New Monocyclopentadienyl Complexes of Tantalum(V) and Titanium(IV) with Chelating Pyrimidinethiolate and Oxypyridine Ligands − Molecular Structure of [Cp*$TaCl_3(SC_6H_7N_2)$]

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New monocyclopentadienyl species of Ta^V, [Cp*TaL_3(XR)] (L = Cl, Me, X = O, S) bearing 4,6-dimethyl-2-pyrimidinethiolate (SR = $SC_6H_7N_2$) or 3-cyano-4,6-dimethyloxypyridine (OR = $OC_8H_7N_2$) ligands were prepared, namely [Cp*$TaCl_3(SC_6H_7N_2)$] (**1**), [Cp*$TaCl_3(OC_8H_7N_2)$] (**2**), [Cp*$TaMe_3(SC_6H_7N_2)$] (**3**). In addition, a bis(oxypyridine)titanium(IV) complex [Cp*$TiMe_2(OC_8H_7N_2)_2$] was isolated. The X-ray structure analysis of **1** revealed that the thiolate group is bonded to the metal center through the sulfur atom and one of the nitrogen atoms in an η^2-fashion. The reactivity of complex **3** with isocyanides (CNR), R = *t*Bu, Xyl (Xyl = 2,6-dimethylphenyl) was also studied showing differences depending on the nature of R group. The reaction with 2,6-dimethylphenyl isocyanide gives the azatantalacyclobutane complex [Cp*TaMe{XylN=CC(Me_2)NXyl}($SC_6H_7N_2$)] (**5**) as the final product, whereas in the reaction with *tert*-butyl isocyanide the η^2-imine-containing complex [Cp*Ta{*t*BuNC(Me_2)}($SC_6H_7N_2$)] (**6**) is proposed to be formed. The dynamic behavior of [Cp*$TaMe_3(SC_6H_7N_2)$] (**3**) was also studied by variable-temperature ^1H NMR spectroscopy.

Introduction

Ligand systems with two different donor atoms are attracting increasing interest in the chemistry of metal complexes. Under appropriate conditions, the remaining donor atom can coordinate reversibly to the metal center and eventually block a vacant coordination site.[1] In this field, complexes that incorporate pyridinethiolate and pyrimidinethiolate, as well as their alkoxide analogues, are interesting for their ability to chelate and bridge transition metal atoms, allowing access to both mono- and oligonuclear products. In addition, they contain functional groups that are common in crude oils and nucleic acids. The thiolate complexes are of particular interest in the field of bioinorganic chemistry due to their relevance to the structure, bonding and function of biologically active reaction centers such as nitrogenase or metalothioneins.[2,3]

Thiolate complexes also play an important role in different reactions, such as the desulfurization of organosulfur compounds [4,5] and metal-catalyzed synthetic reactions involving C−S bond cleavage and formation.[6] All of these features, as well as the propensity of sulfur to form M(μ-SR)M′ bridges, has led to the widespread use of sulfur-containing complexes as synthons for multinuclear transition metal complexes.[7]

Alkoxide and aryloxide ligands have been widely used to stabilize high oxidation states of early transition metals[8] and numerous studies have been reported concerning the catalytic activity of their complexes in alkene metathesis and, in particular, in alkene polymerization.[9]

A systematic study of the chemistry of mono- and bis(cyclopentadienyl) complexes of group-4 transition metals bearing chelating pyrimidinethiolate ligands and analogous oxygen derivatives has been carried out by our research group in recent years.[10] The interesting coordination modes and the reactivity observed along with the scarce number of reported examples of this kind of compounds[11] encouraged us to prepare analogous monocyclopentadienyl complexes of group-5 metals. In particular, this paper will focus on the synthesis, structural details and reactivity of

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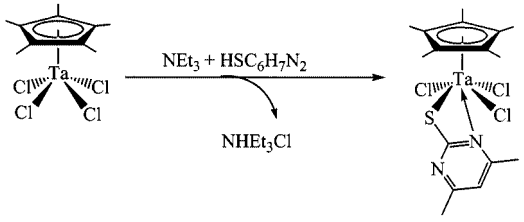
new monocyclopentadienyl complexes of tantalum(v) and titanium(iv) bearing chelating pyrimidinethiolate and oxypyridine ligands.

Results and Discussion

The reaction of [Cp*TaCl$_4$] (Cp* = η^5-C$_5$H$_5$) with 4,6-dimethyl-2-mercaptopyrimidine (HSR, R = C$_6$H$_7$N$_2$) in the presence of 1 equiv. of triethylamine proceeds at room temperature in toluene to yield the complex [Cp*TaCl$_3$(SR)] (**1**) [Equation (1)]. Attempts to perform the substitution of a second chlorine atom by a thiolate ligand were made under a wide variety of conditions but no further reaction was observed and in all cases the only isolated compound was **1**.



(1)

1

Complex **1** was isolated as an air-sensitive orange solid, soluble in toluene and THF and less soluble in pentane or Et$_2$O. It was characterized by ^{1}H and ^{13}C NMR and IR spectroscopy as well as by elemental analysis (see Exp. Sect.). The ^{1}H and ^{13}C NMR spectra indicate that the thiolate ligand is bonded to the metal atom in a bidentate fashion. For example, two resonances at δ = 1.71 and 2.88 ppm are present in the ^{1}H MNR spectrum for the two nonequivalent methyl groups of the thiolate ligand, in accordance with the proposed η^2-*S*,*N* coordination mode.

Crystals of **1**, suitable for an X-ray crystal structure determination, were obtained by slow diffusion of pentane into a saturated solution of the complex in toluene. Figure 1 shows an ORTEP diagram of the molecule; selected bond lengths and angles are given in Table 1.

The structure consists of discrete molecules separated by van der Waals distances. The tantalum atom is bonded to the cyclopentadienyl ring in an η^5-mode, to three chlorine atoms and to the thiolate ligand in the proposed chelate fashion. In this way, the coordination around the metal atom is pseudo-octahedral, with the tantalum atom 0.59 Å out of the plane defined by the S(1), Cl(1), Cl(2) and Cl(3) atoms. The nitrogen atom of the pyrimidinethiolate ligand is located *trans* to the Cp* group. The Ta(1)−S(1) bond length [2.456(2) Å] is as expected for tantalum(v) thiolate complexes[12] and the Ta(1)−N(1) bond [2.327(5) Å] is also in the normal range for pyridyltantalum(v) complexes.[13] Finally, the Ta(1)−S(1)−C(1) angle [84.6(2)°] is in accordance with others observed in this kind of complexes.[10,11]

When 3-cyano-2-hydroxy-4,6-dimethylpyridine was treated with [Cp*TaCl$_4$] in the presence of Et$_3$N in toluene at room temperature [Equation (2)] complex **2** was isolated

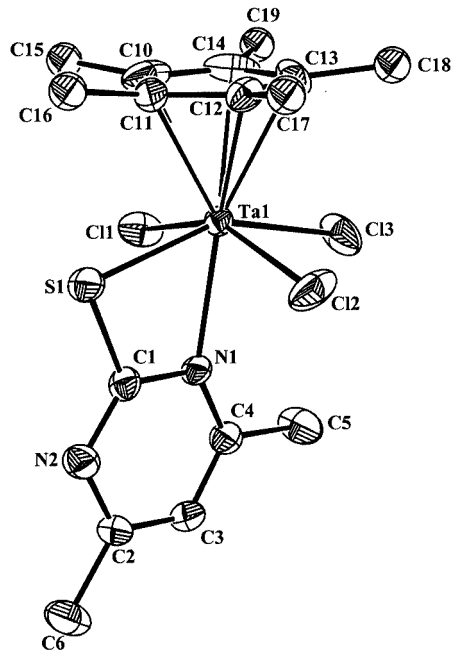
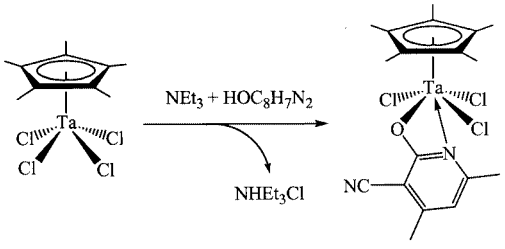


Figure 1. ORTEP drawing of complex **1** with the atomic labeling scheme; hydrogen atoms omitted for clarity; thermal ellipsoids are at the 30% level of probability

Table 1. Bond lengths [Å] and angles [°] for **1**

Ta(1)−N(1)	2.327(5)	N(1)−Ta(1)−Cl(1)	76.2(1)
Ta(1)−Cl(3)	2.393(2)	N(1)−Ta(1)−Cl(2)	76.3(2
Ta(1)−Cl(2)	2.407(2)	N(1)−Ta(1)−Cl(3)	87.6(1)
Ta(1)−Cl(1)	2.407(2)	Cl(2)−Ta(1)−Cl(1)	151.37(8)
Ta(1)−C(14)	2.431(8)	Cl(3)−Ta(1)−Cl(1)	85.4(1)
Ta(1)−C(11)	2.447(7)	Cl(3)−Ta(1)−Cl(2)	85.5(1)
Ta(1)−S(1)	2.456(2)	N(1)−Ta(1)−S(1)	64.3(1)
Ta(1)−C(13)	2.463(8)	Cl(1)−Ta(1)−S(1)	87.87(8)
Ta(1)−C(10)	2.472(8)	Cl(2)−Ta(1)−S(1)	87.49(9)
Ta(1)−C(12)	2.484(7)	Cl(3)−Ta(1)−S(1)	151.96(7)
		C(1)−S(1)−Ta(1)	84.6(2)
		C(1)−N(1)−Ta(1)	99.5(4)
		C(4)−N(1)−Ta(1)	143.8(4)

as a yellow, air-sensitive solid which was sparingly soluble in alkanes but soluble in toluene or THF.



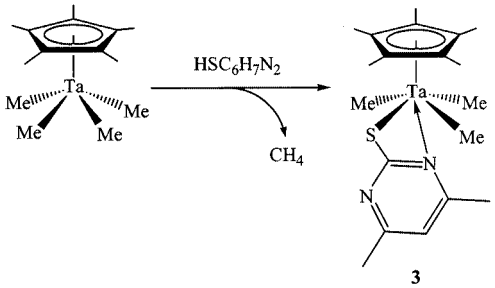
(2)

2

The ^{1}H and ^{13}C NMR spectra for **2** are analogous to those previously described for **1**. For example, the ^{1}H NMR spectrum exhibits two singlet resonances at δ = 1.52 and 2.49 ppm, attributable to the two nonequivalent methyl

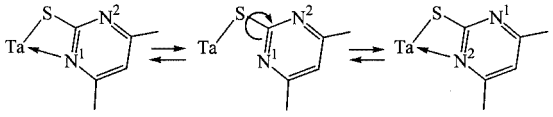
groups of the alkoxide ligand. By analogy with the situation for compound **1**, a bidentate coordination mode for the alkoxide ligand is proposed to be present in this complex.

Another general way to synthesize thiolate complexes is to carry out the protonolysis of metal−alkyl bonds with the corresponding thiol. In this way, the reaction of Cp^*TaMe_4 with 2-mercapto-4,6-dimethylpyrimidine at 80 °C in toluene yields $[Cp^*TaMe_3(SR)]$ (**3**) as an orange solid which is soluble in toluene and THF and scarcely soluble in pentane [Equation (3)]. As in the case of the chlorinated complex **1**, all attempts to increase the number of thiolate ligands around the metal atom were unsuccessful.



3 (3)

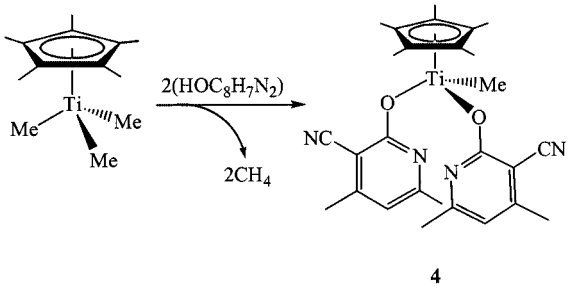
The ^{1}H NMR spectrum of **3** at room temperature shows a broad resonance at δ = 2.43 ppm that integrates for six protons and which is assigned to the methyl groups of the thiolate ligand. The broadness of the peak indicates a fluxional behavior through which both nitrogen atoms interchange their positions in the coordination sphere of the tantalum atom by rotation around the S−C bond (Scheme 1).



Scheme 1

In order to study this fluxional behavior a variable-temperature (VT) ^{1}H NMR experiment was carried out. At −40 °C the methyl groups are inequivalent and appear as two signals at δ = 2.74 and 2.04 ppm, indicating that rotation around the C−S bond is hindered for the thiolate ligand. When the temperature is raised, the peaks coalesce at −10 °C. The two site-exchange equations[14] and the coalescence temperature of 263 K can be used to estimate a value for $\Delta G^{\neq}$ of 12.0(2) kcal·mol^{-1} for the process. This value is in accordance with that previously found for analogous systems, i.e. $[Cp_2ZrMe(SR)]$ (SR = 4,6-dimethylpyrimidine-2-thiolate).[10a]

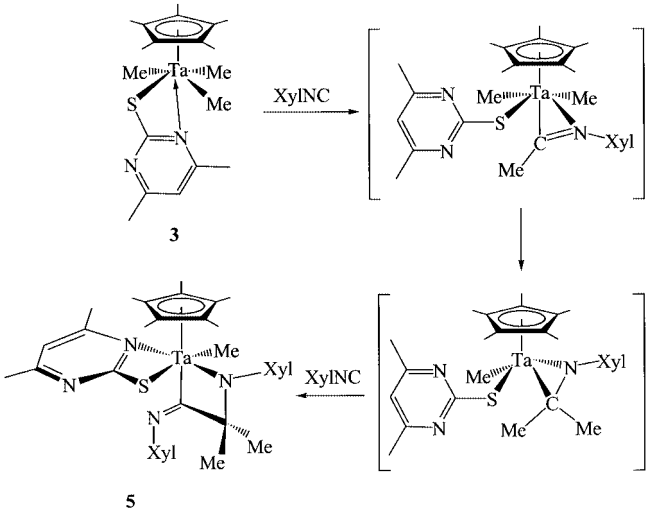
Complex **4** was synthesized in a similar way to **3**, by reaction of $[Cp^*TiMe_3]$ with 2 equiv. of 3-cyano-2-hydroxy-4,6-dimethylpyridine in toluene [Equation (4)].



4 (4)

This compound was isolated as a red solid which is soluble in toluene and THF but less soluble in pentane. The ^{1}H NMR spectrum shows a singlet at δ = 1.00 ppm, corresponding to the methyl group bonded to the titanium atom and a further singlet at δ = 1.77 ppm for the Cp* methyl groups. The pyridine ligands give rise to three signals, two of them at δ = 1.71 and 1.82 ppm are assigned to the methyl groups bonded to the pyridine rings, and the other, at δ = 5.46 ppm, corresponds to the aromatic proton. It can be inferred from these results that in complex **4** the two pyridine ligands are in the same chemical environment, and an η^1-*O* coordination is proposed for both ligands.

Finally, the reactivity of **3** toward isocyanide ligands has been considered. Compound **3** reacts readily in toluene at room temperature with 2,6-dimethylphenyl isocyanide in a 1:2 molar ratio to give the azatantalacyclobutane complex **5** containing an iminoacyl fragment (Scheme 2).



3 **5**

Scheme 2

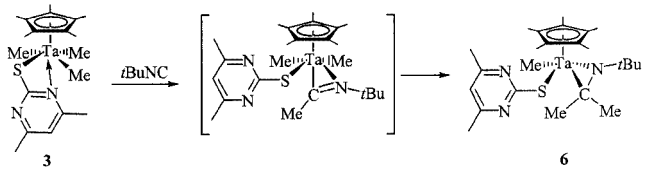
The ^{1}H NMR spectrum of compound **5** shows a singlet signal at δ = 1.39 ppm which is assigned to the Cp* protons and nine singlet signals between δ = 1.00 and 2.45 ppm, each of them integrating for three protons, corresponding to the methyl groups present in the molecule (see Exp. Sect.).

Furthermore, the ^{13}C NMR spectrum shows, among others, two signals at δ = 230.0 and 86.7 ppm, which we tentatively assign to an iminoacyl carbon atom and to the quaternary carbon atom of the Ta−N−C−C metallacycle.[15]

We propose (see Scheme 2) that, initially, complex **3** reacts with one molar equivalent of xylyl isocyanide by insertion into one Ta−Me bond to form an η^2-iminoacyl-containing complex. A second methyl migration would then occur, forming an η^2-imine-containing species. Finally, the insertion of a second isocyanide molecule into the newly formed Ta−C bond would lead to **5**.

Recently, we reported a mechanism for the reaction of xylyl isocyanide with $[Cp^*TaMe_2(SCH_2CH_2)_2O]$ in which the proposed η^2-imine intermediate was isolated .[16] Attempts to isolate this type of intermediate in the reaction of **3** were unsuccessful.

Furthermore, compound **3** reacts readily with *tert*-butyl isocyanide, at room temperature, in C_6D_6 on an NMR-tube scale, to give the η^2-imine complex **6** as the only detectable compound by ^1H NMR spectroscopy (Scheme 3). Isolation of **6** on a preparative scale with an acceptable level of purity was not possible.



Scheme 3

In contrast to the reactivity observed for complex **3** with xylyl isocyanide, no further reaction was observed when an excess of *tert*-butyl isocyanide was added.

The ^1H and ^{13}C NMR spectroscopic data point to an η^2-coordination of the imine ligand, while the thiolate would act as a monodentate ligand (see Exp. Sect.). The ^1H NMR spectroscopic data exhibit a singlet signal at $\delta = 0.04$ ppm corresponding to the methyl group bonded to the tantalum atom, a singlet at $\delta = 1.31$ ppm integrating for nine protons assignable to the *tert*-butyl group and a broad signal at $\delta = 1.79$ ppm due to the methyl groups of the thiolate ligand, indicating that a fluxional behavior similar to that described for **3** takes place. The methyl groups bonded to the quaternary carbon atom of the imine ligand appear as two singlets at $\delta = 1.66$ and 1.99 ppm, respectively. The ^{13}C NMR spectrum shows, as its outstanding feature, a signal at $\delta = 68.1$ ppm corresponding to the quaternary carbon atom of the imine ligand. The high-field shift of this resonance seems to confirm the η^2-coordination of the imine group.[17]

Conclusion

In this paper we report the synthesis of some new monocyclopentadienyl-containing tantalum(V) and titanium(IV) complexes with chelating pyrimidinethiolate and oxypyridine ligands. These compounds were prepared by halide or methyl displacement. The molecular structure of **1**, as determined by X-ray diffraction studies, shows a pseudo-octahedral geometry around the tantalum atom with the thiolate ligand chelating two coordination positions. This structural situation can be considered to also be present in the related tantalum complexes **2** and **3**, on the basis of spectroscopic data. We have also studied the reactivity of complex **3** with xylyl and *tert*-butyl isocyanides. With the first reagent the azatantalacyclobutane complex **5** was isolated, whereas with the second isocyanide the η^2-imine-containing complex **6** was obtained.

Experimental Section

General Remarks: The preparation and handling of the described compounds was performed with rigorous exclusion of air and moisture under nitrogen using standard vacuum line and Schlenk techniques. All solvents were dried and distilled under nitrogen. The following reagents were prepared by literature procedures: $[Cp^*TaCl_4]$[18] $[Cp^*TaMe_4]$[19] and $[Cp^*TiMe_3]$.[20] The commercially available compounds Cp*H, MeLi in diethyl ether, xylyl isocyanide, *tert*-butyl isocyanide, 2-mercapto-4,6-dimethylpyrimidine and 3-cyano-2-hydroxy-4,6-dimethylpyridine were used as received from Aldrich. ^1H and ^{13}C NMR spectra were recorded with a 200 Mercury Varian Fourier Transform spectrometer. Trace amounts of protonated solvents were used as reference, and chemical shifts are reported in units of ppm relative to $SiMe_4$. IR spectra were recorded in the region 4000−400 cm^{-1} with a Nicolet Magna-IR 550 spectrophotometer as Nujol mulls using PET cells.

$[Cp^*TaCl_3(SC_6H_7N_2)]$ (1): $HSC_6H_7N_2$ (0.136 g, 0.97 mmol) and Et_3N (0.140 mL, 0.97 mmol) were added to a solution of Cp^*TaCl_4 (0.446 g, 0.97 mmol) in 5 mL of toluene. The mixture was stirred at room temperature for 1 h. After filtration, the solid was washed twice with 5 mL of THF. The resulting solution was concentrated to dryness and the solid obtained was washed with diethyl ether to give an orange solid, which was characterized as **1** (0.425 g, 78%). IR (Nujol/PET): $\tilde{\nu} = 1591$ cm^{-1} (s), 1558 (w), 1520 (s), 1342 (m), 1271 (s), 1021 (m), 956 (w), 848 (m). ^1H NMR (200 MHz, C_6D_6): $\delta = 1.71$ (s, 3 H, CH_3), 2.24 (s, 15 H, Cp*), 2.88 (s, 3 H, CH_3), 5.67 (s, 1 H, CH pyrimidine) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 13.0$ (Cp*), 23.7 (CH_3), 24.8 (CH_3), 119.6 (CH pyrimidine), 130.3 (Cp*), 165.5 ($C-CH_3$), 168.5 (CCH_3), 172.2 (CS) ppm. $C_{16}H_{22}N_2Cl_3STa$ (561.73): calcd. C 34.17, H 3.91, N 4.98; found C 34.17, H 3.90, N 5.09.

$[Cp^*TaCl_3(OC_8H_7N_2)]$ (2): $HOC_8H_7N_2$ (0.517 g, 3.49 mmol) and Et_3N (0.486 mL, 3.49 mmol) were added to a solution of $[Cp^*TaCl_4]$ (1.6 g, 3.49 mmol) in 25 mL of toluene. The mixture was stirred at room temperature for 2 h. After filtration, the resulting solution was concentrated to dryness and the solid obtained was washed with pentane to give a yellow solid, which was characterized as **2** (1.465 g, 74%). IR (Nujol/PET): $\tilde{\nu} = 2216$ cm^{-1} (s), 1666 (w), 1604 (ms), 1551 (s), 1304 (s), 1256 (m), 1026 (w), 651 (w), 570 (s). ^1H NMR (200 MHz, C_6D_6): $\delta = 1.52$ (s, 3 H, CH_3), 2.22 (s, 15 H, Cp*), 2.49 (s, 3 H, CH_3), 5.49 (s, 1 H, CH pyridine) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): $\delta = 12.6$ (Cp*), 20.1 (CH_3), 22.1 (CH_3), 94.1 (*C*CN), 112.9 (CN), 118.7 (Cp*), 131.9 (CH pyridine), 155.9 (CCH_3), 157.3 (CCH_3), 168.3 (CO) ppm. $C_{18}H_{22}N_2Cl_3OTa$ (569.69): calcd. C 37.95, H 3.89, N 4.92; found C 38.14, H 3.75, N 4.66.

[Cp*TaMe$_3$(SC$_6$H$_7$N$_2$)] (3): Toluene (10 mL) was added to a mixture of Cp*TaMe$_4$ (0.379 g, 1.01 mmol) and HSC$_6$H$_7$N$_2$ (0.141 g, 1.01 mmol). The solution was heated slowly to 80 °C and stirred at this temperature for 1 h. After cooling, the mixture was filtered and the solvent removed. The oil obtained was washed with 10 mL of *n*-pentane to afford an orange solid (0.373 g, 75%) which was characterized as **3**. IR (Nujol/PET): $\tilde{\nu}$ = 1623 cm^{-1} (w), 1580 (s), 1532 (s), 1340 (s), 1274 (s), 1138 (m), 1026 (m) 955 (w) 844 (w), 814 (w). ^{1}H NMR (200 MHz, [D$_8$]toluene): δ = 0.23 (s, 6 H, CH$_3$Ta), 0.34 (s, 3 H, CH$_3$Ta), 2.04 (s, 15 H, Cp*), 2.43 (br. s, 6 H, CH$_3$ pyrimidine), 6.04 (s, 1 H, CH pyrimidine) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 11.6 (Cp*), 23.7 (CH$_3$, pyrimidine), 45.6 (CH$_3$Ta), 48.7 (CH$_3$Ta), 119.1 (CH pyrimidine), 120.5 (Cp*), 165.8 (*C*CH$_3$), 174.6 (CS) ppm. C$_{19}$H$_{31}$N$_2$STa (500.48): calcd. C 45.60, H 6.24, N 5.60; found C 45.39, H 5.82, N 5.61.

[Cp*TiMe(OC$_8$H$_7$N$_2$)$_2$] (4): Toluene (2 mL) was added to a mixture of [Cp*TiMe$_3$] (0.209 g, 0.92 mmol) and HOC$_8$H$_7$N$_2$ (0.271 g, 1.83 mmol). The solution was stirred at room temperature for 5 h and filtered. By addition of 4 mL of *n*-pentane and cooling to −30 °C a red solid (0.190 g, 42%) was obtained and characterized as **4**. IR (Nujol/PET): $\tilde{\nu}$ = 2218 cm^{-1} (s), 1560 (s), 1504 (s), 1221 (s), 1157 (m), 1098 (s), 783 (ms). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 1.00 (s, 3 H, CH$_3$-Ti), 1.71 (s, 6 H, CH$_3$), 1.77 (s, 15 H, Cp*), 1.82 (s, 6 H, CH$_3$), 5.46 (s, 2 H, CH pyridine) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 11.9 (Cp*), 20.0 (CH$_3$), 20.9 (CH$_3$), 63.8 (CH$_3$Ti), 91.4 (*C*CN), 114.4 (CN), 115.0 (Cp*), 127.4 (CH pyridine), 155.1 (*C*CH$_3$), 157.5 (*C*CH$_3$), 171.0 (CO) ppm. C$_{27}$H$_{32}$N$_4$O$_2$Ti (492.44): calcd. C 65.85, H 6.55, N 11.38; found calcd. C 65.57, H 6.88, N 11.72.

[Cp*TaMe{XylN=CC(Me$_2$)NXyl}(SC$_6$H$_7$N$_2$)] (5): Toluene (5 mL) was added to a mixture of [Cp*TaMe$_3$(SC$_6$H$_7$N$_2$)] (0.132 g, 0.26 mmol) and XylN≡C (0.70 g, 0.53 mmol). The solution was stirred at room temperature for 30 min. After that, the mixture was filtered and the solvent removed. The oil obtained was washed with 5 mL of cool *n*-pentane to afford a yellow solid (0.110 g, 54%) which was characterized as **5**. IR (Nujol/PET): $\tilde{\nu}$ = 1666 cm^{-1} (w), 1633 (m), 1593 (s), 1553 (m). ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 1.00 (s, 3 H, CH$_3$-Ta), 1.29 (s, 3 H, CH$_3$), 1.39 (s, 15 H, Cp*), 1.44 (s, 3 H, CH$_3$), 1.76 (s, 3 H, CH$_3$), 1.94 (s, 3 H, CH$_3$), 2.11 (s, 3 H, CH$_3$), 2.15 (s, 3 H, CH$_3$), 2.40 (s, 3 H, CH$_3$), 2.45 (s, 3 H, CH$_3$), 5.64 (s, 1 H, CH pyrimidine), 6.57−6.82 (m, 6 H, Xyl) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 10.8 (Cp*), 19.6, 20.1, 21.8, 22.1, 22.3, 23.5, 23.8, 24.3 (CH$_3$), 39.8 (CH$_3$Ta), 86.7 (*C*Me$_2$), 116.9 (CH pyrimidine), 119.6 (Cp*), 119.6 (CH, Xyl), 125.0 (CH, Xyl), 127.1 (CH, Xyl), 127.9 (CH, Xyl), 128.4 (CH, Xyl), 128.6 (CH, Xyl) 136.4 (*C*CH$_3$, Xyl), 137.0 (*C*CH$_3$, Xyl), 146.9 (*C*N=C), 154.8 (CN), 164.9 (*C*CH$_3$, pyrimidine), 165.8 (*C*CH$_3$, pyrimidine), 176.7 (CS), 230.0 (C=N) ppm. C$_{37}$H$_{49}$N$_4$STa (762.83): calcd. C 58.26, H 6.47, N 7.34; found C 57.80, H 7.34, N 7.61.

[Cp*TaMe{*t*BuNC(Me$_2$)}(SC$_6$H$_7$N$_2$)] (6): *t*BuN≡C (7μL, 0.06 mmol) was added to a solution of Cp*TaMe$_3$(SC$_6$H$_7$N$_2$) (0.031 g, 0.06 mmol) in 0.7 mL of C$_6$D$_6$. The mixture was allowed to react at room temperature in an NMR tube during 10 min to yield the proposed complex **6** as only detectable compound. ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 0.04 (s, 3 H, CH$_3$Ta), 1.31 (s, 9 H, *t*Bu), 1.62 (s, 15 H, Cp*), 1.66 (s, 3 H, CH$_3$), 1.79 (br, 6 H, CH$_3$), 1.99 (s, 3 H, CH$_3$), 5.79 (s, 1 H, CH pyrimidine) ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ = 11.4 (Cp*), 23.6 (CH$_3$ pyrimidine), 27.3, 32.8 (*C*H$_3$C=N), 31.5 (*t*Bu), 45.9 (CH$_3$Ta), 62.6 (*C*Me$_3$), 68.1 (*C*Me$_2$), 114.1 (CH pyrimidine), 116.3 (Cp*), 164.40 (*C*CH$_3$), 182.4 (CS) ppm.

Table 2. Crystal data and structure refinement for **1**

Empirical formula	C$_{16}$H$_{22}$Cl$_3$N$_2$STa
Formula mass	561.71
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, $P2_1/c$
Unit cell dimensions	a = 13.328(4) Å b = 8.596(3) Å, β = 90.74(3)° c = 17.224(2) Å
Volume	1973.1(9) Å^3
Z, calculated density	4, 1.891 Mg/m^3
Absorption coefficient	6.082 mm^{-1}
F(000)	1088
Crystal size	0.3 × 0.3 × 0.2 mm
θ range for data collection	2.37−27.97°
Limiting indices	$-17 \le h \le 17$, $0 \le k \le 11$, $0 \le l \le 22$
Reflections collected/unique	9175/4747 [R(int) = 0.0920]
Data/restraints/parameters	4747/0/213
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0351, $wR2$ = 0.0859
R indices (all data)	$R1$ = 0.0542, $wR2$ = 0.1060
Largest diff. peak and hole	1.297 and −2.295 e Å^{-3}

X-ray Crystallographic Study: The crystallographic data and experimental details are given in Table 2. Crystals of complex **1** suitable for an X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of the complex in toluene. A prismatic crystal was selected, sealed in a Lindeman capillary under dry nitrogen and used for data collection. Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 25 randomly distributed and carefully centered reflections. The data collection was performed with a NONIUS-MACH3 diffractometer equipped with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) using an ω/2θ scan technique to a maximum value of 56°. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR92)[21] and refined first isotropically by full-matrix least squares using SHELXL-97[22] program and then anisotropically by blocked full-matrix least-squares techniques for all the non-hydrogen atoms. The hydrogen atoms were included in calculated positions and refined as "riding" on their parent carbon atoms. CCDC-189366 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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