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Phosphorus ylide-containing niobium complexes: preparation and characterization of homo- and heteronuclear compounds with an α-keto ylide ligand

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Abstract

The reactions have been studied between $[\{NbCl_3(dme)\}_n]$ or $[NbCl_3(dme)(RC{\equiv}CR')]$ with a heterocycle containing α-keto stabilized phosphorus ylide, 2-TCMP = [{2-thiazolylcarbonyl}methylene]triphenylphosphorane, and these reactions give the α-keto ylide-containing niobium complexes $[\{NbCl_3(2\text{-TCMP})\}_2]$ (**1**) and $[NbCl_3(2\text{-TCMP})(RC{\equiv}CR')]$, R = R′ = Ph (**2**); R = R′ = Me (**3**); R = R′ = Et (**4**); R = Ph, R′ = Me (**5**); R = Ph, R′ = Et (**6**); R = Ph, R′ = Pr (**7**); R = Ph, R′ = $SiMe_3$ (**8**), respectively. The reactivity of **5** towards different reagents has also been investigated. Compound **5** reacts with MeLi to give, through a deprotonation process of a phenyl ring, the *ortho*-metallated complex $[\overline{NbCl_2\{NOSC_4H_2CHPPh_2(C_6H_4)\text{-}O,N\}}]_2$ (**9**), with the loss of the alkyne ligand. Furthemore, **5** reacts with $[AuPPh_2R]CF_3SO_3$ and $AgCF_3SO_3$ to give the heterometallic complexes $[NbCl_3(2\text{-TCMP})Au\ PPh_2R]_2\ (CF_3SO_3)_2$, R = Ph (**10**), R = C_3H_2SN (**11**), and $[NbCl_3(2\text{-TCMP})Ag]_2\ (CF_3SO_3)_2$ (**12**), respectively, with the loss of the alkyne ligand in each case.

Keywords: Niobium; Phosphorus ylides; α-Keto ylide

1. Introduction

Phosphorus ylides constitute an important class of compound in the field of organometallic chemistry, particularly due to their interesting applications in metal-promoted organic syntheses [1]. The chemistry of early transition metals and ylides is not common and is mainly limited to cyclopentadienyl complexes and ylides of the type $R_3P{=}CR'R''$ [2], although a few examples of oxophilic group 4 metal species containing α-keto stabilized phosphorus ylides $R_3P{=}C(R')COR''$ have also been described [3]. This class of ligand shows an ambidentate character (C versus O coordination) that can be rationalized in terms of the potential resonance forms A–C (Chart 1).

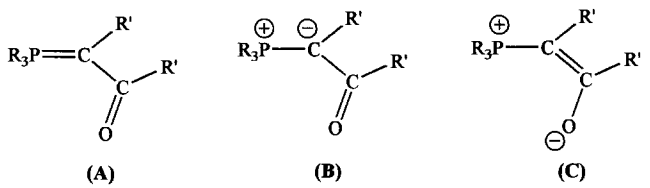

Chart 1

In the complexes reported with this type of ligand, the chemical behavior of the α-keto stabilized phosphorus ylide has been clearly dominated by the C-coordination mode [4] and very few examples of O-coordinated ylides have been described [5]. Examples of O-coordination include the aforementioned ylide-containing group

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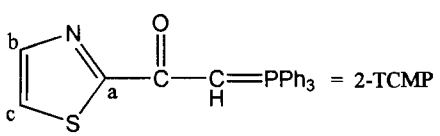
4 metal complexes. With these precedents in mind we initiated a study of the reactivity of an α-keto ylide containing a heterocycle, [{2-thiazolylcarbonyl}methylene]triphenylphosphorane $NOSC_4H_2CHPPh_3$ = 2-TCMP, toward the Nb(III) complexes $[\{NbCl_3(dme)\}_n]$ and $[NbCl_3(dme)(RC{\equiv}CR')]$ (dme = 1,2-dimethoxyethane). We report here the synthesis and structural characterization of the first α-keto ylide niobium complexes and, indeed, the first example of this class of ligand acting in a chelating manner. In this example chelation occurs through N,O-coordination to the metal center. In addition, new examples of early-late heterometallic complexes of gold and silver are also reported. Preliminary results of this work have been published previously [6].

2. Results and discussion

Firstly, the reactions of the heterocycle-containing α-keto ylide [{2-thiazolylcarbonyl}methylene]triphenylphosphorane, $NOSC_4H_2CHPPh_3$ = 2-TCMP, with $[\{NbCl_3(dme)_n\}]$ and $[NbCl_3(dme)(RC{\equiv}CR')]$ (dme = 1,2-dimethoxyethane) were investigated. The standard reaction procedure involved the addition of the ligand to a suspension of the appropriate niobium complex in a 1:1 molar ratio at room temperature. The reaction mixture was stirred for 20 h and gave a new solution or suspension. The products were isolated after the appropriate work-up procedure (see Section 3) as air-sensitive solids corresponding to the complexes $[\{NbCl_3(2\text{-TCMP})\}_2]$ (**1**) (Eq. 1) and $[NbCl_3(2\text{-TCMP})(RC \equiv CR')]$ (**2**–**8**) (Eq. 2).

$$\frac{1}{n}[\{NbCl_3(dme)\}_n] + \text{2-TCMP} \longrightarrow \frac{1}{2}[\{NbCl_3(2\text{-TCMP})\}_2] + dme \quad (1)$$

1



= 2-TCMP

$$[NbCl_3(dme)(RC{\equiv}CR')] + \text{2-TCMP} \longrightarrow [NbCl_3(2\text{-TCMP})(RC{\equiv}CR')] + dme \quad (2)$$

2: R=R'=Ph
3: R=R'=Me
4: R=R'=Et
5: R=Ph; R'=Me
6: R=Ph; R'=Et
7: R=Ph; R'=Pr
8: R=Ph; R'=$SiMe_3$

Complexes **3**, **4** and **6** were obtained from the corresponding reactions as a mixture with complex **1**, resulting from the loss of the corresponding coordinated alkyne. These compounds could, however, be isolated in a pure state by recrystallization (see Section 3). The different complexes were characterized by spectroscopic techniques. These techniques allowed us to distinguish between O-coordination and C(methine)-coordination of the ylide ligand. The ^{1}H-, ^{13}C- and ^{31}P-NMR spectra indicate that the 2-TCMP ligand is bound through the carbonyl oxygen. The ^{1}H-NMR spectra (see Section 3) each show a doublet resonance attributed to the methine proton with coupling constants ($^2J_{PH}$) ranging from 15.0 to 16.4 Hz. In addition, the $^{13}C\{^1H\}$-NMR spectra (see Section 3) show the resonance attributed to the ylidic carbon as a doublet with a coupling constant ($^1J_{PC}$) smaller than that in the free ylide. For example, for compound **2** the value of the coupling constant is 105.3 Hz while for the corresponding free ylide is 111.0 Hz. The values are in accordance with the known coupling constant trend; free ylide > O-coordinated ylide > ylide hydrohalide salt > C-coordinated ylide [7]. ^{31}P-NMR resonances (see Section 3) were observed to occur at slightly lower field with respect to the free ylide. IR spectroscopy has previously been demonstrated to be another reliable indicator of the bonding mode of α-keto ylides ([4]h, [5]a–c, [5]e). Bonding through the carbonyl oxygen (where **C** in Chart 1 is the major resonance contributor) leads to a decrease in the carbonyl stretching frequency with respect to the corresponding free ylide. However, in complexes **1**–**8** the IR spectra (see Section 3) show strong absorptions in the range 1551 to 1557 cm^{-1}, which are shifted to higher wavenumbers than in the free ylide. This behavior, which could be considered surprising, may be justified on the basis of the structure of the complexes. Indeed, in these complexes the α-keto ylide ligand acts as a chelate through N,O-coordination to give five-membered metallacycles in which the O-atom is proposed to be sp^2 hybridized. This situation probably favors effective π-bonding with the ylidic carbon to give a strong C···O bond (see Chart 2). An X-ray crystal study has previously been published [6] that confirmed this proposal.

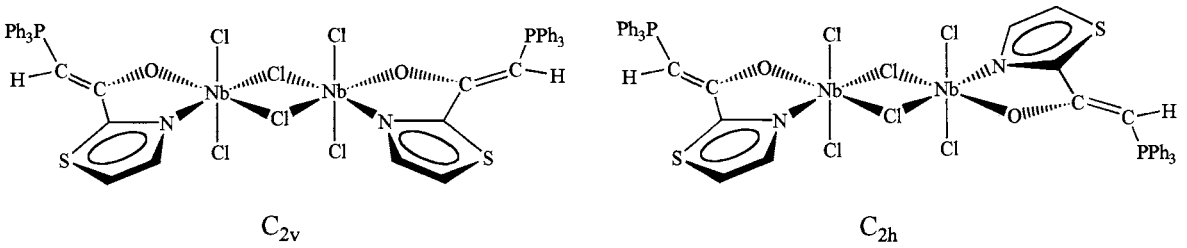


Fig. 1. Proposed structures for complex **1**.

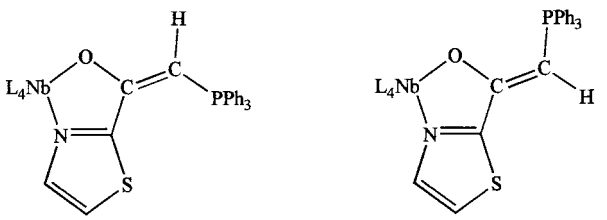


Chart 2

In addition, the different spectroscopic data indicate the presence of only one of the two possible isomers (*cisoid* and *transoid*) in each of these complexes (see Chart 2). The *cisoid* isomer, which would appear to be favored on steric arguments in the complexes, has been proposed to be present both in solution and in the solid state. In fact, as mentioned previously, this structural situation was found for **7** by means of an X-ray crystal structure determination [6]. The mass spectrum of **1** indicates a binuclear formulation. The IR spectrum of **1** shows a strong band at ca. 324 cm^{-1} in the region between 400 and 200 cm^{-1}, which has been assigned to the υ(Nb–Cl) terminal for a C_{2v} or C_{2h} binuclear arrangement with the terminal chloride ligands in a *trans* disposition in an octahedral environment for each niobium atom.

This structural geometry (see Fig. 1) has been described [8] as more favorable in an analogous binuclear complex with both terminal and bridging halide ligands. In the IR spectra of complexes **2**–**8**, absorptions of different intensities (medium to weak) located at ca. 1680 cm^{-1} have been assigned to the υ(C≡C) mode of the bound alkynes. This represents a decrease of about 500 cm^{-1} from free alkyne values, which is consistent with substantial weakening of the triple bond on coordination. With regard to the alkyne moiety, the $^{13}C\{^1H\}$-NMR data for complexes **2**–**8** (see Section 3) indicate that this ligand behaves as a four-electron donor. An empirical correlation between the alkyne π donation and ^{13}C chemical shift for the bound alkyne carbons has been observed [9]. The chemical shift values for complexes **2**–**8** appear at ca. 240 ppm, which is a clear indication that the number of electrons donated per alkyne is four. In this way the role of both bonding $\pi_{\parallel}$ and $\pi_{\perp}$ orbitals in donating electrons is not in conflict with acceptance of electron density from the niobium centre into the antibonding $\pi_{\parallel}^{*}$ orbital of the alkyne. The ^1H- and ^{13}C-NMR spectra of complexes **2**–**4** with symmetrical alkynes exhibit an only one group of signals for the substituted groups. This results can be due to either a simple rotation of the alkyne ligand [10], or that assuming a six-coordinate description of the complexes in which the alkyne occupies a single site, a static structure (see Fig. 2) in which this site located perpendicular to the equatorial plane defined by the N, O, Cl and Nb atoms is proposed. Indeed, this last proposal was confirmed in the X-ray crystal structure determination for **7** [6].

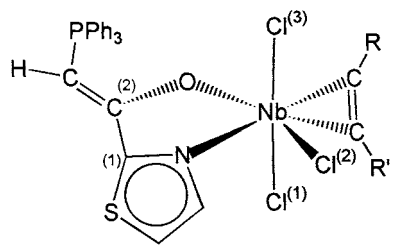
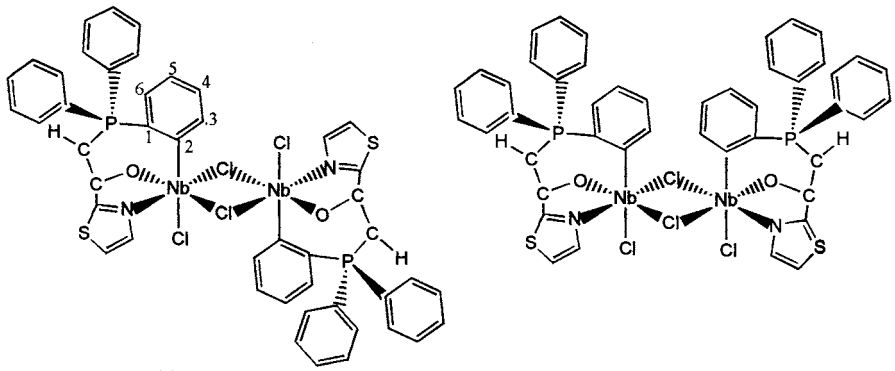


Fig. 2. Proposed structure for complexes **2**–**8**. Selected bond distances (Å) and angles (°) for complex **7**, from a X-ray crystal structure determination [6]: Nb–O 2.148(3), Nb–N 2.344(5), RC=CR′ 1.288(9), Nb–CR 2.066(6), Nb–CR′ 2.026(6), O–Nb–N 72.3(1), O–Nb–Cl(2) 159.0(1), Cl(1)–Nb–Cl(3) 161.28(6), CR–Nb–CR′ 36.7(2), O–C(2)–C(1) 125.4(5).

The reactivity of **5** toward different reagents has also been considered in this study. Firstly, the reaction with MeLi was studied. Compound **5** reacts with one equivalent of MeLi in toluene to give, after the appropriate work-up procedure, the air-sensitive orange-red crystalline compound $[\overline{NbCl_2\{NOSC_4H_2CHPPh_2(C_6H_4)\text{-}O,N\}}]$ (**9**) (Eq. 3).

$$[NbCl_3(2\text{-}TCMP)(PhCCMe)] \;(\mathbf{5}) + LiMe \longrightarrow 1/2[\overline{NbCl_2\{NOSC_4H_2CHPPh_2(C_6H_4)\text{-}O,N\}}]_2 \;(\mathbf{9}) + CH_4 + PhCCMe + LiCl \quad (3)$$



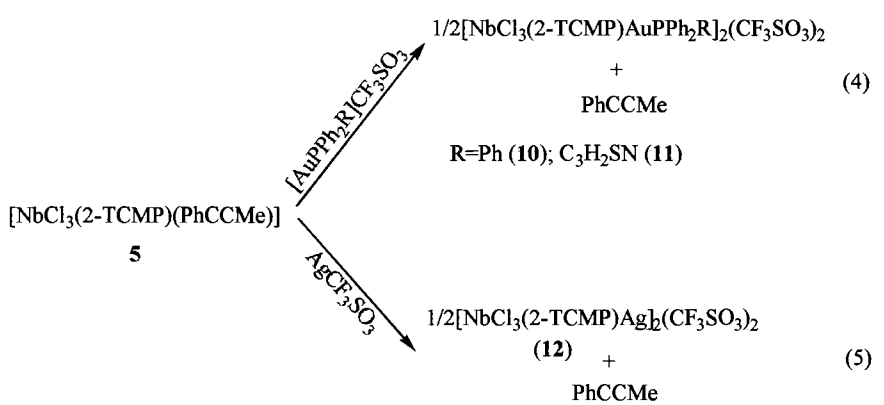
(a) trans, Ci (b) cis, Cs

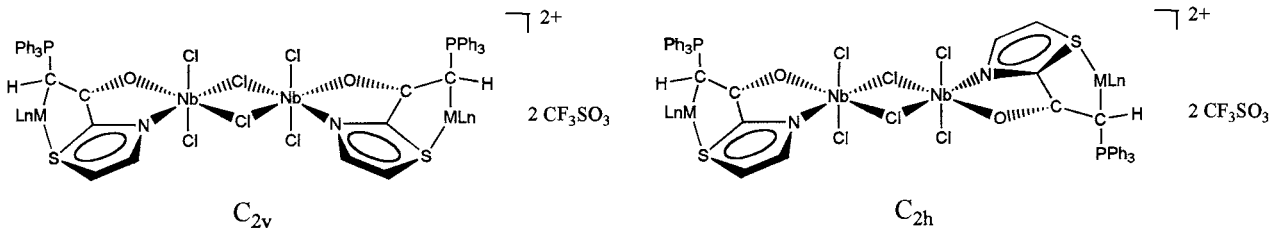
Fig. 3. Proposed structures for complex **9.**

The process takes place through deprotonation of a phenyl ring in the ylide ligand to give the *ortho*-metallated complex **9** with the loss of the coordinated alkyne. The aim of the reaction was to prepare a methyl-containing derivative, but the reaction conditions resulted in a deprotonation process of a phenyl ring-containing ylide to give a new tridentate anionic ligand. Alternatively, the mechanism for the formation of **9** could be methyl substitution at metal followed by σ- bond metathesis to yield the *ortho*-metallated product. The complex was characterized spectroscopically. The mass spectrum of this compound indicates a binuclear formulation (see Section 3).

In the ^{1}H-NMR spectrum the doublet due to the methine proton is observed at a higher field than that in both complex **5** and the free ylide. In the $^{13}C\{^{1}H\}$-NMR spectrum the resonance attributed to the ylidic carbon shows a coupling constant $^{1}J_{PC}$ of 110.8 Hz, which confirms an O-coordination of the ylide ligand. In the $^{13}C\{^{1}H\}$-NMR spectrum, the region in which the resonances corresponding to the phenyl rings occur is more complex than the corresponding area in **5** and in the free ylide. The assignment of the different signals was carried out on the basis of both their intensity and values of their coupling constants J_{PC} (see Section 3). Using of this method it was possible to tentatively assign the resonance that corresponds to the carbon atom bound to the niobium centre of the *ortho*-metallated ring. The $^{31}P\{^{1}H\}$-NMR spectrum shows a resonance at 16.05 ppm, which is attributed to the phosphorus of the ylide. Furthermore, the υ(CO) absorption in the IR spectrum appears at 1560 cm^{-1} and confirms, as previously discussed for **1**–**8**, a bonding of the ylide through the carbonyl oxygen. In addition, two bands at 274 and 267 cm^{-1}, which are probably due to solid state splitting effects, were assigned to the υ(Nb–Cl) terminal of a binuclear species with the terminal chloride ligands *trans* in an octahedral environment for each niobium atom [11].

The structural situation *trans* (Fig. 3a) implies that the two tridentate ligands in the molecule are also mutually *trans*, in a disposition where the steric hindrance is minimum. We have also studied the reaction of complex **5** with different Lewis acidic coinage cationic species, namely $[AuPPh_2R]CF_3SO_3$ and $AgCF_3SO_3$. Compound **5** reacts with one equivalent of $[AuPPh_2R]CF_3SO_3$, prepared in situ from $AuCl(PPh_2R)$ and $AgCF_3SO_3$, or $AgCF_3SO_3$ to give, after appropriate work-up, the corresponding heterometallic complexes $[NbCl_3(2\text{-TCMP})AuPPh_2R]_2(CF_3SO_3)_2$, R = Ph (**10**), R = C_3H_2SN (**11**), and $[NbCl_3(2\text{-TCMP})Ag]_2(CF_3SO_3)_2$ (**12**), respectively (Eq. 4 and 5).





MLn= $AuPPh_3$ (**10**); $AuPPh_2(C_3H_2SN)$ (**11**); Ag (**12**)

Fig. 4. Proposed structures for complexes **10**–**12**.

Niobium-coinage cation heterometallic complexes have not been widely reported in the literature and in these compounds the hydride ligand is frequently present as an ancillary ligand [12]. The different isolated heterometallic complexes were characterized spectroscopically. Their mass spectra (see Section 3) indicate a binuclear formulation as the result of the loss of the coordinated alkyne ligand. In the ^{1}H-NMR spectra of complexes **10**–**12** the doublet due to the methine proton occurs at chemical shift values (see Section 3) that are intermediate between those corresponding to the free ylide (5.00 ppm) and the phosphonium salt (6.65 ppm). These results indicate a probable coordination of the $AuPPh_2R^+$ and Ag^+ fragments to the ylidic carbon atom. In fact, the isolobal analogy suggested between the '$AuPR_3$' and 'H' fragments [13], which has recently stimulated the synthesis and study of gold-containing heterometallic derivatives [14], would justify the formation of the corresponding pseudophosphonium salt coordinated to the niobium center in these reactions. Furthermore, the values of the $^2J_{PH}$ coupling constants are close to the value for the phosphonium salt ($^2J_{PH} = 13.5$Hz). In addition, the signal due to H_c (H_α with respect to the S atom; see Eq. 1) in the thiazolyl ring in the different complexes **10**–**12** was found to be clearly deshielded in relation to the equivalent proton observed in complex **5**. This suggests that a possible coordination of the sulfur atom to the niobium center could be occuring. In the ^{13}C{^{1}H}-NMR spectra for **10**–**12** (see Section 3) the resonances attributed to the ylidic carbon atoms appear at chemical shift values close to those found for the corresponding carbon atom in the phosphonium salt (35.80 ppm). The assignment of all the carbon resonances in the spectra was carried out by means of the appropriate ^{13}C-^{1}H heteronuclear correlations (HETCOR). The ^{31}P{^{1}H}-NMR spectra of **10** and **11** show two signals for the two different phosphorus atoms that are present in each molecule. The resonances of these phosphorus centers were assigned (see Section 3) by an HMQC ^{31}P-^{1}H experiment and it was found that the more shielded signal, close to the value found for the phosphonium salt, corresponds to the phosphorus atom of the ylide ligand. The ^{31}P{^{1}H}-NMR spectrum of **12** exhibits a pseudotriplet, which corresponds to two overlapped doublets by coupling with ^{107}Ag and ^{109}Ag isotopes. Attempts to resolve the complex signal by lowering the temperature (down to -90°C) were unsuccessful. Finally, the ^{19}F{^{1}H}-NMR spectra of complexes **10**–**12** show a signal at -74.4 ppm, which corresponds to the CF_3SO_3 anion. The υ(CO) absorption in the IR spectra appears at ca. 1565 cm^{-1}, indicating a bonding of the pseudophosphonium group through the carbonyl oxygen. The IR spectra also show a strong band at ca. 330 cm^{-1} in the region between 400 and 200 cm^{-1}, which was assigned to the υ(Nb–Cl) terminal for a C_{2v} or C_{2h} binuclear disposition [8], as was previously discussed for complex **1**, with the terminal chloride ligands *trans* in an octahedral environment for each niobium atom (Fig. 4).

In conclusion, the synthesis and characterization of the first α-keto ylide-containing niobium complexes have been described. In addition, the reactivity of one of these complexes toward MeLi and different Lewis acidic coinage cationic species was studied. This work led to the isolation and characterization new *ortho*-metallated and several heterometallic derivatives.

3. Experimental

3.1. General

All reactions were performed using standard Schlenk-tube techniques in an atmosphere of dry nitrogen. Solvents were distilled from appropriate drying agents and degassed before use. Microanalyses were carried out with a Perkin-Elmer 2400 CHN analyser. Infrared spectra were obtained in the region 200–4000 cm^{-1} using a Perkin-Elmer 883 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on Varian-Unity FT-300 and Gemini FT-200 spectrometers and the chemical shifts were determined by reference to the residual deuterated solvent peaks. The complexes [{$NbCl_3$(dme)}$_n$], [$NbCl_3$(dme)(RC≡CR′)] and [AuCl(PPh_3)] were prepared as reported previously [15,16].

3.2. Preparation of $PPh_2(C_3H_2SN)$

A suspension of 2-bromothiazole (13.23 g, 0.08 mol) in toluene (40 cm^3) was cooled to −70°C and a solution of *n*-BuLi in hexane (1.6 M, 53 cm^3, 0.08 mol) and $(C_6H_5)_2PCl$ (14 cm^3, 0.08 mol) were added with vigorous stirring. The cooling bath was kept at −70°C for 1 h, and then allowed to slowly reach room temperature. After 20 h the mixture was filtered through Celite, and the solvent was removed in vacuo to give a yellow oil. (Yield 75%).

3.3. Preparation of $AuClPPh_2(C_3H_2SN)$

To a suspension of AuCl (tht) (1 g, 3 mmol) in acetone (20 cm^3), an equimolar quantity of $PPh_2(C_3H_2SN)$ (840 mg, 3 mmol) was added. The suspension was stirred at room temperature for 1 h. The solvent was removed in vacuo and a greenish-yellow solid was obtained. (Yield 90%).

3.4. Preparation of $[\{NbCl_3(2\text{-}TCMP)\}_2]$ (**1**)

To a suspension of $[\{NbCl_3(dme)\}]$ (240 mg, 0.820 mmol) in THF (20 cm^3), an equimolar quantity of 2-TCMP (321 mg, 0.820 mmol) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo and a greenish-brown solid was obtained. (Yield 80%). NMR: $^1H(CDCl_3)$, δ 5.40 (d, $^2J_{PH} = 16.0$ Hz, CH), 8.20 (d, $^3J_{HH} = 5.7$ Hz, H_b), 7.60 (d, $^3J_{HH} = 5.7$ Hz, H_c), 7.40–7.61 (m, 30H, PPh_3); $^{13}C\text{-}\{^1H\}(CDCl_3)$, δ 71.50 (d, $^1J_{PC} = 101.0$ Hz, CH), 144.30 (s, CO), 168.30 (s, C_a), 142.80 (s, C_b), 124.40 (s, C_c), 120.36 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 130.11 [d, $^2J_{PC} = 13.2$ Hz, $C_o(PPh_3)$], 133.45 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$], 134,48 [d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$]; $^{31}P\text{-}\{^1H\}(CDCl_3, H_3PO_4$ as reference), δ 18.88 (s, PPh_3). IR (Nujol): 1553 [ν(C=O)], 324 [ν(Nb–Cl)]cm^{-1}. (Found: C, 46.7; H, 3.2; N, 2.5. Anal. Calc. for $C_{46}H_{36}Nb_2Cl_6N_2O_2P_2S_2$: C, 47.0; H, 3.1; N, 2.3). Mass spectrum: (*m*/*z* assignment, % intensity): 1175D [M + 1], 6, 1088D [M–C_3H_2NS], 5, 971D [M–2 (C_3H_2NS)], 15, 388D [(2-TCMP)], 100.

3.5. Preparation of $[NbCl_3(2\text{-}TCMP)(PhC{\equiv}CPh)]$ (**2**)

To a suspension of $[NbCl_3(dme)(PhC{\equiv}CPh)]$ (100 mg, 0.210 mmol) in THF (20 cm^3) was added an equimolar quantity of 2-TCMP (81 mg, 0.210 mmol). The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give a brown solid. (Yield 80%). NMR: $^1H(CDCl_3)$, δ 5.15 (d, $^2J_{PH} = 15.0$ Hz, CH), 8.50 (d, $^3J_{HH} = 3.4$ Hz, H_b), 7.56 (d, $^3J_{HH} = 3.4$ Hz, H_c), 7.40–7.80 (m, 25H, PPh_3 and PhC≡); $^{13}C\text{-}\{^1H\}(CDCl_3)$, δ 72.64 (d, $^1J_{PC} = 105.3$ Hz, CH), 165.20 (d, $^2J_{PC} = 19.0$ Hz, CO), 171.00 (s, C_a), 142.80 (s, C_b), 123.20 (s, C_c), 120.81 [d, $^1J_{PC} = 92.3$ Hz, $C_i(PPh_3)$], 129.70[d, $^2J_{PC} = 12.8$ Hz, $C_o(PPh_3)$], 133.41 [d, $^3J_{PC} = 10.7$ Hz, $C_m(PPh_3)$], 133,80[d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$], 139.42 [s, $C_i(PhC{\equiv})$], 126.65 [s, $C_o(PhC{\equiv})$], 129.31 [s, $C_m(PhC{\equiv})$], 128.31 [s $C_p(PhC{\equiv})$], 240.20 (s, C≡C); $^{31}P\text{-}\{^1H\}(CDCl_3, H_3PO_4$ as reference), δ 18.69 (s, PPh_3). IR (Nujol): 1553 [ν(C=O)], 1692 [ν(C≡C)], 382 and 309 [ν(Nb–Cl)]cm^{-1}. (Found: C, 58.4; H, 4.3; N, 2.0. Anal. Calc. for $C_{37}H_{28}NbCl_3NOPS$: C, 58.0; H, 3.8; N, 1.8).

3.6. Preparation of $[NbCl_3(2\text{-}TCMP)(MeC{\equiv}CMe)]$ (**3**)

To a suspension of $[NbCl_3(dme)(MeC{\equiv}CMe)]$ (222 mg, 0.640 mmol) in THF (20 cm^3), an equimolar quantity of 2-TCMP (248 mg, 0.640 mmol) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give a brown solid as a mixture of **1** and **3**. Compound **3** was isolated by crystallization from CH_2Cl_2/Et_2O. (Yield 60%). NMR: $^1H(CDCl_3)$, δ 5.15 (d, $^2J_{PH} = 16.4$ Hz, CH), 8.48 (d, $^3J_{HH} = 3.2$ Hz, H_b), 7.55 (d, $^3J_{HH} = 3.2$ Hz, H_c), 7.56–7.72 (m, 15H, PPh_3), 2.56 (s, 6H, $CH_3C{\equiv}$); $^{13}C\text{-}\{^1H\}(CDCl_3)$, δ 72.40 (d, $^1J_{PC} = 105.3$ Hz CH), 165.00 (d, $^2J_{PC} = 18.0$ Hz, CO), 171.70 (s, C_a), 142.70 (s, C_b), 123.55 (s, C_c), 121.81 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 129.84 [d, $^2J_{PC} = 13.2$ Hz, $C_o(PPh_3)$], 133.36 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$], 133,97 [d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$], 25.59 (s, $CH_3C{\equiv}$), 246.81 (s, C≡C); $^{31}P\text{-}\{^1H\}(CDCl_3, H_3PO_4$ as reference), δ 19.00 (s, PPh_3). IR (Nujol): 1552 [ν(C=O)], 1680 [ν(C≡C)], 377 and 323 [ν(Nb–Cl)]cm^{-1}. (Found: C, 50.5; H, 4.1; N, 2.2. Anal. Calc. for $C_{27}H_{24}NbCl_3NOPS$: C, 50.5; H, 3.9; N, 2.2).

3.7. Preparation of $[NbCl_3(2\text{-}TCMP)(EtC{\equiv}CEt)]$ (**4**)

To a suspension of $[NbCl_3(dme)(EtC{\equiv}CEt)]$ (210 mg, 0.560 mmol) in THF (20 cm^3) was added an equimolar quantity of 2-TCMP (219 mg, 0.560 mmol). The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give an orange solid as a mixture of **1** and **4**. Compound **4** was isolated by crystallization from CH_2Cl_2/Et_2O. (Yield 55%). NMR: $^1H(CDCl_3)$, δ 5.09 (d, $^2J_{PH} = 15.4$ Hz, CH), 8.65 (d, $^3J_{HH} = 7.3$ Hz, H_b), 7.13 (d, $^3J_{HH} = 3.2$ Hz, H_c), 7.55–7.77 (m, 15H, PPh_3), 2.96 (q, 4H, $^3J_{HH} = 3.2$ Hz, $CH_3CH_2C{\equiv}$), 0.97 (t, 6H, $^3J_{HH} = 7.3$ Hz, $CH_3CH_2C{\equiv}$); $^{13}C\text{-}\{^1H\}(CDCl_3)$, δ 71.30 (d, $^1J_{PC} = 105.6$ Hz, CH), 165.30 (d, $^2J_{PC} = 18.0$ Hz, CO), 171.80 (s, C_a), 142.70 (s, C_b), 123.24 (s, C_c), 121.55 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 129.85[d, $^2J_{PC} = 13.2$ Hz, $C_o(PPh_3)$], 133.44 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$], 133,97 [d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$], 30.46 (s, $CH_3CH_2C{\equiv}$), 13.58 (s, $CH_3CH_2C{\equiv}$), 250.30 (s, C≡C); $^{31}P\text{-}\{^1H\}(CDCl_3, H_3PO_4$ as reference), δ 18.98 (s, PPh_3). IR (Nujol): 1551 [ν(C=O)], 1700 [ν(C≡C)], 380 and 322 [ν(Nb–

Cl)]cm^{-1}. (Found: C, 52.0; H, 4.0; N, 1.6. Anal. Calc. for $C_{29}H_{10}NbCl_3NOPS$: C, 51.9; H, 4.4; N, 2.0).

3.8. Preparation of [NbCl$_3$(2-TCMP)(PhC≡CMe)] (5)

To a suspension of [$NbCl_3$(dme)(PhC ≡ CMe)] (260 mg, 0.640 mmol) in THF (20 cm^3), an equimolar quantity of 2-TCMP (248 mg, 0.640 mmol) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give an orange solid. (Yield 85%). NMR: ^{1}H($CDCl_3$), δ 5.10 (d, $^2J_{PH} = 16.1$ Hz, CH), 8.55 (d, $^3J_{HH} = 3.1$ Hz, H_b), 7.58 (d, $^3J_{HH} = 3.1$ Hz, H_c), 7.40–7.80 (m, 20H, PPh_3 and PhC ≡), 2.79 (s, 3H, ≡ CCH_3); ^{13}C-{^{1}H}($CDCl_3$), δ 71.80 (d, $^1J_{PC} = 104.6$ Hz, CH), 165.10 (d, $^2J_{PC} = 18.4$ Hz, CO), 170.90 (s, C_a), 142.70 (s, C_b), 123.33 (s, C_c), 121.22 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 129.80 [d, $^2J_{PC} = 13.2$ Hz, $C_o(PPh_3)$], 133.36 [d, $^3J_{PC} = 10.7$ Hz, $C_m(PPh_3)$], 133,90 [d, $^4J_{PC} = 2.9$ Hz, $C_p(PPh_3)$], 138.06 [s, C_i(PhC ≡)], 127.87 [s, C_o(PhC ≡)], 131.02 [s, C_m(PhC ≡)], 128.67 [s C_p(PhC ≡)], 22.42 (s, ≡ CCH_3), 251.97, 236.24 (s, C ≡ C); ^{31}P-{^{1}H}($CDCl_3$, H_3PO_4 as reference), δ 19.06 (s, PPh_3). IR (Nujol): 1554 [ν(C=O)], 1680 [ν(C ≡ C)], 379 and 313 [ν(Nb–Cl)]cm^{-1}. (Found: C, 54.3; H, 4.0; N, 1.8. Anal. Calc. for $C_{32}H_{26}NbCl_3NOPS$: C, 54.7; H, 3.7; N, 1.9).

3.9. Preparation of [NbCl$_3$(2-TCMP)(PhC≡CEt)] (6)

To a suspension of [$NbCl_3$(dme)(PhC ≡ CEt)] (270 mg, 0.640 mmol) in THF (20 cm^3), an equimolar quantity of 2-TCMP (246 mg, 0.640 mmol) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give an orange solid as a mixture of **1** and **6**. Compound **6** was isolated by crystallization from CH_2Cl_2/Et_2O. (Yield 62%). NMR: ^{1}H($CDCl_3$), δ 5.16 (d, $^2J_{PH} = 16.0$ Hz, CH), 8.55 (d, $^3J_{HH} = 3.0$ Hz, H_b), 7.55 (d, $^3J_{HH} =$ 3.0 Hz, H_c), 7.40–7.80 (m, 20H, PPh_3 and PhC ≡), 3.17 (q, 2H, $^3J_{HH} = 7.5$ Hz, ≡ CCH_2CH_3), 1.10 (t, 3H, $^3J_{HH} = 7.3$ Hz, ≡ CCH_2CH_3); ^{13}C-{^{1}H}($CDCl_3$), δ 71.90 (d, $^1J_{PC} = 104.8$ Hz, CH), 165.22 (d, $^2J_{PC} = 19.0$ Hz, CO), 170.80 (s, C_a), 142.50 (s, C_b), 123.50 (s, C_c), 120.59 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 129.75 [d, $^2J_{PC} =$ 13.3 Hz, $C_o(PPh_3)$], 133.31 [d, $^3J_{PC} = 10.7$ Hz, $C_m(PPh_3)$], 133,87 [d, $^4J_{PC} = 2.9$ Hz, $C_p(PPh_3)$], 138.50 [s, C_i(PhC ≡)], 127.65 [s, C_o(PhC ≡)], 130.73[s, C_m(PhC ≡)], 128.65 [s C_p(PhC ≡)], 30.88 (s, ≡ CCH_2CH_3), 12.58 (s, ≡ CCH_2CH_3), 254.66, 236.75 (s, C ≡ C); ^{31}P-{^{1}H}($CDCl_3$, H_3PO_4 as reference), δ 18.98 (s, PPh_3). IR (Nujol): 1557 [ν(C = O)], 1692 [ν(C ≡ C)], 377 and 298 [ν(Nb–Cl)]cm^{-1}. (Found: C, 55.8; H, 4.2; N, 1.6. Anal. Calc. for $C_{33}H_{28}NbCl_3NOPS$: C, 55.2; H, 3.9; N, 1.9).

3.10. Preparation of [NbCl$_3$(2-TCMP)(PhC≡CPr)] (7)

To a suspension of [$NbCl_3$(dme)(PhC ≡ CPr)] (174 mg, 0.400 mmol) in THF (20 cm^3), an equimolar quantity of 2-TCMP (155 mg, 0.400 mmol) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give a brown solid. (Yield 86%). NMR: ^{1}H($CDCl_3$), δ 5.10 (d, $^2J_{PH} =$ 16.1 Hz, CH), 8.57 (d, $^3J_{HH} = 2.9$ Hz, H_b), 7.57 (d, $^3J_{HH} = 2.9$ Hz, H_c), 7.46–7.69 (m, 20H, PPh_3 and PhC ≡), 3.19 (t, 2H, $^3J_{HH} = 7.6$ Hz, ≡ $CCH_2CH_2CH_3$), 1.50 (m, 2H, ≡ $CCH_2CH_2CH_3$), 0.69 (t, 3H, $^3J_{HH} = 7.6$ Hz, ≡ $CCH_2CH_2CH_3$); ^{13}C-{^{1}H}($CDCl_3$), δ 71.53 (d, $^1J_{PC} = 105.0$ Hz, CH), 165.20 (d, $^2J_{PC} = 19.0$ Hz, CO), 171.00 (s, C_a), 142.80 (s, C_b), 123.20 (s, C_c), 120.79 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$], 129.79 [d, $^2J_{PC} = 12.8$ Hz, $C_o(PPh_3)$], 133.35 [d, $^3J_{PC} = 11.4$ Hz, $C_m(PPh_3)$], 133,88 [d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$], 139.01 [s, C_i(PhC ≡)], 127.62 [s, C_o(PhC ≡)], 130.42 [s, C_m(PhC ≡)], 128.10 [s C_p(PhC ≡)], 39.68 (s, ≡ $CCH_2CH_2CH_3$), 21.29 (s, ≡ $CCH_2CH_2CH_3$), 14.52 (s, ≡ $CCH_2CH_2CH_3$), 253.38, 237.17 (s, C ≡ C); ^{31}P-{^{1}H}($CDCl_3$, H_3PO_4 as reference), δ 18.95 (s, PPh_3). IR (Nujol): 1556 [ν(C=O)], 1692 [ν(C ≡ C)], 378 and 311 [ν(Nb–Cl)]cm^{-1}. (Found: C, 55.4; H, 4.7; N, 2.1. Anal. Calc. for $C_{34}H_{30}NbCl_3NOPS$: C, 55.8; H, 4.2; N, 1.9).

3.11. Preparation of [NbCl$_3$(2-TCMP)(PhC≡CSiMe$_3$)] (8)

To a suspension of [$NbCl_3$(dme)(PhC≡CSiMe_3)] (200 mg, 0.430 mmol) in THF (20 cm^3) was added an equimolar quantity of 2-TCMP (167 mg, 0.430 mmol). The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give a brown solid. (Yield 75%). NMR: ^{1}H($CDCl_3$), δ 5.11 (d, $^2J_{PH} =$ 15.6 Hz, CH), 8.58 (d, $^3J_{HH} = 2.8$ Hz, H_b), 7.61 (d, $^3J_{HH} = 2.8$ Hz, H_c), 7.50–7.98 (m, 20H, PPh_3 and PhC ≡), 0.30 (s, 9H, ≡ $CSiMe_3$); ^{13}C-{^{1}H}($CDCl_3$), δ 71.80 (d, $^1J_{PC} = 105.6$ Hz, CH), 165.40 (d, $^2J_{PC} = 18.0$ Hz, CO), 171.70 (s, C_a), 142.60 (s, C_b), 123.32 (s, C_c), 120.58 [d, $^1J_{PC} = 92.3$ Hz, $C_i(PPh_3)$], 129.70 [d, $^2J_{PC} =$ 13.3 Hz, $C_o(PPh_3)$], 133.23 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$], 134.31 [d, $^4J_{PC} = 2.9$ Hz, $C_p(PPh_3)$], 139.56 [s, C_i(PhC ≡)], 127.37 [s, C_o(PhC ≡)], 131.89 [s, C_m(PhC ≡)], 128.74 [s C_p(PhC ≡)], 0.04 (s, ≡ $CSiMe_3$), 260.40, 244.87 (s, C ≡ C); ^{31}P-{^{1}H}($CDCl_3$, H_3PO_4 as reference), δ 18.65 (s, PPh_3). IR (Nujol): 1551 [ν(C=O)], 1653 [ν(C ≡ C)], 381 and 305 [ν(Nb–Cl)]cm^{-1}. (Found: C, 53.4; H, 4.2; N, 2.0. Anal. Calc. for $C_{34}H_{42}NbCl_3NOPSSi$: C, 53.7; H, 4.1; N, 1.8).

3.12. Preparation of [NbCl$_2${NOSC$_4$H$_2$CHPPh$_2$(C$_6$H$_4$)-O,N}]$_2$ (9)

A suspension of [$NbCl_3$(2-TCMP)(PhC≡CMe)] (**5**) (250 mg, 0.356 mmol) in toluene (40 cm^3) was cooled to

−40°C and an ethereal solution of CH_3Li (1.6 m, 0.24 cm^3, 0.384 mmol) was added with vigorous stirring. The cooling bath was kept at −40°C for 1 h and then allowed to slowly reach room temperature. After 20 h the mixture was filtered through Celite, and the solvent was removed in vacuo to give a orange-red solid. (Yield 75%). NMR: $^1H(CDCl_3)$, δ 4.68 (d, $^2J_{PH} = 19.5$ Hz, CH), 7.51 (d, $^3J_{HH} = 3.2$ Hz, H_b), 7.37 (d, $^3J_{HH} = 3.2$ Hz, H_c), 7.40–7.70 [m, 28H, $PPh_2(C_6H_4)$]; ^{13}C-$\{^1H\}(CDCl_3)$, δ 62.63 (d, $^1J_{PC} = 110.8$ Hz, CH), 169.70 (d, $^2J_{PC} = 21.1$ Hz, CO), 173.74 (s, C_a), 142.50 (s, C_b), 121.69 (s, C_c), 123.51 [d, $^1J_{PC} = 92.1$ Hz, $C_i(PPh_2)$], 129.82 [d, $^2J_{PC} = 12.6$ Hz, $C_o(PPh_2)$], 133.31 [d, $^3J_{PC} = 10.3$ Hz, $C_m(PPh_2)$], 133.42 [d, $^4J_{PC} = 3.1$ Hz, $C_p(PPh_2)$], 128.41 [d, $^1J_{PC} = 71.0$ Hz, $C_1(C_6H_4)$], 138.83 [d, $^2J_{PC} = 11.0$ Hz, $C_2(C_6H_4)$], 132.42 [d, $^3J_{PC} = 10.6$ Hz, $C_3(C_6H_4)$], 132.74 [d, $^4J_{PC} = 3.0$ Hz, $C_4(C_6H_4)$], 130.61 [d, $^3J_{PC} = 11.0$ Hz, $C_5(C_6H_4)$], 128.82 [d, $^2J_{PC} = 12.6$ Hz, $C_6(C_6H_4)$]; ^{31}P-$\{^1H\}(CDCl_3$, H_3PO_4 as reference), δ 16.05 [s, $PPh_2(C_6H_4)$]. IR (Nujol): 1560 [ν(C=O)], 274 and 267 [ν(Nb–Cl)]cm^{-1}. (Found: C, 50.8; H, 3.0; N, 2.3. Calcd. for $C_{46}H_{34}Nb_2Cl_4N_2O_2P_2S_2$: C, 50.2; H, 3.1; N, 2.5). Mass spectrum (m/z assignment, % intensity): 1086 D [M–C_3H_2NS], 7; 971 D [M–$2C_3H_2NS$], 12; 800 D [M-OCHCPPh_3], 15; 388 D [(2-TCMP)], 100.

3.13. Preparation of $[NbCl_3(2\text{-}TCMP)(AuPPh_3)]_2(CF_3SO_3)_2$ (**10**)

To a suspension of [$NbCl_3$(2-TCMP)(PhC≡CMe)] (**5**) (235 mg, 0.334 mmol) in toluene (40 cm^3), an equimolar quantity of [$AuPPh_3$](CF_3SO_3) (204 mg, 0.334 mmol) in dichloromethane (30 cm^3) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give an orange solid. (Yield 75%). NMR: $^1H(CDCl_3)$, δ 5.78 (d, $^2J_{PH} = 13.1$ Hz, CH), 8.04 (d, $^3J_{HH} = 2.7$ Hz, H_b), 7.73 (d, $^3J_{HH} = 2.7$ Hz, H_c), 7.44–7.86 (m, 60 H, PPh_3 and $AuPPh_3$); ^{13}C-$\{^1H\}(CDCl_3)$, δ 34.99 (d, $^1J_{PC} = 67.5$ Hz, CH), 179.13 (s, CO), 183.90 (s, C_a), 145.51 (s, C_b), 129.18 (s, C_c), 117.90, 117.72 [d, $^1J_{PC} = 87.5$, 88.8 Hz, $C_i(PPh_3$ or $AuPPh_3)$], 130.51, 130.42 [d, $^2J_{PC} = 13.2$, 12.7 Hz, $C_o(PPh_3$ or $AuPPh_3)$], 134.01, 133.83 [d, $^3J_{PC} = 10.3$, 10.7 Hz, $C_m(PPh_3$ or $AuPPh_3)$], 135.32, 135.22 [d, $^4J_{PC} = 3.1$, 2.5 Hz, $C_p(PPh_3$ or $AuPPh_3)$]; ^{31}P-$\{^1H\}(CDCl_3$, H_3PO_4 as reference), δ 21.69 (s, PPh_3), 23.08 (s, $AuPPh_3$); $^{19}F(CDCl_3$, $CFCl_3$ as reference) δ −79.40 (s, CF_3SO_3); IR (Nujol): 1562 [ν(C=O)], 326 [ν(Nb–Cl)]cm^{-1}. (Found: C, 42.3; H, 2.8; N, 1.3. Anal. Calc. for $C_{84}H_{66}Nb_2Au_2Cl_6F_6N_2O_8P_4S_4$: C, 42.2; H, 3.0; N, 1.4). Mass spectrum (m/z assignment, % intensity): 1572 D [M^+–$2PPh_3$], 5; 1417 D [M^+–$2PPh_3$–C_3H_2NS], 9; 721 D [$Au(PPh_3)_2]^+$, 42; 459 D [$Au(PPh_3)]^+$, 40; 388 D [(2-TCMP)], 6; 303 D [(2-TCMP)–C_3H_2NS], 100.

3.14. Preparation of $[NbCl_3(2\text{-}TCMP)\{AuPPh_2(C_3H_2SN)\}]_2(CF_3SO_3)_2$ (**11**)

To a suspension of [$NbCl_3$(2-TCMP)(PhC≡CMe)] (**5**) (235 mg, 0.334 mmol) in toluene (40 cm^3), an equimolar quantity of [$AuPPh_2(C_3H_2SN)$](CF_3SO_3) (206 mg, 0.334 mmol) in dichoromethane (30 cm^3) was added. The suspension was stirred at room temperature for 20 h. The solvent was removed in vacuo to give a brown solid. (Yield 70%). NMR: $^1H(CDCl_3)$, δ 5.73 (d, $^2J_{PH} = 13.4$ Hz, CH), 8.33 (d, $^3J_{HH} = 3.8$ Hz, H_b), 7.78 (d, $^3J_{HH} = 2.9$ Hz, H_c), 8.01 [d, $^3J_{HH} = 2.9$ Hz, $H_b\{PPh_2(C_3H_2SN)\}$, 7.80 [d, $^3J_{HH} = 2.9$ Hz, $H_c\{PPh_2(C_3H_2SN)\}$, 7.44–7.85 [m, 50 H, PPh_3 and $PPh_2(C_3H_2SN)$]; ^{13}C-$\{^1H\}(CDCl_3)$, δ 34.53 (d, $^1J_{PC} = 57.7$ Hz, CH), 177.28 (s, CO), 183.94 (s, C_a), 145.38 (s, C_b), 129.04 (s, C_c), 117.80 [d, $^1J_{PC} = 88.9$ Hz, $C_i(PPh_3)$], 130.35 [d, $^2J_{PC} = 13.3$ Hz, $C_o(PPh_3)$], 133.80 [d, $^3J_{PC} = 10.7$ Hz, $C_m(PPh_3)$], 135.22 [d, $^4J_{PC} = 3.4$ Hz, $C_p(PPh_3)$], 164.28 [d, $^1J_{PC} = 41.5$ Hz, $C_a\{PPh_2(C_3H_2SN)\}$], 134.08 [d, $^3J_{PC} = 10.7$ Hz, $C_b\{PPh_2(C_3H_2SN)\}$], 126.01 [s, $C_c\{PPh_2(C_3H_2SN)\}$], 130.50 [d, $^1J_{PC} = 30.3$ Hz, $C_i\{PPh_2(C_3H_2SN)\}$], 134.00 [d, $^2J_{PC} = 19.1$ Hz, $C_o\{PPh_2(C_3H_2SN)\}$], 129.60 [d, $^3J_{PC} = 10.3$ Hz, $C_m\{PPh_2(C_3H_2SN)\}$], 132.10 [d, $^4J_{PC} = 2.0$ Hz, $C_p\{PPh_2(C_3H_2SN)\}$]; ^{31}P-$\{^1H\}(CDCl_3$, H_3PO_4 as reference), δ 21.68 (s, PPh_3), 23.01 [s, $\{PPh_2(C_3H_2SN)\}$]; $^{19}F(CDCl_3$, $CFCl_3$ as reference) δ −79.49 (s, CF_3SO_3); IR (Nujol): 1568 [ν(C=O)], 328 [ν(Nb–Cl)]cm^{-1}. (Found: C, 38.4; H, 2.8; N, 2.2. Anal. Calc. for $C_{78}H_{60}Nb_2Au_2Cl_6F_6N_4O_8P_4S_6$: C, 38.9; H, 2.5; N, 2.3). Mass spectrum (m/z assignment, % intensity): 1566 D [M^+–$2\{PPh_2(C_3H_2SN)\}$], 5; 735 D [$Au\{PPh_2(C_3H_2SN)\}_2]^+$, 20; 466 D [$Au\{PPh_2(C_3H_2SN)\}]^+$, 35; 388 D [(2-TCMP)], 100.

3.15. Preparation of $[NbCl_3(2\text{-}TCMP)Ag]_2(CF_3SO_3)_2$ (**12**)

To a suspension of [$NbCl_3$(2-TCMP)(PhC≡CMe)] (**5**) (200 mg, 0.284 mmol) in acetone (40 cm^3), an equimolar quantity of $AgCF_3SO_3$ (73 mg, 0.284 mmol) was added. The suspension was stirred at room temperature for 1 h. The solvent was removed in vacuo to give a red solid. (Yield 50%). NMR: $^1H(CDCl_3)$, δ 5.87 (d, $^2J_{PH} = 13.2$ Hz, CH), 8.15 (d, $^3J_{HH} = 2.9$ Hz, H_b), 7.97 (d, $^3J_{HH} = 2.9$ Hz, H_c), 7.42–7.75 (m, 30H, PPh_3); ^{13}C-$\{^1H\}(CDCl_3)$, δ 35.11 (d, $^1J_{PC} = 59.4$ Hz, CH), 164.47 (d, $^2J_{PC} = 14.2$ Hz, CO), 182.96 (s, C_a), 144.35 (s, C_b), 129.17 (s, C_c), 118.00 [d, $^1J_{PC} = 89.1$ Hz, $C_i(PPh_2)$], 130.35 [d, $^2J_{PC} = 13.6$ Hz, $C_o(PPh_2)$], 133.85 [d, $^3J_{PC} = 11.0$ Hz, $C_m(PPh_2)$], 135.22 [d, $^4J_{PC} = 3.1$ Hz, $C_p(PPh_2)$]; ^{31}P-$\{^1H\}(CDCl_3$, H_3PO_4 as reference), δ 21.15, 21.10 (dd, $^2J_{107AgP} = 6.7$ Hz or $^2J_{109AgP} = 6.1$ Hz, PPh_3). IR (Nujol): 1560 [ν(C=O)], 335 [ν(Nb–Cl)]cm^{-1}. (Found: C, 33.9; H, 2.0; N, 1.8. Anal. Calc. for

$C_{48}H_{36}Nb_2Ag_2Cl_6F_6N_2O_8P_2S_4$: C, 34.1; H, 1.6; N, 2.1). Mass spectrum (m/z assignment, % intensity): 1309D $[M^+ - C_3H_2SN]$, 7; 667D $[\frac{1}{2}M^+ - Cl]$, 15; 388 D [(2-TCMP)], 100; 370 D $[AgPPh_3]^+$, 20.

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