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Zirconium Alkyl Thiolate Complexes: Synthesis and Reactivity. Molecular Structures of $[Zr(\eta^5\text{-}C_5H_5)_2(\eta^2\text{-}C_6H_7N_2S)(Me)]$ and $[Zr(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_6H_7N_2S)(\eta^2\text{-}CH_3CNXylyl)]$ (Xylyl = 2,6-Dimethylphenyl)

Rosa Fandos,*,[†] Maurizio Lanfranchi,[‡] Antonio Otero,*,[§]
Maria Angela Pellinghelli,[‡] María José Ruiz,[†] and Pilar Terreros[||]

Departamento de Química Inorgánica, Orgánica y Bioquímica, Universidad de Castilla-La Mancha, Facultad de Químicas: Campus de Toledo, C/ S. Lucas, 6, 45001 Toledo, Spain, and Campus de Ciudad Real, 13071 Ciudad Real, Spain, Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Universitá degli Studi di Parma, Centro di Studio per la Structturistica Diffractometrica del CNR, Vialle delle Scienze 78, I-43100 Parma, Italy, and Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco, 28049 Madrid, Spain

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The thiolate−alkylzirconocene complex $Cp_2ZrMe(SR)$ (**2**) (Cp = η^5-C_5H_5; SR = 4,6-dimethylpyrimidine-2-thiolate) can be prepared by reacting the corresponding dialkylmetallocene complex Cp_2ZrMe_2 (**1**) with 1 equiv of 4,6-dimethyl-2-mercaptopyrimidine. X-ray structure analysis of complex **2** revealed that the thiolate group is bonded in an η^2 fashion through the sulfur and one of the nitrogen atoms. Complex **2** reacts with 2,6-dimethylphenyl isocyanide (CNXylyl) to yield the corresponding iminoacyl derivative, $Cp_2Zr(\eta^2$-MeCNXylyl)(SR) (**4**). The molecular structure of **4** shows that the thiolate group is η^1-bonded while the iminoacyl group behaves as a bidentate ligand. Reaction of compound **2** with different acidic reagents gives formation of methane and different zirconium complexes. Reaction with HSR renders $Cp_2Zr(SR)_2$ (**3**) and with $(NHEt_3)(BPh_4)$ the cationic complex $[Cp_2Zr(SR)][BPh_4]$ (**5**). An hydride thiolate complex, $Cp^*{}_2ZrH(SR)$ (Cp^* = η^5-C_5Me_5) (**6**) can also be prepared by reaction of "$Cp^*{}_2Zr$" with HSR by an oxidative addition reaction.

Introduction

In the last few years there has been a growing interest in transition metal thiolate complexes due to the important role that such compounds are believed to play as intermediates in different reactions such as desulfurization of organosulfur compounds[1−2] and metal-catalyzed synthetic reactions involving C−S bond cleavage and formation.[3] On the other hand, 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 and so a number of zirconocene thiolate complexes have been prepared.[4]

Moreover, thiolate complexes are the focus of much attention due to their relevance to the structure, bonding, and function of biologically active reaction centers such as nitrogenase or metallothioneins.[5] In the last aspect, thiolate ligands containing nitrogen atoms are specially interesting.[6]

From recent literature it appears that the number of studies concerning the interaction modes and reactivity of transition metal complexes containing pyridinethiolate and pyrimidinethiolate ligands is growing rapidly.[7] Such ligands are especially interesting because (i) they contain functional groups common in crude oils (thiolate-S and aromatic-N), (ii) the pyrimidine group is a constituent of nucleic acids, and (iii) they have the ability to chelate and bridge transition metals, allowing access to both mononuclear and oligonuclear products.

We herein report the synthesis and reactivity of the first examples of pyrimidinethiolate-containing zirconocene complexes as well as the X-ray crystal structure characterization of two of them.

[†] Campus de Toledo, Universidad de Castilla-La Mancha.

[‡] Universitá degli Studi di Parma.

[§] Campus de Ciudad Real, Universidad de Castilla-La Mancha.

[||] Instituto de Catálisis y Petroleoquímica.

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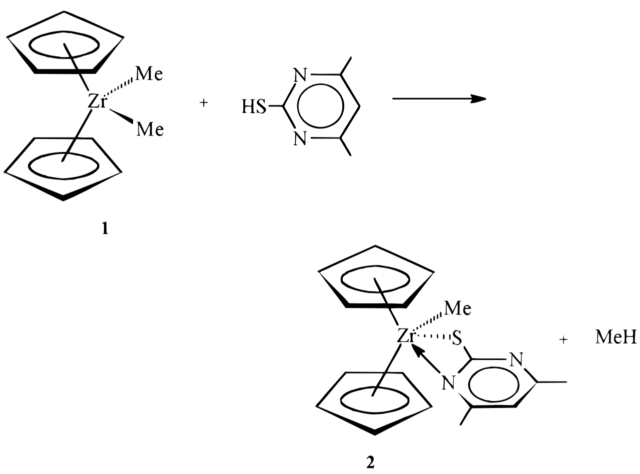
Scheme 1



Results and Discussion

Early transition metal alkyl complexes react with acidic reactives such as alcohols or mercaptans to the corresponding alkane and the alkoxide or thiolate complexes, respectively. A likely mechanism of the protonolysis of carbon−zirconium bonds requires initial donation of an oxygen or sulfur lone pair to the metal center.[8] This methodology is useful in the synthesis of alkyl thiolate zirconocene complexes. 4,6-Dimethyl-2-mercaptopyrimidine reacts with Cp_2ZrMe_2 (**1**) in 1:1 ratio according to Scheme 1.

Synthesis of $Cp_2ZrMe(SR)$ (**2**) was carried out with pentane used as the solvent. Complex **2** is prepared in high yield (92%) as a white precipitate in the reaction solvent from which it is separated by filtration. Complex **2** is air sensitive, insoluble in alkanes, sparsely soluble in toluene and benzene, and partially soluble in THF and acetonitrile. At room temperature, and over a period of 48 h, complex **2** does not react with an excess of mercaptan.

The lack of reactivity of the remaining alkyl group indicates that the coordination of the sulfur atom from a second mercaptan molecule is prevented by coordination of the nitrogen atom of the pyrimidine group. This expectation is confirmed by the structure of complex **2**, which has been determined by X-ray diffraction. X-ray-quality crystals were prepared by slow diffusion of pentane on a THF-saturated solution. An ORTEP drawing of the structure of complex **2** is shown in Figure 1. Selected bond distances and angles are given in Table 1 and atomic coordinates for all non-hydrogen atoms appear in Table 2.

Complex **2** exhibits the typical bent metallocene structure. The cyclopentadienyl rings are bonded to the zirconium atom in a nearly symmetric η^5-fashion. The Zr−CE1 and Zr−CE2 (CE = ring centroid) distances of 2.241(4) and 2.229(5) Å compare well with those of other $Cp_2Zr(^{IV})$ reported complexes.[9]

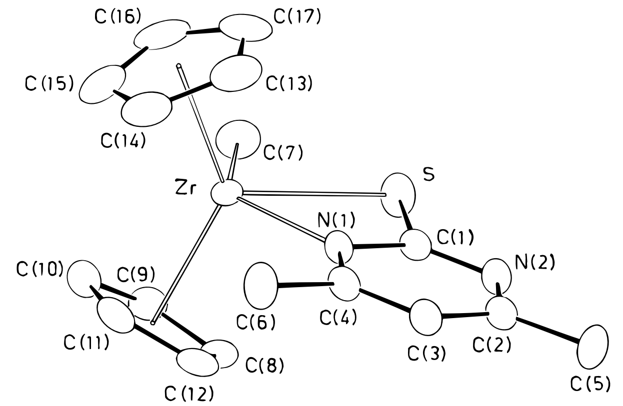


Figure 1. An ORTEP drawing of complex **2** with the atomic labeling scheme (30% probability ellipsoids).

Table 1. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for 2[a]

Zr−CE(1)	2.241(4)	N(1)−C(4)	1.355(4)
Zr−CE(2)	2.229(5)	N(2)−C(1)	1.329(4)
Zr−S	2.629(1)	N(2)−C(2)	1.343(4)
Zr−N(1)	2.440(2)	C(2)−C(3)	1.379(5)
Zr−C(7)	2.359(4)	C(3)−C(4)	1.377(4)
S−C(1	1.723(3)	C(2)−C(5)	1.500(5)
N(1)−C(1)	1.358(4)	C(4)−C(6)	1.504(4)
CE(1)−Zr−CE(2)	130.0(2)	C(1)−N(1)−C(4)	117.3(2)
CE(1)−Zr−S	114.4(1)	S−C(1)−N(1)	111.7(2)
CE(1)−Zr−N(1)	99.0(1)	S−C(1)−N(2)	122.4(2)
CE(1)−Zr−C(7)	99.1(1)	N(1)−C(1)−N(2)	125.9(3)
CE(2)−Zr−S	115.5(1)	C(1)−N(2)−C(2)	116.5(3)
CE(2)−Zr−N(1)	102.5(1)	N(2)−C(2)−C(3)	121.2(3)
CE(2)−Zr−C(7)	98.5(2)	N(2)−C(2)−C(5)	116.4(3)
S−Zr−N(1)	60.5(1)	C(3)−C(2)−C(5)	122.3(3)
S−Zr−C(7)	72.2(1)	C(2)−C(3)−C(4)	119.9(3)
N(1)−Zr−C(7)	132.6(1)	N(1)−C(4)−C(3)	119.3(3)
Zr−S−C(1)	85.5(1)	N(1)−C(4)−C(6)	119.2(3)
Zr−N(1)−C(1)	101.9(2)	C(3)−C(4)−C(6)	121.5(3)
Zr−N(1)−C(4)	140.4(2)		

[a] CE(1) and CE(2) are the centroids of the C(8)···C(12) and C(13)···C(17) cyclopentadienyl rings, respectively.

The zirconium atom is also bonded to the bidentate 4,6-dimethylpyrimidine-2-thiolate-*N,S* ligand and to the carbon atom of the methyl group. To the best of our knowledge this complex, together with complex **4** (see below), represents the first structurally characterized pyrimidine-2-thiolate zirconium complex. The Zr, C(7), S, and N(1) atoms are practically coplanar (max dev 0.033(4) Å for C(7)) and lie roughly in the equatorial plane which bisects the dihedral angle formed by the cyclopentadienyl rings. The 4,6-dimethylpyrimidine-2-thiolate ligand chelates ligand through the N(1) and S atoms. The four-membered ZrSC(1)N(1) ring is not strictly planar and the dihedral angle between the ZrSN(1) and SC(1)N(1) planes is 172.9(2)°.

The bonding of the bidentate thiolate to the metal center can be considered as an intermediate between the two possible bonding situations represented in Scheme 2.[10] In agreement with this proposal is that the C(1)−S bond (1.723(3) Å) is slightly shorter than the one observed in complex **4** (1.752(4) Å) where the thiolate ligand is mononodentate. The value falls into the range 1.696−1.761 Å observed in pyrimidine-2-thiolate transition metal complexes.[11]

The Zr−S bond distance (2.629(1) Å) falls into the range 2.561−2.660 Å found in zirconocene complexes

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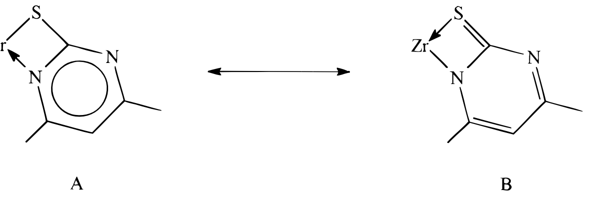
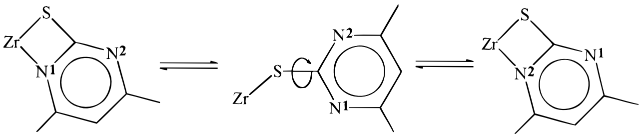
Scheme 2



Scheme 3



with N and S atoms coordinated to the metal. In $Cp_2ZrCl[SC(H)NC_6H_5]$,[12] which is the only X-ray structurally characterized zirconium complex containing similar four-membered N,S chelation, the Zr−S (2.659(4) Å) bond distance is larger than in complex **2**. On the other hand, the Zr−N bond length (2.408(9) Å) is shorter than in complex **2** (2.440(4) Å).

The Zr−C7 distance (2.359(4) Å) is longer than the one observed in Cp_2ZrMe_2 (2.273 Å)[9a] but is within the range expected for 18 e^- zirconium complexes.[13]

The room temperature ^{1}H NMR spectrum of complex **2** (toluene-d_8) shows a broad resonance at 1.85 ppm that integrates to six protons and which is assigned to the methyl groups attached to the phenyl ring in the thiolate ligand. The width of the peak indicates fluxional behavior through which both nitrogen atoms interchange their positions in the coordination sphere of the zirconium atom (see Scheme 3). Variable-temperature ^{1}H NMR spectroscopy showed that at −40 °C methyl groups are unequivalent and appear as two singlets at 1.99 and 1.54 ppm. The peaks coalesce at 14 °C. The two site exchange equations and the coalescence temperature of 287 K can be used to estimate a value for $\Delta G^{\ddagger}$ of 13.5 ± 2 kcal mol^{-1} for the rotation. That means that although complex **2** in the solid state is, formally, a 18 e^- molecule, in solution, due to the fluxional interchange, a free coordination position at the metal atom could be available for some reactions to take place.

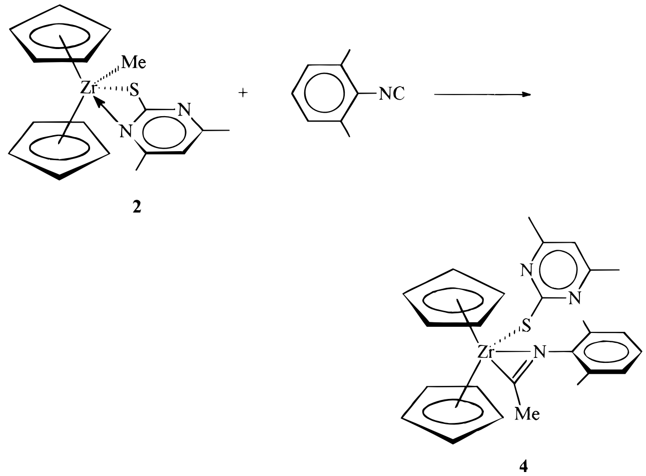
Accordingly, when the reaction of Cp_2ZrMe_2 with 2 equiv of 4,6-dimethyl-2-mercaptopyrimidine is carried out at high temperature, in refluxing toluene, it is possible to synthesize the corresponding bis-thiolate complex as depicted in eq 1

$$\underset{\mathbf{1}}{Cp_2ZrMe_2} + 2HSR \rightarrow \underset{\mathbf{3}}{Cp_2Zr(SR)_2} + 2MeH \qquad (1)$$

Complex **3** can also be prepared by reaction of **2** with one more equivalent of mercaptan under the same experimental conditions. Compound **3** is insoluble in pentane and scarcely soluble in toluene or THF. It has been characterized by ^{1}H NMR and IR spectroscopy and elemental analysis.

^{1}H NMR spectrum, at room temperature, shows singlets at 6.23 (10H), 5.92 (1H), and 5.54 (1H) ppm assigned to Cp and the pyrimidine protons, respectively.

Scheme 4



Methyl groups appear as three singlets at 2.04 (3H), 1.96 (3H), and 1.78 (6H) ppm, indicating that while one thiolate acts as a bidentate ligand the other is bonded to the zirconium atom only by the sulfur atom.

Compound **2** reacts readily in THF, at room temperature, with 2,6-dimethylphenyl isocyanide in 1:1 ratio to give the corresponding η^2-iminoacyl complex **4** (Scheme 4) in 82% yield, which was isolated as the hemi-THF adduct. It is air sensitive, moderately soluble in THF, less soluble in toluene and other aromatic solvents, and practically insoluble in pentane.

All spectroscopic data point to an η^2-coordination of the iminoacyl group while the thiolate acts as a monodentate ligand. This is in agreement with the expectation based on the literature precedents in which early transition metal iminoacyl complexes are described to be normally stabilized by coordination of the nitrogen atom to the metal center on a η^2-coordination mode.[14] Accordingly, the IR spectrum shows several absorptions in the region near to 1500 cm^{-1} and one of them may be assigned to the ν(C=N), and the iminoacyl carbon appears at 241.8 ppm in the $^{13}C\{^1H\}$ NMR spectrum.[15]

On the other hand, the ^{1}H NMR spectrum shows that the two methyl groups in the pyrimidine moiety are equivalent as they appear as a singlet at 1.92 ppm which means free rotation around the C-S bond. In the same way, rotation of the xylyl group is fast on the NMR time scale and the two methyl groups are equivalent giving a singlet at 2.17 ppm.

The structure of complex **4** has been determined by X-ray diffraction. An ORTEP drawing is shown in Figure 2. Selected bond distances and angles are given in Table 3 and the atomic coordinates for all nonhydrogen atoms appear in Table 4.

Like **2**, complex **4** exhibits the typical bent metallocene structure with the cyclopentadienyl groups η^5-bonded to the Zr atom. The coordination sphere around the metal is completed by the S atom of the monodentate thiolate ligand and by the N(3) and C(7) atoms of the η^2-iminoacyl. The Zr, C(7), N(3), and S atoms are practically coplanar and lie in the equatorial plane which bisects the dihedral angle formed by the cyclopentadienyl rings. The Zr−S bond (2.623(1) Å) is quite

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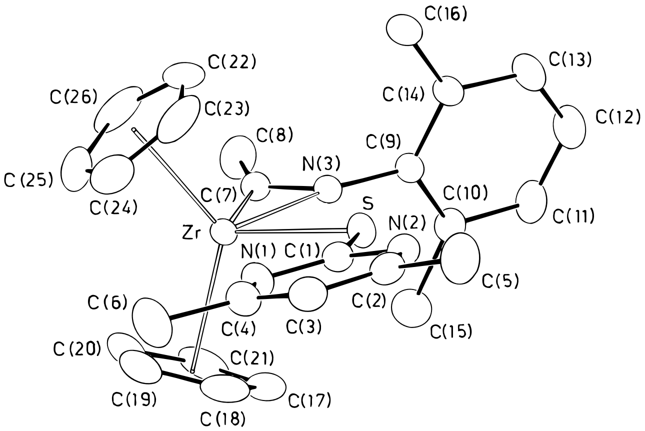


Figure 2. An ORTEP drawing of complex **4** with the atomic labeling scheme (30% probability ellipsoids).

Table 3. Selected Bond Distances (Å) and Angles (deg) with Esd's in Parentheses for $4\cdot{}^1/_2C_4H_8O$[a]

Zr−CE(1)	2.237(5)	N(2)−C(2)	1.338(5)
Zr−CE(2)	2.244(5)	C(2)−C(3)	1.380(6)
Zr−S	2.623(1)	C(3)−C(4)	1.373(7)
Zr−N(3)	2.271(3)	C(2)−C(5)	1.505(7)
Zr−C(7)	2.206(4)	C(4)−C(6)	1.504(7)
S−C(1)	1.752(4)	N(3)−C(7)	1.268(5)
N(1)−C(1)	1.341(5)	N(3)−C(9)	1.439(4)
N(1)−C(4)	1.342(6)	C(7)−C(8)	1.489(6)
N(2)−C(1)	1.349(5)		
CE(1)−Zr−CE(2)	126.9(2)	C(1)−N(2)−C(2)	116.2(3)
CE(1)−Zr−S	105.6(1)	N(2)−C(2)−C(3)	122.1(4)
CE(1)−Zr−N(3)	110.3(1)	N(2)−C(2)−C(5)	116.5(4)
CE(1)−Zr−C(7)	103.2(2)	C(3)−C(2)−C(5)	121.4(4)
CE(2)−Zr−S	107.9(2)	C(2)−C(3)−C(4)	117.6(4)
CE(2)−Zr−N(3)	116.5(2)	N(1)−C(4)−C(3)	121.8(4)
CE(2)−Zr−C(7)	102.6(2)	N(1)−C(4)−C(6)	115.9(4)
S−Zr−N(3)	77.2(1)	C(3)−C(4)−C(6)	122.2(4)
S−Zr−C(7)	109.9(1)	Zr−N(3)−C(7)	70.8(2)
N(3)−Zr−C(7)	32.9(1)	Zr−N(3)−C(9)	161.2(2)
Zr−S−C(1)	111.5(1)	C(7)−N(3)−C(9)	128.0(3)
C(1)−N(1)−C(4)	116.6(3)	Zr−C(7)−N(3)	76.4(2)
S−C(1)−N(1)	119.7(3)	Zr−C(7)−C(8)	156.4(3)
S−C(1)−N(2)	114.6(3)	N(3)−C(7)−C(8)	127.1(3)
N(1)−C(1)−N(2)	125.6(3)		

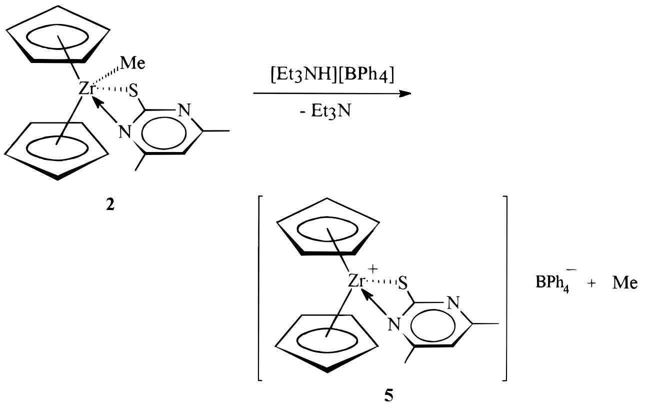
[a] CE(1) and CE(2) are the centroids of the C(17)···C(21) and C(22)···C(26) cyclopentadienyl rings respectively.

similar to that previously described for **2**, while the S−C(1) bond length (1.752(4) Å) is longer than the one found in complex **2**. The S−C(1) bond distance, observed for complex **4,** agrees well with the the unweighted sample mean value (1.761(20) Å) reported for terminal arenethiolates.[16] The Zr−C(7) bond distance (2.206(4) Å) falls into the range 2.164−2.363 Å while the Zr−N(3) bond distance (2.271(3) Å) is slightly out of the range 2.148−2.250 Å obtained from 10 crystal structures from CSD which contain the $Cp_2Zr(\eta^2\text{-}C{=}N-)$ moiety (Zr−C and Zr−N mean bond lengths: 2.25(6) and 2.21(3) Å, respectively). The length of the N(3)−C(7) bond distance (1.268(5) Å) is consistent with a double-bond character and falls into the range 1.242−1.322 Å obtained in the above-mentioned system.

Reaction of compound **2** with $[NEt_3H]^+[BPh_4]^-$, in THF, at room temperature yields the cationic complex **5** (Scheme 5).

Some thiolate cationic complexes of zirconium have been previously reported.[17] They have been prepared by treatment of the well-known cationic complex $[Cp_2ZrMe(THF)][BPh_4]$ with $HS(t\text{-}C_4H_9)$. $[Cp_2Zr(S\text{-}t\text{-}C_4H_9)(THF)][BPh_4]$ is unstable in THF solution, and the decomposition occurs through cleavage of the carbon−sulfur bond and formation of the known sulfide-bridged dimmer $[Cp_2ZrS]_2$. Dissociation of the THF ligand is proposed to be the step prior to the cleavage.

Scheme 5



Complex **5** is stable in THF solution, at room temperature, at least, 24 h. The higher stability of this complex can be explained, on one the hand, by the strong coordination of the nitrogen atom which is enhanced by the chelate effect. On the other hand a possible contribution of form B to the bond (see Scheme 2) strengthens the C−S bond, preventing its cleavage.

^1H NMR spectrum of **5** shows two singlets at 2.41 and 2.46 ppm, indicating that the two methyl groups are clearly different, at room temperature. That implies that one of the two nitrogen atoms of the pyrimidine group is bonded to the metal and than the bond is stronger than that in complex **2**, as expected for a cationic complex. Dissociation which would allow rotation around the S−C bond and would make the two methyl groups equivalent is not possible. The protons from the Cp groups appear at 6.37 ppm as a singlet which indicates that both ligands are equivalent. The proton of the pyrimidine group appears at 5.41 ppm. ^{13}C NMR spectrum agrees well with the proposed η^2-coordination of thiolate group. ^{13}C NMR resonances for C−Me pyrimidinethiolato atoms at 167.0 and 114.2 ppm respectively suggest that an important contribution of the bonding situation of form B (Scheme 2) may be considered.

In an effort to get a deeper insight on the reactivity of the 4,6-dimethyl-2-mercaptopyrimidine group with different zirconium moieties we have studied the oxidative addition reactions of the thiol on Zr(II) precursors.

Reaction of "Cp^*_2Zr"[18] with 4,6-dimethyl-2-mercaptopyrimidine gives via oxidative addition the hydride−thiolate complex **6** as depicted in Scheme 6.

It is a colorless compound and very soluble in most of the common organic solvents. It has been characterized by elemental analysis, ^1H and ^{13}C NMR, and IR spectroscopy. ^1H NMR shows singlets at 1.89 (30H), 2.04 (3H), and 2.34 ppm (3H) corresponding to the methyl groups in the Cp* ring and the pyrimidine

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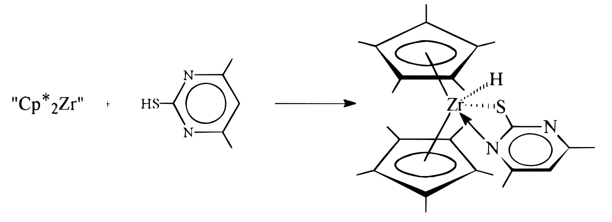
Scheme 6



6

moiety. It means that, at room temperature, the thiolate ligand is bidentate, and rotation around the C−S bond is obstructed. The aromatic proton of the thiolate group appears at 5.49 ppm and the hydride signal at 5.95 ppm which agrees well with the shift expected according to that found in other hydride−zirconocene complexes, like $Cp*_2ZrH(NH_2)$[19] (4.83 ppm) or $(Cp*_2ZrH)_2O$[20] (5.50 ppm).

In conclusion, we would like to call the attention to the great potential offered by this versatile thiolate ligand. On one hand it is possible to stabilize unsaturated compounds due to the assistance of the nitrogen atom without preventing its further reactivity and so, it is possible to synthesize, in a stepwise manner, monoalkyl−thiolate zirconium compounds and the corresponding bis-thiolate zirconium complexes. The ligand is also useful in the stabilization of the cationic thiolate complex, and it is able to undergo oxidative addition reactions in a selective way. On the other hand, it can also behave as a monodentate ligand as is the case in the iminoacyl complex.

Experimental Section

General Procedures. All reactions were carried out by using Schlenk techniques. Toluene was distilled from sodium. Pentane was distilled from sodium/potassium alloy. Diethyl ether and THF were distilled from sodium benzophenone. All solvents were deoxygenated prior to use.

The following reagents were prepared by literature procedures: Cp*H,[21] $Cp*_2ZrCl_2$,[22] Cp_2ZrMe_2,[23] CNXylyl.[24] The commercially available compounds LiMe in diethyl ether, 4,6-dimethyl-2-mercaptopyrimidine, Cp_2ZrCl_2, and ${}^tBuLi$ were used as received from Aldrich.

${}^1H$ and ${}^{13}C$ NMR spectra were obtained on either 200 Gemini or 300 Unity MHz Varian Fourier transform spectrometers. Trace amounts of protonated solvents were used as references, and chemical shifts are reported in units of parts per million relative to $SiMe_4$.

Synthesis of $Cp_2Zr(\eta^2\text{-}SC_6H_7N_2)(Me)$ (2). A mixture of Cp_2ZrMe_2 (0.36 g, 1.43 mmol) and $HS(C_6H_7N_2)$ (0.20 g, 1.43 mmol) was stirred with 20 mL of pentane, at room temperature for 5 h. The white precipitate was separated by filtration and washed twice with 10 mL of pentane and vacuum dried yielding 0.50 g (93%) of **2**: IR (Nujol / PET, cm^{-1}) 3096 (m), 3079 (m), 3056 (m), 2668 (w), 1621 (w), 1575 (s), 1526 (s), 1364 (s), 1336 (s), 1271 (s), 1235 (m), 1186 (w), 1168 (m), 1124 (w), 1063 (w), 1022 (m), 1010 (m), 980 (w), 951 (m), 906 (w), 894 (w), 837 (m), 811 (s), 765 (m), 668 (w), 637 (w), 594 (w), 566 (w), 549 (w), 461 (w), 420 (w), 336 (m), 228 (w), 203 (w); ${}^1H$ NMR (300 MHz, toluene-d_8, −40 °C) δ 0.47 (s, 3 H, CH_3Zr), 1.54 (s, 3H, CH_3), 1.99 (s,, 3H, CH_3), 5.42 (s, 10H, Cp), 5.62 (s, 1H, pyrimidine). Anal. Calcd for $C_{17}H_{20}N_2SZr$: C, 54.36; H, 5.37; N, 7.46. Found: C, 53.93; H, 5.36; N, 7.58.

Synthesis of $Cp_2Zr(SC_6H_7N_2)_2$ (3). A mixture of Cp_2ZrMe_2 (0.46 g, 1.83 mmol) and $HS(C_6H_7N_2)$ (0.51 g, 3.66 mmol) was stirred under reflux, in 15 mL of toluene, for 3 h. The solution was allowed to reach the room temperature, and the white solid that formed was filtered and then washed with pentane (2 × 5 mL) and characterized as **3**: Yield 0.43 g (47%); IR (Nujol/PET, cm^{-1}) 2671 (w), 2329 (w), 2019 (w), 1563 (m), 1266 (s), 1241 (s), 1061 (m), 1014 (m), 967 (w), 874 (w), 820 (m), 796 (s), 764 (m), 552 (m); ${}^1H$ NMR (200 MHz, C_6D_6) δ 1.78 (s, 6H, CH_3), 2.04 (br s, 3H, CH_3), 1.96 (br s, 3H, CH_3), 5.54 (s, 1H, pyrimidine), 5.92 (s, 1H, pyrimidine), 6.23 (s, 10H, Cp). Anal. Calcd for $C_{22}H_{24}N_4S_2Zr$: C, 52.87; H, 4.84; N, 11.21. Found: C, 52.53; H, 4.77; N, 11.13.

Synthesis of $Cp_2Zr(\eta^2\text{-}MeCNXylyl)$ $(\eta^1\text{-}SC_6H_7N_2)\cdot({}^1/{}_2C_4H_8O)$($4\cdot{}^1/{}_2$THF). A mixture of $Cp_2Zr(SC_6H_7N_2)(Me)$ (0.20 g, 0.53 mmol) and 2,6-dimethylphenyl isocyanide (0.07 g, 0.53 mmol) in 20 mL of THF was allowed to react at room temperature for 5 h. After this time, the solvent was partially evaporated under vacuum. Slow diffusion of pentane in the saturated THF solution yielded 0.22 g of insertion product **4**$\cdot{}^1/{}_2$THF in 81% yield: IR (Nujol/PET, cm^{-1}) 2360(w), 1611(m), 1599 (m), 1568 (m), 1556 (m), 1537 (m), 1532 (m), 1519 (m), 1244 (s), 1175 (m), 1159 (w), 1133 (w), 789 (s), 766 (s); ${}^1H$ NMR (200 MHz, C_6D_6) δ 1.44 (m, 2H, THF), 1.92 (s, 6H, CH_3), 1.94 (s, 3H, CH_3), 2.17 (s, 6H, CH_3), 3.59 (m, 2H, THF), 5.85 (s, 10H, Cp), 6.11 (s, 1H, pyrimidine), 6.9 (m, 3H, Xylyl); ${}^{13}C\{H\}$ NMR (300 Mhz, C_6D_6) δ 19.2 (CH_3), 23.6 (CH_3), 23.8 (CH_3), 25.8 (THF), 67.8 (THF), 108.7 (Cp), 112.9 (CH, pyrimidine), 125.6, 128.8 (CH, Xylyl), 130.3 (C−CH_3, Xylyl), 142.8 (C−N, Xylyl), 164.5 (C−CH_3, pyrimidine), 181.4 (C−S), 241.8 (C═N). Anal. Calcd for $C_{28}H_{33}N_3O_{0,5}SZr$: C, 61.95; H, 6.12; N, 7.74. Found: C, 61.61; H, 6.10; N, 7.78.

Synthesis of $[Cp_2Zr(\eta^2\text{-}SC_6H_7N_2)][BPh_4]$ (5). A mixture of complex **2** (0.51 g, 1.36 mmol) and $[NEt_3H][BPh_4]$ (0.57 g, 1.36 mmol) was stirred at room temperature, in 20 mL of THF, for 7 h. After this time, the solvent was partially evaporated under vacuum. Slow diffusion of pentane gave 0.80 g (87%) of the microcrystalline cationic complex **5**: IR (Nujol/PET, cm^{-1}) 1611 (m), 1574 (m), 1567 (m), 1525 (m), 1307 (m), 1264 (m), 1228 (m), 1013 (m), 706 (s). ${}^1H$ NMR (200 MHz, CD_3CN) δ 2.41 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 5.41 (s, 1H, pyrimidine), 6.37 (s, 10H, Cp), 6.92−7.40 (m, 20 H, Ph); ${}^{13}C\{H\}$ NMR (300 MHz, CD_3CN) δ 22.9 (CH_3), 24.4 (CH_3), 114.2 (C−CH_3), 114.8 (Cp), 118.2 (CH, pyrimidine), 122.7, 126.5, 136.7 (CH, BPh_4), 164.7 (${}^1J_{C-B}$ = 49.4 Hz, C−B), 167.0 (C−CH_3), 171.7 (C-S). Anal. Calcd for $BC_{40}H_{37}N_2SZr$: C, 70.67; H, 5.49; N, 4.12. Found: C, 70.55; H, 5.60; N, 4.19.

Synthesis of $Cp*_2Zr(\eta^2\text{-}SC_6H_7N_2)(H)$ (6). To a solution of $Cp*_2ZrCl_2$ (0.37 g, 0.85 mmol) in 10 mL of Et_2O at −78 °C was added 1 mL (1.70 mmol) of a pentane solution of ${}^tBuLi$. The mixture was allowed to reach room temperature and to react for 1 h. The solution was then cooled again at −78 °C and 0.12 g (0.85 mmol) of 4,6-dimethyl-2-mercaptopyrimidine were added. After that the cooling was removed and the mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum, and the residue was extracted with pentane. Partial evaporation of the solvent and cooling at −30 °C for 24 h gave 0.20 g (47%) of a microcrystalline solid which was characterized as **6**: IR (Nujol/PET, cm^{-1}) 1645 (w, broad), 1570 (s), 1552 (w), 1524 (m), 1332 (m), 1259 (s), 1063 (w), 1022 (m), 952 (w), 788 (w), 358 (m); ${}^1H$ NMR (200 MHz, C_6D_6) δ 1.89 (s, 30H, Cp*), 2.04 (s, 3H, CH_3), 2.34 (s, 3H, CH_3), 5.49 (s, 1H, C−H), 5.95 (s, 1H, Zr−H); ${}^{13}C$ NMR (300 MHz, C_6D_6) δ 12.2 (q, ${}^1J_{C-H}$ = 127.4 Hz, Cp*), 23.7 (q, ${}^1J_{C-H}$ = 127.9 Hz, CH_3), 24.0 (q, ${}^1J_{C-H}$ = 127.4 Hz, CH_3), 113.9 (d, ${}^1J_{C-H}$ =

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Table 5. Experimental Data for the X-ray Diffraction Studies

	2	$\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$
mol formula	$C_{17}H_{20}N_2SZr$	$C_{26}H_{29}N_3SZr\cdot{}^{1}/_{2}C_4H_8O$
mol wt	375.638	542.869
cryst syst	monoclinic	monoclinic
space group	$P2_{1/n}$	$P2_{1/c}$
radiation (Mo Kα)	$\lambda = 0.71073$ Å graphite-monochromated	
a, Å	13.905(2)	8.706(2)
b, Å	15.677(2)	22.790(5)
c, Å	7.683(1)	13.607(2)
β, deg	94.20(1)	100.89(2)
V, Å^3	1670.3(4)	2651.1(9)
Z	4	4
D_{calcd}, g cm^{-3}	1.494	1.360
$F(000)$	768	1128
cryst dimens, mm	0.15 × 0.22 × 0.25	0.20 × 0.25 × 0.30
μ(Mo Kα), cm^{-1}	7.78	5.16
diffractometer	Philips PW 1100	Siemens AED
2θ range, deg	6−60	6−60
reflns measd	$\pm h,k,l$	$\pm h,k,l$
unique total data	4866	7718
unique obsd data $[I \geq 2\sigma(I)]$	2360	5141
goodness of fit	1.04	1.07
R,[a] R_w[b]	0.0291, 0.0336	0.0479, 0.0718

[a] $R = \sum| |F_o| - |F_c| |/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

169.2 Hz, CH), 115.1 (s, Cp*), 166.1 (s, C−CH$_3$), 169.0 (s, C−CH$_3$), 184.6 (S, C−S). Anal. Calcd for $C_{26}H_{38}N_2SZr$: C, 62.22; H, 7.63; N, 5.58. Found: C, 62.06; H, 7.89; N, 5.30.

General Procedures Employed in the Crystallographic Studies. A single crystal of each compound was sealed in Lindemann capillary under dry nitrogen atmosphere and used for data collection. Crystallographic data are summarized in Table 5.

Accurate unit cell parameters were determined by least-squares treatment of the setting angles of 30 carefully centered reflections in the θ range 10.8−18.5° for **2** and 11.1−18.9° for $\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$. Data ($3 < \theta < 30°$) were collected at 22 °C on a Philips PW 1100 single-crystal diffractometer (**2**) and on a Siemens AED ($4\cdot{}^{1}/_{2}C_4H_8O$), using the graphite-monochromated Mo Kα radiation ($\lambda = 0.710$ 73 Å) and the $\theta/2\theta$ scan method. The reflections were collected with a variable scan speed of 3−9° min^{-1} and a scan width of $1.20 + 0.34 \tan \theta$. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collections. The individual profiles have been analyzed following the method of Lehmann and Larsen:[25] Intensities were corrected for Lorentz and polarization effects. Only the observed reflections were used in the structure refinements.

The structures were solved by direct and Fourier methods and refined by full-matrix least-squares methods, first with isotropic thermal parameters and then with anisotropic thermal parameters for all the non-hydrogen atoms, except the carbon and the oxygen atoms of the solvent for $\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$. All hydrogen atoms of **2** were clearly located in the ΔF map and refined isotropically, while the hydrogen atoms of $\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$ (except those of the THF molecule which were not calculated) were placed at their geometrically calculated positions (C−H = 0.96 Å) and refined "riding" on the corresponding carbon atoms (with isotropic thermal parameters). The final cycles of refinement were carried out on the basis of 256 (**2**) and 307 ($\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$) variables; after the last cycles no parameters shifted more than 0.51 (**2**) and 0.54 ($\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$). The biggest remaining peak in the final difference map was equivalent to about 0.40 (**2**) and 0.84 (**4**) e/Å^3. In the final cycles of refinement a weighting scheme, $w = k[\sigma(F_o) + gF_o^2]^{-1}$, was used; at convergence the k and g values were 0.4224 and 0.0010 (**2**), 0.5929 and 0.0056 ($\mathbf{4}\cdot{}^{1}/_{2}C_4H_8O$), respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersions.[26] All calculations were carried out on the OULD POWERNODE 6040 and ENCORE 91 of the "Centro di Studio per la Strutturistica Diffrattometrica" of the CNR, Parma. The system of computer programs SIR92,[27] SHELXS-86 and SHELX-76,[28] Parts[29] and ORTEP[30] were used.

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Supporting Information Available: Tables 2 and 4, tables of hydrogen atom coordinates, anisotropic thermal parameters, complete bond distances and angles, and complete crystallographic data (12 pages). Ordering information is given on any current masthead page. A list of structure factors is available upon request from the authors.

OM960396G

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