6): δ −7.61 (d, 1H, J_{PH} = 34.1 Hz, Nb-*H*); 0.28 (s, 18H, Si*Me*$_3$); 3.31 (d, 9H, J_{PH} = 11.1 Hz, O*Me*); 4.12 (2H); 4.36 (2H); 4.71 (2H); 5.15 (2H) (each a complex signal, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6): δ −0.40 (Si*Me*$_3$); 50.5 (O*Me*); 91.3 (C^1); 84.4, 86.4, 88.3, 88.9 (C^2, C^3, C^4, C^5; exact assignment not possible). Yield 95%. **7**: IR (Nujol) ν(Nb–H) 1677 cm^{-1}. ^{1}H NMR (C_6D_6): δ −8.39 (d, 1H, J_{PH} = 33.6 Hz, Nb-*H*); 0.33 (s, 18H, Si*Me*$_3$); 1.10 (m, 9H, OCH_2CH_3); 3.83 (m, 6H, OCH_2CH_3); 3.83 (2H); 4.14 (2H); 4.51 (2H); 4.79 (2H) (each a complex signal, C_5H_4). ^{13}C{^{1}H} NMR (C_6D_6): δ 0.45 (Si*Me*$_3$); 16.0 (OCH_2CH_3); 59.4 (OCH_2CH_3); 90.5 (C^1); 85.0, 86.1, 88.8, 89.1 (C^2, C^3, C^4, C^5; exact assignment not possible). Yield: 95%. **8**: IR (Nujol) ν(Nb–H) 1714 cm^{-1}. ^{1}H NMR (C_6D_6): δ −7.17 (d, 1H, J_{PH} = 35.2 Hz, Nb-*H*); 0.18 (s, 18H, Si*Me*$_3$); 4.21 (2H); 4.47 (2H); 4.59 (2H); 5.33 (2H) each a complex signal, C_5H_4); 6.90–7.30 (m, 15H, O*Ph*). ^{13}C{^{1}H} NMR (C_6D_6): δ 0.56 (Si*Me*$_3$); 94.4 (C^1); 87.4, 87.6, 89.4, 89.6 (C^2, C^3, C^4, C^5; exact assignment not possible); 153.1 (d, J_{PC} = 8.56 Hz, *Cipso* phenyl group); 129.5, 129.9, 152.2 (phenyl group). Yield: 95%.

3.3. [Nb(η^5-$C_5H_4SiMe_3$)$_2$(S(S)CH)(CO)] 10, [Nb(η^5-$C_5H_4SiMe_3$)$_2$(SCHS)] 11

CS_2 (0.88 mmol) was added to a light brown THF solution (50 ml) of **9** (350 mg, 0.88 mmol). The mixture was stirred for 1 h at room temperature. The solution became increasingly red and a deep garnet solution was finally obtained which was evaporated to dryness. The oily residue was extracted with hexane and a garnet solid of **10** was obtained after concentrating and cooling the solution. Complex **11** was prepared in a similar way. After stirring the solution for 2 h an orange solution was formed which was evaporated to dryness. The residue was washed with cold hexane and complex **11** was isolated as an orange solid. **10**: IR (Nujol) ν(CO) 1905 cm^{-1}, ν(C=S) 1000 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 18H, Si*Me*$_3$); 5.13 (4H); 5.33 (2H); 5.60 (2H) (each a complex signal, C_5H_4); 11.67 (s, 1H, S(C)S*H*. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.0 (Si*Me*$_3$); 103.6 (C^1); 95.1, 97.8, 104.0, 104.9 (C^2, C^3, C^4, C^5; exact assignment not possible); 148.6 (S(*C*)SH); 240.2 (*C*O). Anal. Found (Calc. for $C_{18}H_{27}NbOS_2Si_2$): C, 45.81(45.77); H, 5.70(5.72)%. Yield: 70%. **11**: ^{1}H NMR ($CDCl_3$): δ 0.22 (s, 18H, Si*Me*$_3$); 5.05 (4H); 5.44 (4H) (each a complex signal C_5H_4); 4.17 (S, 1H, SSC*H*). ^{13}C {^{1}H} NMR ($CDCl_3$): δ 0.5 (Si*Me*$_3$); 98.6 (C^1); 103.6, 106.9 (C^2, C^5 and C^3, C^4; exact assignment not possible); 120.0 (S*C*HS). Anal. Found (Calc. for $C_{17}H_{27}NbS_2Si_2$): C, 45.81(45.95); H, 5.96(6.08)%. Yield: 80%.

3.4. [Nb(η^5-$C_5H_4SiMe_3$)$_2$Cl(μ-CS_2)(C(S)S-MPPh$_3$)][PF$_6$] (M = Cu 12; Ag 13; Au 14)

A THF solution (20 ml) of [CuPPh$_3$]PF$_6$ was prepared *in situ* by reaction of [Cu(PPh$_3$)Cl] (148 mg, 0.41 mmol) with TlPF$_6$ (143 mg, 0.41 mmol). The white precipitate (TlCl) was separated by filtration and the filtrate was added to a THF solution (30 ml) of **1** (200 mg, 0.41 mmol). The mixture was stirred for 1.5 h to give a solution which was evaporated to dryness to give a red residue. Complex **12** was obtained as a red crystalline solid by crystallization from diethyl ether-hexane. Complexes **13** and **14** were isolated similarly as red **13** and green **14** crystalline solids. **12**: IR (Nujol) ν(C–S) 630 cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): δ 0.21 (s, 18H, Si*Me*$_3$); 5.88 (4H); 6.37 (2H); 6.52 (H) (each a complex signal, C_5H_4); 7.43–7.50 (m, 15H, P*Ph*$_3$). ^{13}C{^{1}H} NMR($(CD_3)_2CO$): δ −0.39 (Si*Me*$_3$); 115.6 (C^1); 107.1, 112.3, 122.1, 124.8, (C^2, C^3, C^4, C^5; exact assignment not possible); 128.9, 130.4, 133.8, 135.5 (P*Ph*$_3$); 307.8 (*C*S$_2$). Anal. Found (Calc. for $C_{35}H_{41}ClF_6CuNbP_2S_2Si_2$): C, 44.45(44.30); H, 4.40(4.32)%. Yield: 75%. **13**: IR (Nujol) ν(C–S) 632 cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): δ 0.20 (s, 18H, Si*Me*$_3$); 5.89 (4H); 6.25 (2H); 6.47 (2H) (each a complex signal, C_5H_4); 7.30–7.65 (m, 15H, P*Ph*$_3$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ −0.47 (Si*Me*$_3$); 126.3 (C^1); 108.0, 112.4, 125.5, 126.3 (C^2, C^3, C^4, C^5; exact assignment not possible); 129.9, 131.4, 134.5, 136.6 (P*Ph*$_3$); 303.4 (*C*S$_2$). Anal. Found (Calc. for $C_{35}H_{41}ClF_6AgNbP_2S_2Si_2$): C, 42.45(42.37); H, 4.10(4.13)%. Yield: 70%. **14**: IR (Nujol) ν(C–S) 630 cm^{-1}. ^{1}H NMR ($(CD_3)_2CO$): δ 0.21 (s, 18H, Si*Me*$_3$); 5.97 (4H); 6.29 (2H); 6.50 (2H) (each a complex signal, C_5H_4); 7.50–7.69 (m, 15H, P*Ph*$_3$). ^{13}C{^{1}H} NMR ($(CD_3)_2CO$): δ 0.50 (Si*Me*$_3$); 122.8 (C^1); 107.8, 112.3, 118.6, 119.2 (C^2, C^3, C^4, C^5; exact assignment not possible); 130.4, 133.7, 134.9, 135.6 (P*Ph*$_3$); 303.4 (*C*S$_2$). Anal. Found (Calc. for $C_{35}H_{41}ClF_6AuNbP_2S_2Si_2$): C, 38.98(38.87); H, 3.70(3.79)%. Yield: 65%.

3.5. [Nb(η^5-$C_5H_4SiMe_3$)$_2$L(μ-H)(AuPPh$_3$)][PF$_6$] [L = P(OMe)$_3$ 15; P(OEt)$_3$ 16; P(OPh)$_3$ 17]

To a THF solution (30 ml) of **6** (400 mg, 0.81 mmol) at −78°C was added a THF solution (20 ml) of [AuPPh$_3$]PF$_6$ obtained *in situ* from the reaction of [Au(PPh$_3$)Cl] (370 mg, 0.81 mmol) and TlPF$_6$ (280 mg, 0.81 mmol). The mixture was stirred and allowed to warm to room temperature for 1.5 h. The resulting suspension was filtered through a layer of Celite and the filtrate was evaporated to dryness. The resulting oily residue was washed with diethyl ether to give a brown solid of **15**. Complexes **16** and **17** were isolated similarly as brown and orange-yellow solids respectively. **15**: ^{1}H NMR($(CD_3)_2CO$): δ −6.76 (d, 1H, J_{PH}

= 69 Hz; Nb–H–Au); 0.23 (s, 18H, SiMe_3); 3.65 (d, 9H; $J_{\mathrm{PH}} = 12$ Hz, OMe); 4.87 (2H); 5.26 (2H); 5.45 (2H); 5.73 (2H) (each a complex signal, C$_5H_4$); 7.55–7.78 (m, 15H, PPh_3). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO): δ 0.33 (SiMe$_3$); 53.3 (d, $J_{\mathrm{PC}} = 16.5$ Hz, OMe); 102.0 (C^1); 92.2, 92.7, 94.5, 96.1 (C^2, C^3, C^4, C^5; exact assignment not possible); 130.7, 132.5, 133.6, 134.2 (PPh_3). Anal. Found (Calc. for $C_{34}H_{38}O_3AuF_6P_3Si_2$): C, 40.54(40.51); H, 4.73(4.65)%. Yield: 85%. **16**: ^{1}H NMR((CD$_3$)$_2$CO): δ −6.57 (d, 1H, $J_{\mathrm{PH}} = 65.3$ Hz, Nb–H–Au); 0.23 (s, 18H, SiMe_3); 1.18 (m, 6H, $J_{\mathrm{PH}} = 14$ Hz, $J_{\mathrm{HH}} = 7.3$ Hz, OCH$_2$CH_3); 3.99 (m, 9H; $J_{\mathrm{PH}} = 14$ Hz, $J_{\mathrm{HH}} = 6.7$ Hz, OCH_2CH$_3$); 4.87 (2H); 5.26 (2H); 5.45 (2H); 5.73 (2H) (each a complex signal, C$_5H_4$); 7.58–7.72 (m, 15H, PPh_3). ^{13}C{1H} NMR((CD$_3$)CO): δ 0.60 (SiMe_3); 16.5 (d, $J_{\mathrm{PC}} = 6.6$ Hz, OCH$_2$$CH_3$); 63.3 (d, $J_{\mathrm{PC}} = 9.1$ Hz, OCH$_2$CH$_3$); 102.1 (C^1); 92.1, 92.4, 95.3, 96.2 (C^2, C^3, C^4, C^5; exact assignment not possible); 130.2, 132.5, 134.9 (PPh_3). Anal. Found (Calc. for $C_{37}H_{44}O_3AuF_6P_3Si_2$): C, 42.75(42.45); H, 5.37(5.04)%. Yield: 88%. **17**: ^{1}H NMR((CD$_3$)$_2$CO): δ −5.95 (d, 1H, $J_{\mathrm{PH}} = 66$ Hz, Nb–H–Au); 0.23 (s, 18H, SiMe_3); 5.16 (4H); 5.31 (2H); 5.81 (2H) (each a complex signal, C$_5H_4$); 6.84–7.48 (m, 15H, P(OPh)$_3$); 7.58–7.72 (m, 15H, PPh_3). ^{13}C{^{1}H} NMR((CD$_3$)$_2$CO): δ 0.76 (SiMe_3); 103.3 (C^1); 92.1, 93.8, 94.7, 97.3 (C^2, C^3, C^4, C^5; exact assignment not possible); 122.4, 126.2, 130.8 (P(OPh)$_3$); 152.6 (d, $J_{\mathrm{PC}} = 14$ Hz, C*ipso* P(OPh)$_3$); 130.3, 132.5, 134.9 (PPh_3). Anal. Found (Calc. for $C_{52}H_{44}O_3AuF_6P_3Si_2$): C, 48.12(48.42); H, 4.37(4.39)%. Yield: 89%.

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