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Synthesis and spectroscopic characterization of α-keto ylide-containing Group 4 metal complexes. The X-ray molecular structure of [Cp*$ZrCl_3$(2-TCMP)], Cp* = η^5-C_5Me_5, 2-TCMP = [{2-thiazolylcarbonyl}methylene]triphenylphosphorane

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Abstract

The species $TiCl_4(thf)_2$ and $ZrCl_4$ reacted with a heterocycle-containing α-keto stabilized phosphorus ylide, 2-TCMP = [{2-thiazolylcarbonyl}methylene]triphenylphosphorane, to give the complexes [MCl_4(2-TCMP)], M = Ti (**1**), M = Zr (**2**). Reactions of **1** and **2** with $AgCF_3SO_3$ afforded the heterometallic complexes [MCl_4(2-TCMP)Ag]CF_3SO_3, M = Ti (**3**), M = Zr (**4**), and **2** also reacted with LiCp*, Cp* = C_5Me_5, to give the cyclopentadienyl-containing complex [Cp*$ZrCl_3$(2-TCMP)] (**5**). Complex **5** was also isolated, in greater yield, by an alternative method involving the reaction of $[Cp^*ZrCl_3]_n$ with the 2-TCMP ligand. The X-ray molecular structure of **5** was established and an X-ray study of the ligand was also carried out in order to compare the ligand and complex. Finally, the reactions of **5** with $PhCH_2MgCl$ and $AgCF_3SO_3$ gave rise to the corresponding complexes [Cp*$ZrCl_2(CH_2Ph)$(2-TCMP)] (**6**) and [Cp*$ZrCl_3$(2-TCMP)Ag]CF_3SO_3 (**7**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Titanium; Zirconium; α-Keto ylide; Silver; Cyclopentadienyl

1. Introduction

In organometallic chemistry the field of phosphorus ylides has undergone much development in the last few years, particularly due to the interesting applications of these materials in metal-promoted syntheses [1]. The chemistry of early transition metals and ylides is not widely studied and is mainly focused on cyclopentadienyl-containing species and $R_3P{=}CR'R''$ ylides [2]. However, we have recently described [3] 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≡CR′)] (dme = 1,2-dimethoxyethane), and new families of α-keto ylide-containing complexes [{$NbCl_3$-(2-TCMP)}$_2$] and [$NbCl_3$(2-TCMP)(RC≡CR′)] were isolated and characterized. In these complexes the ligand acts in a chelating manner and this chelation occurs through N,O-coordination to the metal center. In general, the α-keto stabilized phosphorus ylides $R_3P{=}C(R')COR''$ exhibit an ambidentate character (C vs O coordination), which can be rationalized in terms of the potential resonance forms A–C (Chart 1). In the complexes reported with this type of ligand, the chemi-

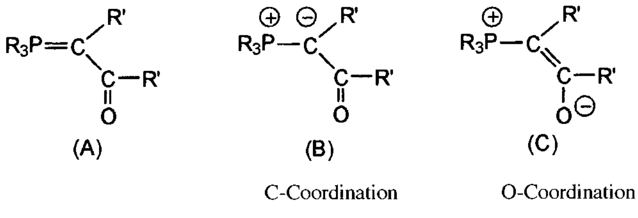

Chart 1.

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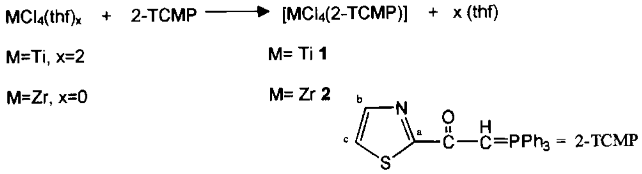
cal behavior of the α-keto stabilized phosphorus ylides has been clearly dominated by the C-coordination mode [4] and very few examples of O-coordinated ylides have been described [5].

In addition to the aforementioned niobium complexes, a few examples of O-coordinated α-keto stabilized phosphorus ylide-containing Group 4 metal complexes are known [6]. With these precedents in mind, we have studied the reactivity of our α-keto ylide, 2-TCMP, towards Group 4 metal halide species. We report here the preparation and structural characterization of new α-keto ylide-containing titanium and zirconium complexes and describe some aspects of their reactivity toward the formation of early–late heterometallic complexes and alkylation reactions.

2. Results and discussion

Firstly, the reactions of $TiCl_4(thf)_2$ and $ZrCl_4$ with the heterocycle-containing α-keto ylide [{2-thiazolylcarbonyl}methylene]triphenylphosphorane, $NOSC_4H_2$-$CHPPh_3$=2-TCMP, were considered. The standard reaction procedure involved the addition of the ligand to a suspension of the halide in THF in a 1:1 molar ratio at room temperature. The reaction mixture was stirred for 20 h to give a suspension that was yellow-green for Ti and red-orange for Zr. The products were isolated as air-sensitive solids after the appropriate work-up procedure (Section 3), and were characterized as complexes [$TiCl_4$(2-TCMP)] (**1**) and [$ZrCl_4$(2-TCMP)] (**2**) (Eq. (1)).



(1)

Analogous complexes were previously described by Burmeister et al. [6b] from the reactions of $MCl_4(thf)_2$ and the α-keto ylides Ph_3P=CHCOR, namely [$MCl_4(Ph_3PCHCOR)(thf)$] complexes, where a monodentate O-coordination was found. In our complexes an N,O-coordination to the metal center occurs because the ligand acts in a chelating manner (see below), totally replacing the thf in the titanium complex. The reactivity of **1** and **2** toward different reagents was also considered. Alkylation reactions were attempted but, unfortunately, the use of several sets of experimental conditions with different alkylating reagents gave only a mixture of products, which were not identified. We also studied the reactions of **1** and **2** with a Lewis acid coinage cationic species, $AgCF_3SO_3$. It was found that **1** and **2** react with $AgCF_3SO_3$ in a 1:1 molar ratio in acetone at room temperature to give, after appropriate work-up (Section 3), the corresponding heterometallic complexes [MCl_4(2-TCMP)Ag]CF_3SO_3, M = Ti (**3**), M = Zr (**4**) (Eq. (2)). In these complexes, a probable coordination of the Ag^+ fragment of the ylide carbon atom can be considered on the basis of spectroscopic evidence (see Eq. (2)).

$$[MCl_4(2\text{-TCMP})] + AgCF_3SO_3 \longrightarrow [MCl_4(2\text{-TCMP})Ag]CF_3SO_3 \quad \begin{matrix}M= Ti\ \mathbf{3}\\ M= Zr\ \mathbf{4}\end{matrix} \qquad (2)$$

A similar structural situation was previously proposed in the analogous niobium complex [$NbCl_3$(2-TCMP)Ag](CF_3SO_3) [3b]. In this investigation, we were also interested in the preparation of α-keto ylide-containing species that incorporate the cyclopentadienyl ligand. In order to prepare this type of species for Zr, two synthetic pathways were considered. The first consists of the addition to a suspension of **2** in THF of LiCp*, Cp* = C_5Me_5, in a 1:1 molar ratio at −78°C. After the appropriate work-up procedure (Section 3) complex [Cp*$ZrCl_3$(2-TCMP)] (**5**) was isolated in low yield (Eq. (3)).

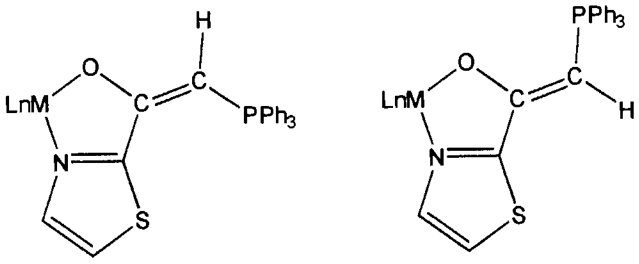
$$[ZrCl_4(2\text{-TCMP})] + LiCp^* \rightarrow \underset{\mathbf{5}}{[Cp^*ZrCl_3(2\text{-TCMP})]} + LiCl \qquad (3)$$

Alternatively, **5** was prepared in greater yield by the reaction of a THF suspension of $[Cp^*ZrCl_3]_n$ with 2-TCMP in an 1/n:1 molar ratio, followed by the appropriate work-up (Section 3) (Eq. (4)).

$$1/n[Cp^*ZrCl_3]_n + 2\text{-TCMP} \rightarrow \underset{\mathbf{5}}{[Cp^*ZrCl_3(2\text{-TCMP})]} \qquad (4)$$

It is known that in the presence of chelating ligands, such as dme, the polymeric species $[Cp^*ZrCl_3]_n$ gives rise to the more stable mononuclear species [Cp*$ZrCl_3$(dme)] [7]. In our example the α-keto ylide 2-TCMP acts as a chelating ligand toward the aforementioned polymer to afford the mononuclear complex **5**. Analogous reactions for titanium yield only decomposition products. Finally, the reactivity of **5** was also considered. Alkylation reactions were performed using several organomagnesium reagents, namely RMgCl, R = Me, Et, $PhCH_2$, in order to prepare the corresponding alkyl/aryl-containing species. For RMgCl in which R = Me or Et, the reactions afforded an intractable mixture of products. The reaction of **5** with $PhCH_2MgCl$ in diethyl ether at −70°C, on the other hand, led to the isolation of the complex [Cp*$ZrCl_2$(CH_2Ph)(2-TCMP)] (**6**) (Eq. (5)) after the appropriate work-up.

$$[Cp^*ZrCl_3(2\text{-TCMP})] + PhCH_2MgCl \rightarrow \underset{\mathbf{6}}{[Cp^*ZrCl_2(CH_2Ph)(2\text{-TCMP})]} + MgCl_2 \qquad (5)$$



Transoid isomer.
M=Ti, Zr.

Cisoid isomer.
M=Ti, Zr.

Chart 2.

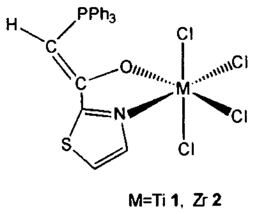


Fig. 1. Proposed structure for complexes **1** and **2**.

An acetone solution of **5** also reacted with $AgCF_3SO_3$ in a 1:1 molar ratio at room temperature to afford, after the appropriate work-up, the heterometallic complex $[Cp^*ZrCl_3(2\text{-}TCMP)Ag]CF_3SO_3$ (**7**) (Eq. (6)).

$$[Cp^*ZrCl_3(2\text{-}TCMP)] + AgCF_3SO_3 \rightarrow \underset{7}{[Cp^*ZrCl_3(2\text{-}TCMP)Ag]CF_3SO_3} \qquad (6)$$

A probable coordination of the Ag^+ cation fragment to the ylidic carbon atom can be considered as being present in this complex on the basis of spectroscopic data. A similar situation has already been mentioned for complex **4**.

The different complexes were characterized by spectroscopic techniques, which allowed us to distinguish between O-coordination and C(methine)-coordination of the ylide ligand. The ^1H-, ^{13}C- and ^{31}P-NMR spectra of all complexes indicate that the 2-TCMP ligand is bound to the metal center through the carbonyl oxygen. The ^1H-NMR spectra (Section 3) of **1** and **2** show a doublet resonance attributed to the methine proton with coupling constants ($^2J_{PH}$) of 15.1 and 14.9 Hz, respectively. In addition, the signal due to H_b (H_α with respect to the N atom, see Eq. (1)) in the thiazolyl ring in these complexes was found to be clearly deshielded in relation to the equivalent proton observed in the free ligand (7.81 ppm). This suggests that a possible additional coordination of the N atom to the metal center could be occurring, with the ylide acting as an N,O-bidentate ligand. Furthermore, the $^{13}C\{^1H\}$-NMR spectra (see Section 3) show the resonance attributed to the ylidic carbon as a doublet with a coupling constant ($^1J_{PC}$) that is smaller than that in the free ylide (111.3 Hz). The values are in accordance with the known coupling constant trend: free ylide > O-coordinated ylide > ylide hydrohalide salt > C-coordinated ylide [8].

Single ^{31}P-NMR resonances (see Section 3) were observed at slightly lower field with respect to the corresponding signals in the free ylide (14.40 ppm). The IR spectra of **1** and **2** exhibit bands at 1560 and 1550 cm^{-1}, respectively, which correspond to the $\nu(CO)$ and are shifted to higher wavenumbers than in the free ylide (1540 cm^{-1}). Analogous values were found for the niobium complexes $[NbCl_3(2\text{-}TCMP)(RC{\equiv}CR')]$ [3] and they were justified on the basis of the proposed N,O-coordination of the ligand to give five-membered metallacycles in which the O-atom was proposed to be sp^2 hybridized. This situation was claimed to favor effective π-bonding with the ylidic carbon to give a strong $C\underline{\cdots}O$ bond (see Chart 2).

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 in the complexes on steric grounds, has been proposed to be present both in solution and in the solid state (Fig. 1).

It is noteworthy that the ^1H-NMR spectra of complexes **3** and **4** show significant deshielding of the methine proton with regard to the equivalent proton in complexes **1** and **2**. Similar behavior was previously described for the analogous heterometallic-niobium complexes $[NbCl_3(2\text{-}TCMP)Ag]CF_3SO_3$ [3b]. Another feature of importance noticed in these spectra is that the resonance of H_b (H_α with respect to the N atom) is shielded and the resonance of H_c (H_α with respect to the S atom, see Eq. (1)) is deshielded with regard to the resonances of the corresponding protons in complexes **1** and **2**. This suggests that a possible coordination of the sulfur atom to the silver center could be occurring in addition to the coordination through the ylidic carbon atom. In the $^{13}C\{^1H\}$-NMR spectra the resonance attributed to the ylidic carbon atoms appears at chemical shifts 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–^1H heteronuclear correlations (HETCOR). The $^{31}P\{^1H\}$-NMR spectra exhibit a pseudotriplet, which corresponds to two overlapped doublets by coupling with ^{107}Ag and ^{109}Ag isotopes. Finally, the $^{19}F\{^1H\}$-NMR spectra show a signal at ca. -74.4 ppm, which corresponds to the CF_3SO_3 anion. The $\nu(CO)$ absorption in the IR spectrum appears at ca. 1560 cm^{-1}, indicating a bonding of the pseudophosphonium group through the carbonyl oxygen. On the basis of the spectroscopic data we propose a pseudooctahedral structure for complexes **3** and **4**, where the silver atom could be coordinated to both C and S atoms (see Fig. 2).

The mass spectrum of **5** indicates a mononuclear formulation. The ^{1}H-NMR spectra of this complex shows a singlet for the Cp* ring while the resonance for the methine proton exhibits chemical shift and $^{2}J_{PH}$ coupling constant values that are comparable to those found in complexes **1** and **2**. This situation is consistent with an N,O-coordination of the ylide ligand, which was corroborated by means of an X-ray crystal structure determination (see below). ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR data for these complexes are comparable with those previously described for complexes **1** and **2**. The IR spectrum exhibits the ν(CO) absorption at 1542 cm^{-1}. On the basis of these spectroscopic data, three structural arrangements in an octahedral situation can be considered for this complex (see Scheme 1). The X-ray crystal structure study was carried out and confirmed that situation (b) is the one present in the solid state. The X-ray study of the ylide ligand was also carried out in order to make comparisons with complex **5**.

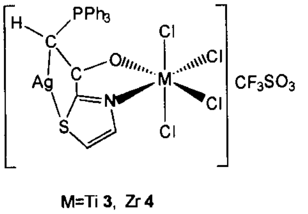
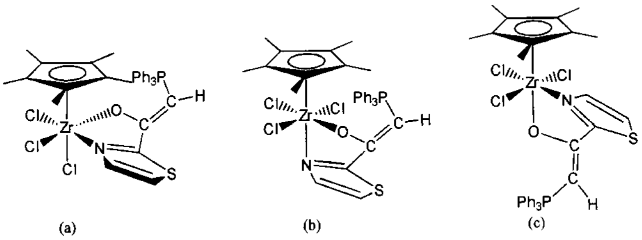


Fig. 2. Proposed structure for complexes **3** and **4**.



Scheme 1.

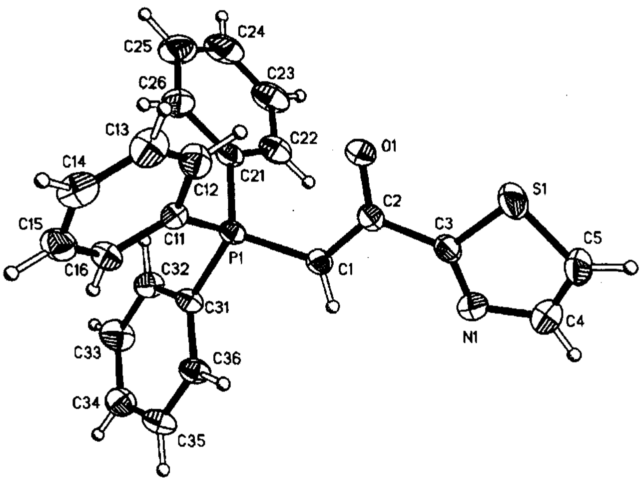


Fig. 3. Molecular structure and atom-labeling scheme for 2-TCMP (30% probability ellipsoids).

An ORTEP drawing of both the ligand and complex **5** are represented in Figs. 3 and 4, respectively. Selected bond lengths and angles for 2-TCMP and complex **5** are given in Table 1.

The zirconium atom in complex **5** shows a typical geometry for pseudooctahedral zirconium(IV) monocyclopentadienyl derivatives. The cyclopentadienyl ring is bound to the metal in a η^{5} mode. The 2-TCMP ligand is bound to the zirconium center through the nitrogen and oxygen in a five-membered chelate-ring conformation, as one would expect for this type of compound. The nitrogen atom is in an axial position *trans* to the cyclopentadienyl ring. The environment of the zirconium atom is completed by three chlorine atoms in the equatorial plane. The zirconium atom is out of the plane defined by O1, Cl1, Cl2 and Cl3 by 0.602(1) Å.

The 2-TCMP ligand adopts a quasi-planar structure after N,O-coordination to the zirconium atom, with the angle between S1, N1, C3, C4, C5 and P1, C1, C2, O1 being 13.0(3)° for the ligand and 4.8(2)° for complex **5**. The angle between the chelate ring and the heterocyclic ring is 1.1(2)°. This planarity increases the delocalization of the electron density throughout the ylide system.

Bond distances and angles are quite similar in 2-TCMP and complex **5**, and are also similar to those reported previously for these kinds of complex [3,5]. Thus, the P1–C1 bond distances of 1.725(4) and 1.743(4) Å for 2-TCMP and **5**, respectively, are typical for ylide systems and are intermediate between double and single bond distances [6]. The C2–O1 bond distance in 2-TCMP is 1.256(5) Å but is slightly longer in complex **5** [1.296(4) Å] as a consequence of the O-coordination to the zirconium atom.

The Zr1–Cl2 bond distance of 2.488(1) Å is slightly shorter than the Zr1–Cl1 and Zr1–Cl3 lengths of 2.519(1) and 2.537(1) Å, respectively, probably due to the *trans* effect of the oxygen atom. The Zr1–O1 and Zr1–N1 bond distances of 2.200(2) and 2.389(3) are in the normal range for zirconium complexes [9].

A weak intermolecular CH···Cl hydrogen bond can be postulated between Cl1 and H45 [Cl1···H45 = 2.780 Å, Cl1···C45 = 3.557(4) Å, Cl1–H45–C45 = 141.8°, symmetry operation: $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$].

The ^{1}H-NMR spectrum of **6** exhibits a doublet for the methine proton and this signal experiences significant shielding with respect to the equivalent proton in complexes **1** and **2**. The spectrum also shows the corresponding resonance for the methylene protons of the benzyl ligand, which appears as an AB spin system (see Section 3). The ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectra show resonances for the 2-TCMP ligand (see Section 3) that are in accordance with those described for the spectra of **5**, indicating that an N,O-coordination for

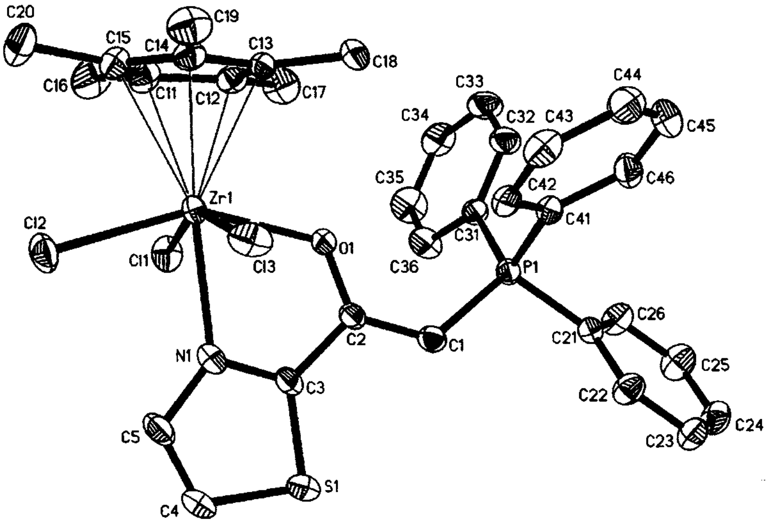


Fig. 4. Molecular structure and atom-labeling scheme for complex **5** (30% probability ellipsoids).

the ylide ligand can be envisaged. On the basis of the spectroscopic data, two structural arrangements for **6** can be proposed (see Scheme 2) and, by considering steric arguments, arrangement (b) is proposed as being more stable.

The ^{1}H-NMR spectrum of **7** exhibits the same features as those already described in the spectrum of complex **4**; indeed, significant deshielding of the methine proton and H_c (H_α with respect to the S atom) in comparison to the equivalent protons in **5** was observed (see Section 3). In addition, the $^{31}P\{^{1}H\}$-NMR spectrum contains a pseudotriplet which corresponds to two overlapped doublets by coupling with ^{107}Ag and ^{109}Ag isotopes. Based on the spectroscopic data, a pseudooctahedral structure in which the silver atom is coordinated to both C and S atoms (see Fig. 5) can be proposed for complex **7**.

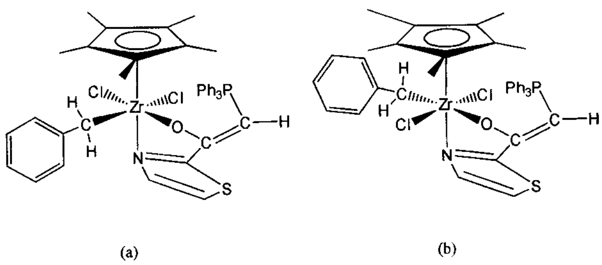
In conclusion, the preparation and characterization of new α-keto ylide-containing Group 4 metal complexes has been described. In addition, reactivity studies have allowed the preparation of new heterometallic and alkyl complexes.

3. Experimental

All the reactions were performed using standard Schlenk-tube techniques under 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 analyzer. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as the matrix. Infrared spectra were obtained in the region 4000–200 cm^{-1} using a Perkin–Elmer 883 spectrophotometer. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded on a Varian Unity FT-300 spectrometer and referenced to the residual deuterated solvent. The NOE difference spectra were recorded with the following

Table 1
Selected bond lengths (Å) and angles (°) for 2-TCMP and **5**

	2-TCMP	**5**
Zr1–Cl1		2.519(1)
Zr1–Cl2		2.488(1)
Zr1–Cl3		2.537(1)
Zr1–O1		2.200(2)
Zr1–N1		2.389(3)
O1–C2	1.256(5)	1.296(4)
C2–C3	1.496(6)	1.485(5)
N1–C3	1.304(6)	1.312(5)
C1–C2	1.389(5)	1.367(5)
P1–C1	1.725(4)	1.743(4)
O1–Zr1–N1		70.5(1)
O1–Zr1–Cl1		84.40(7)
Cl1–Zr1–Cl2		90.87(4)
Cl2–Zr1–Cl3		89.13(4)
Cl3–Zr1–O1		81.55(7)
P1–C1–C2	121.0(3)	124.1(3)
C1–C2–O1	126.2(4)	126.6(3)
O1–C2–C3	116.6(4)	114.1(3)
C2–C3–N1	127.0(4)	118.9(3)



(a) (b)

Scheme 2.

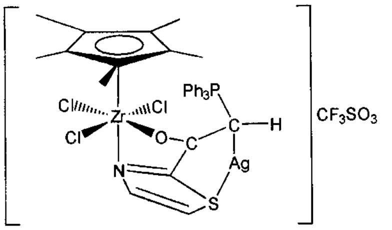


Fig. 5. Proposed structure for complex **7**.

acquisition parameters: spectrum width 5000 Hz, acquisition time 3.27 s, pulse width 90°, relaxation delay 4 s, irradiation power 5–10 dB, number of scans 120. Two-dimensional NMR and simulated spectra were acquired using standard VARIAN-FT software and processed using an IPC-Sun computer.

The compound [{2-thiazolylcarbonyl}methylene]-phosphorane ($NOSC_4H_2CHPPh_3$=2-TCMP) and the complex $[Cp^*ZrCl_3]_n$ were prepared as reported previously [3,10].

3.1. Preparation of [$TiCl_4$(2-TCMP)] (*1*)

To a suspension of $[TiCl_4(thf)_2]$ (0.700 g, 2.100 mmol) in THF (200 cm^3) was added an equimolar quantity of 2-TCMP (0.810 g, 2.100 mmol). The suspension was stirred at room temperature (r.t.) for 20 h. The solvent was removed under vacuum and a yellow-green solid was obtained. Yield 75%. Anal. Found: C, 47.25; H, 3.63; N, 2.43. Calc. for $C_{23}H_{18}TiCl_4NOPS$: C, 47.86; H, 3.14; N, 2.42%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 5.27 (d, $^2J_{PH} = 15.1$ Hz, CH); 8.35 (d, $^3J_{HH} = 3.0$ Hz, H_b); 7.57 (d, $^3J_{HH} = 3.0$ Hz, H_c); 7.40–7.80 (m, 15 H, PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 72.7 (d, $^1J_{PC} = 103.2$ Hz, CH); 163.2 (d, $^2J_{PC} = 18.8$ Hz, CO); 169.3 (s, C_a); 143.6 (s, C_b); 123.4 (s, C_c); 120.5 [d, $^1J_{PC} = 99.6$ Hz, $C_i(PPh_3)$], 130.1 [d, $^2J_{PC} = 12.6$ Hz, $C_o(PPh_3)$], 133.7 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$], 134.2 [d, $^4J_{PC} = 2.6$ Hz, $C_p(PPh_3)$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 16.17 (s, PPh_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1560; ν(Ti–Cl) 392, 348. FABMS (*m*/*z* assignment, % intensity): 579D [M + 1], 45, 388D [2-TCMP], 100.

3.2. Preparation of [$ZrCl_4$(2-TCMP)] (*2*)

To a suspension of $[ZrCl_4]$ (0.700 g, 2.975 mmol) in THF (200 cm^3) was added an equimolar quantity of 2-TCMP (1.153 g, 2.975 mmol). The suspension was stirred at r.t. for 20 h. The solvent was removed under vacuum and a red-orange solid was obtained. Yield 70%. Anal. Found: C, 45.00; H, 3.01; N, 2.22.Calc. for $C_{23}H_{18}ZrCl_4NOPS$: C, 44.98; H, 2.96; N, 2.22%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 5.40 (d, $^2J_{PH} = 14.9$ Hz, CH); 8.30 (d, $^3J_{HH} = 2.9$ Hz, H_b); 7.61 (d, $^3J_{HH} = 2.9$ Hz, H_c); 7.45–7.86 (m, 15 H, PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 75.0 (d, $^1J_{PC} = 102.7$ Hz, CH); 164.2 (d, $^2J_{PC} = 18.0$ Hz, CO); 168.2 (s, C_a); 143.8 (s, C_b); 123.6 (s, C_c); 120.3 [d, $^1J_{PC} = 92.7$ Hz, $C_i(PPh_3)$]; 130.1 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 133.5 [d, $^3J_{PC} = 10.5$ Hz; $C_m(PPh_3)$]; 134.8 [d, $^4J_{PC} = 2.6$ Hz, $C_p(PPh_3)$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 16.06 (s, PPh_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1550; ν(Zr–Cl) 375, 316. FABMS (*m*/*z* assignment, % intensity): 621D [M + 1], 58, 388D [2-TCMP], 100.

3.3. Preparation of [$TiCl_4$(2-TCMP)Ag]CF_3SO_3 (*3*)

To a suspension of [$TiCl_4$(2-TCMP)] (**1**) (0.200 g, 0.340 mmol) in dry Me_2CO (60 cm^3) was added an equimolar quantity of $AgCF_3SO_3$ (0.089 g, 0.340 mmol). The suspension was stirred at r.t. for 1 h. The solvent was removed under vacuum and a yellow solid was obtained. The solid was crystallized from a mixture of THF–Et_2O. Yield 60%. Anal. Found: C, 34.58; H, 2.71; N, 1.50. Calc. for $C_{24}H_{18}TiAgCl_4F_3NO_4PS_2$: C, 34.55; H, 2.71; N, 1.50%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 6.05 (d, $^2J_{PH} = 12.7$ Hz, CH); 8.29 (d, $^3J_{HH} = 3.0$ Hz, H_b); 8.06 (d, $^3J_{HH} = 3.0$ Hz, H_c); 7.45–7.90 (m, 15 H, PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 34.4 (d, $^1J_{PC} = 57.1$ Hz, CH); 164.2 (s, CO); 183.9 (s, C_a); 145.5 (s, C_b); 129.2 (s, C_c); 118.5 [d, $^1J_{PC} = 89.1$ Hz, $C_i(PPh_3)$]; 130.3 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 133.8 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$]; 135.2 [d, $^4J_{PC} = 3.1$ Hz, $C_p(PPh_3)$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 21.56, 21.50 (dd, $^2J_{^{107}AgP} = 6.7$ Hz or $^2J_{^{109}AgP} = 6.7$ Hz, PPh_3). ^{19}F($CDCl_3$, $CFCl_3$ as reference, δ ppm): -74.36 (s, CF_3SO_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1560; ν(Ti–Cl) 348. FABMS (*m*/*z* assignment, % intensity): 608D [M–Cl], 23, 388D [2-TCMP], 100, 370D [$AgPPh_3$], 19.

3.4. Preparation of [$ZrCl_4$(2-TCMP)Ag]CF_3SO_3 (*4*)

To a suspension of [$ZrCl_4$(2-TCMP)] (**2**) (0.200 g, 0.320 mmol) in dry Me_2CO (60 cm^3) was added an equimolar quantity of $AgCF_3SO_3$ (0.083 g, 0.320 mmol). The suspension was stirred at r.t. for 1 h. The solvent was removed under vacuum and a pink solid was obtained. The solid was crystallized from a mixture of THF–Et_2O. Yield 70%. Anal. Found: C, 33.02; H, 2.16; N, 1.88. Calc. for $C_{24}H_{18}ZrAgCl_4F_3NO_4PS_2$: C, 32.86; H, 2.06; N, 1.59%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 5.79 (d, $^2J_{PH} = 12.9$ Hz, CH); 8.31 (d, $^3J_{HH} = 3.0$ Hz, H_b); 8.05 (d, $^3J_{HH} = 3.0$ Hz, H_c); 7.49–7.90 (m, 15 H, PPh_3). $^{13}C\{^1H\}$-NMR ($CDCl_3$, δ ppm): 34.6 (d, $^1J_{PC} = 58.4$ Hz, CH); 164.3 (s, CO); 183.9 (s, C_a); 145.5 (s, C_b); 129.1 (s, C_c); 117.8 [d, $^1J_{PC} = 88.7$ Hz, $C_i(PPh_3)$]; 130.4 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 133.8 [d, $^3J_{PC} = 10.5$ Hz, $C_m(PPh_3)$]; 135.3 [d, $^4J_{PC} = 3.1$ Hz, $C_p(PPh_3)$]. $^{31}P\{^1H\}$-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 21.70, 21.65 (dd, $^2J_{^{107}AgP} = 6.8$ Hz or $^2J_{^{109}AgP} = 6.6$ Hz, PPh_3). ^{19}F-NMR ($CDCl_3$, $CFCl_3$ as reference, δ ppm): −74.14 (s, CF_3SO_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1565; ν(Zr–Cl) 348. FABMS (*m*/*z* assignment, % intensity): 615D [M+1], 43, 388D [2-TCMP], 100, 370D [$AgPPh_3$], 39.

3.5. Preparation of [Cp*ZrCl$_3$(2-TCMP)] (**5**)

(a) To a cooled (−78°C) solution of Cp*H (0.5 cm^3, 4.218 mmol) in dry THF (100 cm^3) was added a 1.6 M solution of ^{n}BuLi in hexane (2.6 cm^3, 4.218 mmol). After 1 h a solution of [$ZrCl_4$(2-TCMP)] (**2**) (2.617 g, 4.218 mmol) in THF (100 cm^3) was added and the reaction mixture was stirred for 5 h at r.t. The solvent was removed under vacuum and, after extraction with CH_2Cl_2 (2 × 50 cm^3), a red solid was obtained. This solid was crystallized from a mixture of THF–hexane. Yield 50%.

(b) To a suspension of Cp*$ZrCl_3$ (0.700 g, 2.100 mmol) in THF (200 cm^3) was added an equimolar quantity of 2-TCMP (0.810 g, 2.100 mmol). The suspension was stirred at r.t. for 12 h. The solvent was removed under vacuum and a red solid was obtained. Yield 85%. Anal. Found: C, 55.12; H, 4.82; N, 2.01. Calc. for $C_{33}H_{33}ZrCl_3NOPS$: C, 55.03; H, 4.61; N, 1.94%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 4.74 (d, $^2J_{PH} = 14.8$ Hz, CH); 8.80 (d, $^3J_{HH} = 3.3$ Hz, H_b); 7.41 (d, $^3J_{HH} = 3.3$ Hz, H_c); 7.32–7.95 (m, 15 H, PPh_3); 1.71 [s, 15H, Me(Cp*)]. ^{13}C{^{1}H}-NMR ($CDCl_3$, δ ppm): 66.4 (d, $^1J_{PC} = 106.7$ Hz, CH); 165.2 (d, $^2J_{PC} = 20.1$ Hz, CO); 171.9 (s, C_a); 144.8 (s, C_b); 121.4 (s, C_c); 122.0 [d, $^1J_{PC} = 92.2$ Hz, $C_i(PPh_3)$]; 130.0 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 133.6 [d, $^3J_{PC} = 11.1$ Hz, $C_m(PPh_3)$]; 134.0 [d, $^4J_{PC} = 3.0$ Hz, $C_p(PPh_3)$]; 125.2 [s, C_i(Cp*)]; 12.4 [s, Me(Cp*)]. ^{31}P{^{1}H}-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 12.60 (s, PPh_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1542; ν(Zr–Cl) 360, 300, 276. FABMS (*m*/*z* assignment, % intensity): 684D [M–Cl], 60, 388D [2-TCMP], 100.

3.6. Preparation of [Cp*ZrCl$_2$(CH$_2$Ph)(2-TCMP)] (**6**)

To a cooled (−70°C) suspension of [Cp*$ZrCl_3$(2-TCMP)] (**5**) (0.250 g, 0.290 mmol) in dry Et_2O (100 cm^3) was added a 1 M solution of $MgCH_2PhCl$ in Et_2O (0.298 cm^3, 0.290 mmol). The reaction mixture was stirred for 1 h at −78°C and the temperature was slowly allowed to reach at r.t. during 12 h. The solvent was removed under vacuum and, after extraction with hexane (2 × 50 cm^3), a yellow solid was obtained. Yield 66%. Anal. Found: C, 61.81; H, 5.18; N, 1.92. Calc. for $C_{40}H_{40}ZrCl_2NOPS$: C, 61.91; H, 5.19; N, 1.80%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 3.25 (d, $^2J_{PH} = 17.0$ Hz, CH); 8.86 (d, $^3J_{HH} = 3.3$ Hz, H_b); 6.98–7.95 (m, 21 H, H_c, PPh_3, CH_2*Ph*); A 3.84, B 3.49 [AB, $J_{AB} = 13.5$ Hz, (*CH*$_2$Ph)]; 1.74 [s, 15H, Me(Cp*)]. ^{13}C{^{1}H}-NMR ($CDCl_3$, δ ppm): 64.5 (d, $^1J_{PC} = 105.7$ Hz, CH); 164.8 (s, CO); 173.6 (s, C_a); 136.9 (s, C_b); 127.1 (s, C_c); 125.6 [d, $^1J_{PC} = 46.3$ Hz, $C_i(PPh_3)$]; 128.7 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 129.6 [d, $^3J_{PC} = 12.5$ Hz, $C_m(PPh_3)$]; 132.0 [d, $^4J_{PC} = 2.8$ Hz, $C_p(PPh_3)$]; 131.8 [s, C_i(CH_2*Ph*)]; 132.2 [s, C_o(CH_2*Ph*)]; 133.6 [s, C_m(CH_2*Ph*)]; 133.8 [s, C_p(CH_2*Ph*)]; 72.4 (s, *CH*$_2$Ph); 122.8 [s, C_i(Cp*)]; 12.1 [s, Me(Cp*)]. ^{31}P{^{1}H}-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm), 13.80 (s, PPh_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1557; ν(Zr–Cl) 363. FABMS (*m*/*z* assignment, % intensity): 776D [M–Cl], 12, 388D [2-TCMP], 100.

3.7. Preparation of [Cp*ZrCl$_3$(2-TCMP)Ag]CF$_3$SO$_3$ (7)

To a suspension of [Cp*$ZrCl_3$(2-TCMP)] (**5**) (0.215 g, 0.290 mmol) in dry Me_2CO (60 cm^3) was added an equimolar quantity of $AgCF_3SO_3$ (0.077 g, 0.290 mmol). The suspension was stirred at r.t. for 1 h. The solvent was removed under vacuum and a red solid was obtained. The solid was crystallized from a mixture of THF–Et_2O. Yield 75%. Anal. Found: C, 41.81; H, 3.81; N, 1.62. Calc. for $C_{34}H_{33}ZrAgCl_3F_3NO_4PS_2$: C, 41.79; H, 3.40; N, 1.43%. ^{1}H-NMR ($CDCl_3$, 295 K, δ ppm): 5.04 (d, $^2J_{PH} = 11.7$ Hz, CH); 8.43 (d, $^3J_{HH} = 3.2$ Hz, H_b); 7.97 (d, $^3J_{HH} = 3.2$ Hz, H_c); 7.25–7.90 (m, 15H, PPh_3); 1.74 [s, 15H, Me(Cp*)]. ^{13}C{^{1}H}-NMR ($CDCl_3$, δ ppm): 42.1 (d, $^1J_{PC} = 60.2$ Hz, CH); 170.1 (d, $^2J_{PC} = 21.3$ Hz, CO); 183.0 (s, C_a); 144.2 (s, C_b); 129.5 (s, C_c); 117.8 [d, $^1J_{PC} = 88.7$ Hz, $C_i(PPh_3)$]; 130.4 [d, $^2J_{PC} = 13.1$ Hz, $C_o(PPh_3)$]; 133.8 [d, $^3J_{PC} = 10.5$ Hz, $C_m(PPh_3)$]; 135.3 [d, $^4J_{PC} = 3.1$ Hz, $C_p(PPh_3)$]; 125.6 [s, C_i(Cp*)]; 11.2 [s, Me(Cp*)]. ^{31}P{^{1}H}-NMR ($CDCl_3$, H_3PO_4 as reference, δ ppm): 22.31, 22.29 (dd, $^2J_{^{107}AgP} = 6.4$ Hz or $^2J_{^{109}AgP} = 6.4$ Hz, PPh_3). ^{19}F-NMR ($CDCl_3$, $CFCl_3$ as reference, δ ppm): −75.39 (s, CF_3SO_3). IR (Nujol mull, cm^{-1}): ν(C=O) 1570; ν(Zr–Cl) 325. FABMS (*m*/*z* assignment, % intensity): 589D [M−Cl], 33, 388D [2-TCMP], 100, 370D [$AgPPh_3$], 58.

4. X-ray structure determinations for 2-TCMP and complex 5

Crystals of 2-TCMP and complex **5** were mounted at low temperature in inert oil on a glass fiber. Intensity data were collected on a NONIUS-MACH3 diffractometer equipped with a graphite monochromator (Mo–Kα radiation, $\lambda = 0.71073$ Å) using an $\omega/2\theta$ scan technique at 250 K to a maximum value of 56. The final unit cell parameters were determined from 25 well centered reflections and refined by the least-squares method. Analysis of systematic absences in the data was consistent with the monoclinic space group $P2_1/n$ for both compounds. The structures were solved by direct methods using the SHELXS computer program [11] and refined on F^2 by full-matrix least-squares

Table 2
Crystal data and structure refinement for 2-TCMP and **5**

	2-TCMP	**5**
Empirical formula	$C_{23}H_{18}NOPS\cdot C_4H_8O$	$C_{33}H_{33}Cl_3NOPSZr\cdot CH_2Cl_2$
Formula weight	459.52	805.13
Temperature (K)	250(2)	250(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	9.187(1)	10.756(1)
b (Å)	27.207(1)	24.281(1)
c (Å)	9.734(1)	14.610(1)
β (°)	99.26(1)	101.04(1)
V (Å^3)	2401.3(4)	3745.0(5)
Z	4	4
D_{calc} (g cm^{-3})	1.271	1.428
μ (mm^{-1})	0.225	0.776
F(000)	968	1640
Crystal size (mm)	$0.5\times0.4\times0.4$	$0.3\times0.3\times0.2$
Theta range for data collection (°)	2.25–27.97	2.10–27.85
Index ranges	$-12\leq h\leq 12$, $0\leq k\leq 35$, $0\leq l\leq 12$	$-14\leq h\leq 14$, $0\leq k\leq 31$, $0\leq l\leq 19$
Reflections measured	6075	9202
Independent reflections	5760	8872
Observed reflections	3746	5947
Goodness-of-fit on F^2	1.351	0.989
Final R indices [$I>2\sigma(I)$]	$R_1=0.0963$ [a], $wR_2=0.2752$ [b]	$R_1=0.0467$ [a], $wR_2=0.1015$[b]
Largest difference peak (e Å^{-3})	0.718/−1.28	0.631/−0.614

[a] $R_1=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$.
[b] $wR_2=[\Sigma\,[w(F_o{}^2-F_c{}^2)^2]/\Sigma\,[w(F_o{}^2)^2]]^{0.5}$.

(SHELXL-97) [12]. All non-hydrogen atoms were refined with anisotropic thermal parameters. 2-TCMP crystallizes with one THF molecule, whereas complex **5** crystallizes with one dichloromethane molecule as solvent. The hydrogen atoms were included in calculated positions and were refined with an overall isotropic temperature factor using a riding model. Crystallographic date are shown in Table 2.

5. Supporting information available

Details of data collection, refinement, atom coordinates, anisotropic displacement parameters, and bond lengths and angles for compounds 2-TCMP and **5** are available free of charge via the Internet at http://pubs.acs.org.

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