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Synthesis of Titanium and Zirconium Complexes with 2-Pyridonate and 2,6-Pyridinedithiolate Ligands

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Dedicated to Prof. Ekkehardt Hahn on the Occasion of his 60th birthday with our most sincere congratulations for his outstanding contributions to chemistry and best wishes.

Keywords: Titanium; Zirconium; Cyclopentadienyl Ligands; Heterocyclic Ligands

Treatment of complex $[Cp_2TiCl_2]$ with the lithium salt of 2-hydroxypyridine afforded complex $[Cp_2Ti(Opy)_2]$ (**1**), while the same synthetic strategy applied to the analogous zirconium compound $[Cp_2ZrCl_2]$ did not worked. However, the use of the metallocene $[Cp^{tt}_2ZrMe_2]$ with protic ligands allowed directing the reactivity towards protonation of the methyl groups attached to zirconium. To check this approach we reacted $[Cp^{tt}_2ZrMe_2]$ with methanol affording complex $[Cp^{tt}_2ZrMe(OMe)]$ (**2**), which was characterized *in situ* by NMR techniques. In the same line, the reaction of $[Cp^{tt}_2ZrMe_2]$ with 2-hydroxypyridine gave complex $[Cp^{tt}_2Zr(Me)(Opy)]$ (**3**); forcing the conditions of this reaction did not lead to the expected complex $[Cp^{tt}_2Zr(Opy)_2]$, most probably due to the steric hindrance exerted by the bulky cyclopentadienyl ligands.

Further reactions of complex **3** with ligands having acidic protons also led to the recovery of the starting complex. However, when shifting to the bifunctional ligand 2,6-dimercaptopyridine ($py(SH)_2$) a double protonation of the methyl ligands in $[Cp^{tt}_2ZrMe_2]$ occurred, allowing the isolation of mononuclear complex $[Cp^{tt}_2Zr(\kappa S,\kappa S,\kappa N\text{-}pyS_2)]$ (**4**), upon evolution of methane. The molecular structure of complex **4** has been determined by X-ray methods, showing the zirconium atom in a highly distorted trigonal bipyramidal geometry; structural parameters indicate a conventional Zr-N bond, but rather weak Zr-S interactions.

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Introduction

The synthesis and study of early-late heterobimetallic complexes (ELBH) have been the subject of an intense research. The chemical behaviour of complexes having metallic centers of distinct electronic properties located at close distances could lead to unusual reactivity patterns both in stoichiometric and catalytic processes.[1] The combination in the same system of early metals, considered as electron-poor Lewis acid compounds, and basic late metals suggests the possibility of a cooperative reactivity among them,[2] and also novel modes of intermetallic interactions.[3]

Rational synthetic strategies towards ELBH complexes mainly rely on the preparation of designed metalloligands based on early or late metals, which may induce the coordination of electronic disparate metallic complexes. In this context, the use of early transition metal metallocenes bearing donor atoms around their coordination environment susceptible to coordinate to late metal fragments has allowed the characterization of an important number of ELHB complexes based on thiolate,[4] phosphane[5] and bifunctional[6] early metal-based metalloligands. In this line, hydrosulfido transition metal complexes have proven to be efficient precursors for the preparation of sulfido-bridged homo- and heterometallic ELBH clusters.[7] As a matter of fact, hydrosulfido metallocene early-metal based complexes have been successfully used as metalloligands towards late metallic fragments.[8] In particular, we have reported the compounds $[Cp_2Ti(SH)_2]$ and $[Cp^{tt}_2Zr(SH)_2]$ (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclpentadienyl) as very efficient precursors for the preparation of d^0-d^8 ELBH complexes through additive deprotonation processes with mono- and dinuclear rhodium and iridium compounds having protonable ligands.[9] This synthetic approach has led to the formation of heterotrinuclear complexes with triangular $[MM'_2]$ (M = Ti, M´ = Rh, Ir;[10] M = Zr, M´ = Rh, Ir)[11] cores capped with two sulfido ligands, and also to rare complexes with $[TiM_3]$ (M = Rh, Ir) cores with incomplete cubane structures,[12] and $[Ti_2Rh_4]$ oxo-sulfido clusters, with a double-fused cubane tetrametallic core.[13]

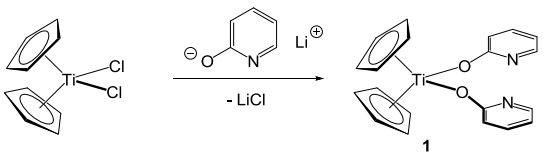
On the other hand, early transition metal metallocenes have also been successfully assembled into homometallic

molecular squares because of their usually distorted tetrahedral geometry.[14] However, only a few early-late heterobimetallic macrocycles containing early metallocenes and late transition metals have been described. An illustration of this statement is based on the tetranuclear Ti/Pt macrocycles,[15] formed through the assembly of bis(pyridine-4-carboxylate)titanocene moieties, but also titanocene or zirconocene halide complexes bearing phophanealkylcyclopentadienyl ligands have been assembled to form tetranuclear M/Rh (M = Ti, Zr) metallomacrocycles.[16] In this context, we have also shown the usefulness of flexible early metallodiphosphines for the synthesis of a series of d^0-d^8 early-late heterobimetallic M/Ir (M = Ti, Zr) tetranuclear 16-membered metallomacrocycles.[17]

In our search towards the preparation potential early metal based metalloligands adapted for the construction of ELBH complexes,[11b, 17] herein we report on the synthesis and characterization of a series of titanium and zirconium mononuclear complexes having functionalized pyridine ligands containing N-C-X (X = O, S) framework.

Results and Discussion

Treatment of complex $[Cp_2TiCl_2]$ with the salt LipyO, generated *in situ* by deprotonation of pyOH (pyOH = 2-hydroxypyridine) with ^{n}BuLi at 0 °C in thf afforded complex $[Cp_2Ti(Opy)_2]$ (**1**), which was isolated as a yellow solid with moderate yield (30%) (Scheme 1). The yield of the reaction increases when using a weaker base such as triethylamine. In this case, the reaction is slower and consequently it needs prolonged reaction time (16h). However, although the yield is higher (70%) recrystallization is required in order to get an analytically pure sample. Complex **1** is soluble in dichloromethane, chloroform and toluene and it is highly unstable towards air and humidity.



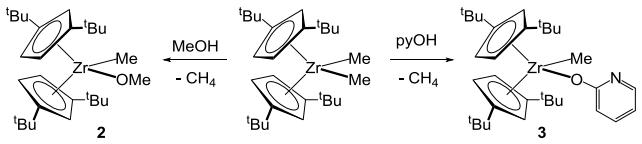
Scheme 1. Synthesis of complex $[Cp_2Ti(Opy)_2]$ (**1**).

The ^{1}H NMR spectrum of **1** in $CDCl_3$ showed four separated multiplets (8.15, 7.48, 6.70, and 6.60 ppm) of relative intensities of 2H in the aromatic region corresponding to the protons of the pyO^- ligand, which confirmed the chemical equivalence of the two pyridine ligands in the molecule, while the cyclopentadienyl ligand was observed at 6.41 ppm as a singlet. The micro-analytical data obtained for complex **1** agreed with the proposed formulation. On the other hand, the mass spectrum of **1** showed a peak at *m/z*: 301 whose isotopic distribution matched with the molecular ion $[CpTi(Opy)_2]^+$, and several peaks corresponding to the sequential loss of the cyclopentadienyl and pyridine ligands. The existence of a symmetry element that relates both the Cp and the 2-pyridonate ligands in the molecule indicates that both pyO^- ligands are coordinated through the same donor atom. The presence of an oxophilic titanium center suggests that both 2-pyridonate ligands should be coordinated through the oxygen atom, which is the most reasonable stereochemistry if one takes into account that this is the less congested coordination mode of the pyridine ligands.

The synthetic strategy shown in Scheme 1 is not operative for the zirconium complex $[Cp_2ZrCl_2]$. In this case, independently of the nature of the base used, mixtures of species are obtained, as confirmed by NMR spectroscopy. However, the change of the nature of the cyclopentadienyl ring allowed us preparing discrete zirconium complexes with bifunctional pyridine ligands. In particular, we have used 1,3-ditertbutylcyclopentadieny ligands, which contains two ^{t}Bu groups that exert a considerable steric effect, which in turn release electronic density to the metal center. Surprisingly, the reaction of the *in situ* generated salt LipyO with complex $[Cp^{tt}_2ZrCl_2]$ does not work, a situation that can be explained considering the steric hindrance of the two ^{t}Bu groups at the cyclopentadienyl rings, which could complicate the metathetical reaction.

An alternative and very attractive synthetic strategy is based on compound $[Cp^{tt}_2ZrMe_2]$ as starting complex, since it contains two methyl groups that in principle can be protonated with ligands bearing acidic protons. One can expect that after protonation and release of methane, the coordination vacant sites should be occupied by the pyO^- ligands. An additional advantage of this synthetic protocol is that the byproduct formed is a gas, which is easily removed and it avoids the separation of LiCl salts. To check the consistency of this approach we treated complex $[Cp^{tt}_2ZrMe_2]$ with an excess of methanol in sealed NMR tube. While at room temperature no changes were observed, at 60 °C slow evolution of methane was observed along with the clean and quantitative formation of the new compound, further characterized as complex $[Cp^{tt}_2ZrMe(OMe)]$ (**2**) by NMR techniques (Scheme 2). The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of complex **2** are in agreement with the expected C_s symmetry, since both cyclopentadienyl ligands were chemically equivalent; additionally, the methyl and methoxo fragments were observed at 0.01 and 3.64 ppm in the ^{1}H NMR spectra, and at 19.3 and 61.3 ppm in the $^{13}C\{^1H\}$ NMR spectra, respectively. Having succeeded in the aforementioned transformation, we decided to apply this strategy with the pyOH ligand.

In this way, the reaction of $[Cp^{tt}_2ZrMe_2]$ with pyOH in a 1:2 molar ratio produced the evolution of methane and the formation of a pale yellow solution. Monitoring of the reaction by NMR spectroscopy showed the formation of a new compound and the presence of unreacted pyOH. Forcing the reaction conditions (90 °C) did not lead to the completion of the process, since free pyOH is always observed. However, reaction of $[Cp^{tt}_2ZrMe_2]$ with pyOH in an 1:1 molar ratio in en toluene at 85 °C led to the clean and quantitative formation of complex $[Cp^{tt}_2Zr(Me)(Opy)]$ (**3**), isolated as an oil which solidified after two days standing at 4 °C (Scheme 2). Complex **3** is soluble in toluene, thf and acetone and partially soluble in diethyl ether. The mass spectrum of **3** showed two peaks at *m/z*: 538 and 443 corresponding to the molecular ions $[Cp_2{}^{tt}Zr(Opy)]^+$ and $[Cp_2{}^{tt}Zr]^+$ respectively, whose isotopic distributions nicely matched with the theoretical values.



Scheme 2. Synthesis of complexes [Cp$^{tt}_2$ZrMe(OMe)] (**2**) and [Cp$^{tt}_2$ZrMe(Opy)] (**3**).

The ^{1}H NMR spectrum of **3** in C_6D_6 at room temperature showed four distinct multiplets with relative intensities of one proton at 8.04, 7.13, 6.33 y 6.28 ppm respectively, which corresponded to the protons of the pyO$^-$ ligand, while the resonances for the Cp^{tt} rings were observed as pseudo triplets at 6.42 ppm (J_{H-H} = 2.52 Hz), 6.00 ppm (J_{H-H} = 2.98 Hz) y 5.80 ppm (J_{H-H} = 2.75 Hz). The pattern of signals observed in the ^{1}H NMR spectrum of **3** indicated the chemical equivalence of both cyclopentadienyl ligands, which are related by a symmetry plane that contains the methyl group and the pyridine ligand. The ^{t}Bu fragments of the cyclopentadienyl rings were observed as two sharp singlets at 1.30 and 1.40 ppm. The methyl group attached to zirconium appeared as a singlet at 0.75 ppm. The ^{13}C{^{1}H} spectrum of **3** in C_6D_6 is also in agreement with the structure proposed in Scheme 2. The carbon atom bonded to both nitrogen and oxygen atoms of the pyridine ligand was observed deshielded, at 172.3 ppm, while that bonded to nitrogen appeared at 156.7 ppm; the rest of the carbon atoms from the pyO$^-$ ligand were located at 139.4, 112.8 and 112.4 ppm. Concerning the Cp^{tt} ligands, two signals at 138.6 and 138.4 ppm were assigned to the carbons of the aromatic rings attached to the tert-butyl groups, and three additional resonances at 114.4, 103.6 and 102.6 ppm corresponded to the remaining carbon atoms from the cyclopentadienyl rings. The ^{t}Bu substituents were observed at 33.7 and 33.3 ppm for the quaternary carbon atoms, and two additional intense resonances at 31.4 and 31.3 ppm. Finally, the methyl group was observed at 27.3 ppm.

In order to further functionalize complex **3** we attempted the protonation of the methyl ligand with selected ligands bearing acidic protons, such as the phosphanes PPh_2CH_2OH and $PPh_2CH_2CH_2SH$ and the thiol compound 2-mercaptopyridine (pySH). Disappointingly no transformations were observed (NMR evidence), even working in refluxing toluene. The low reactivity of phosphane PPh_2CH_2OH could be explained by the low acidity of the hydroxylic proton. However, the acidity of compounds pySH and $PPh_2CH_2CH_2SH$ should be high enough to protonate the methyl group in **3**, a situation that suggests that the lack of reactivity in the latter cases could be explained in terms of steric hindrance exerted by the two cyclopentadienyl derivatives.

However, complex [Cp$^{tt}_2$ZrMe(Opy)] (**3**) does react with SH_2(g). The monitoring of the reaction of **3** with SH_2 (g) in C_6D_6 in a sealed NMR tube at room temperature showed total and clean conversion to a new compound, along with free pyOH. Characteristic resonances were observed at 6.51 (t) y 5.71 (d) from the Cp^{tt} ligands, and a triplet at 2.50 ppm assigned to a SH functionality and a sharp singlet at 2.50 ppm from the ^{t}Bu groups. The NMR data fits with the known complex [Cp$^{tt}_2$Zr(SH)$_2$], which has been confirmed through the comparison of a pure sample of the complex prepared by an established method.[18]

In this line, the related zirconium complex [Cp^{tt}Zr(Spy)$_2$] having 2-pyridinethiol (pySH) ligands is not accessible from reaction of [Cp$^{tt}_2$ZrMe$_2$] with pySH in a 1:2 molar ratio. Both compounds did not react at room temperature; forcing the reaction conditions by heating the reaction mixture led to a mixture of compounds difficult to identify and to separate. This reaction was carried out at different temperatures (40, 60 and 90 ºC), and even changing the molar ration of the reactants no satisfactory results were obtained. We decided at this point shifting to the known 2,6-dimercaptopyridine (py(SH)$_2$) compound;[19] with the aim that the presence of two acidic protons[20] could lead to a double deprotonation process induced by complex [Cp$^{tt}_2$ZrMe$_2$].

In this way, reaction of py(SH)$_2$ with [Cp$^{tt}_2$ZrMe$_2$] in a 1:1 molar ratio in toluene allowed observing the evolution of methane, and afforded after work-up a yellow solid with excellent yield, whose elemental analytic data agreed with the formula [Cp$^{tt}_2$Zr(pyS$_2$)]$_x$. This compound is soluble in chlorinated solvents, thf and insoluble in nonpolar solvents such as hexane and pentane. The new complex has been fully characterized as [Cp$^{tt}_2$Zr(κ*S*,κ*S*,κ*N*-pyS$_2$)] (**4**) (*vide infra*). The ^{1}H RMN spectrum of **4** in $CDCl_3$ showed a Cp^{tt}:pyS$_2^{2-}$ ratio of 2:1. The cyclopentadienyl ligands were chemically equivalent, where the C–H protons of the Cp^{tt} ligands were observed as a doublet at 5.99 ppm (4H) and a triplet at 7.07 ppm (2H) (Figure 1). On the other hand, the resonances from the pyridine ligand were detected as a doublet at 6.21 ppm (2H) and a triplet at 7.01 ppm (1H), the latter from the hydrogen atom bonded to the *para* position of the pyridinic ring. Finally, the ^{t}Bu groups appeared as a singlet at 1.12 ppm. On the other hand, the ^{13}C{^{1}H} RMN spectrum of **4** showed both C–S carbon atoms from the pyS$_2^{2-}$ ligand at 172.7 ppm, and the three remaining carbons were found at 120.5 y 105.9 ppm. The Cp^{tt} ligands gave signals at the usual chemical shifts (see Experimental Section). The NMR data indicates that in complex **4** both Cp^{tt} ligands are related by a symmetry element. Furthermore, there exists a symmetry plane that bisects the two Cp^{tt} ligands and relates both halves of the pyS$_2^{2-}$ ligand.

While the elemental analysis of **4** fits nicely with the formula [Cp$^{tt}_2$Zr(pyS$_2$)]$_n$, the mass spectrum was not conclusive due to the observations of peaks difficult to assign; moreover, molecular weight calculations in solutions did not give any satisfactory information. Due to the rigidity of the 2,6-dimercaptopyridine ligand, one would expect the formation of a dinuclear structure in which two 2,6-pyridinedithiolate ligands are bridging two "Cp$^{tt}_2$Zr" moieties through the sulfur donor atoms, whit a D_{2h} symmetry. Since other structures are also compatible with the spectroscopic information available, we decided to study the molecular structure of **4** by X-ray methods.

The molecular structure of complex [Cp$^{tt}_2$Zr(pyS$_2$)] (**4**) has been determined by a X-ray diffraction study. Figure 1 shows a molecular drawing of complex **4** and Table 1 contains the most representative bond distances and bond angles. Complex **4** results to be mononuclear, with two Cp^{tt} ligands bonded to the metal in their usual η^5-coordination mode. The pyridine-2,6-thiolate ligand is coordinated through both sulfur atoms and the pyridine nitrogen atom. The coordination environment around zirconium can be described as a highly distorted trigonal bipyramid, in which

the axial sites are occupied by the two sulfur atoms and the equatorial plane is defined by pyridine nitrogen atom and the two centroids (T(1) and T(2)) of the aromatic rings. The biggest deviation from an ideal trigonal bipyramidal geometry is associated to the chelate coordination of the 2,6-pyridinedithiolate ligand. In this way, the S(1)-Zr-S(2) angle, 115.12(2)º, is quite small as a consequence of the intrinsic rigidity of the pyridine ligand. Within the equatorial plane, the T(1)-Zr-T(2) angle of 132.84(4)º deviates from the theoretical value (120º) most likely due to the steric needs generated by the presence of the bulky tert-butyl groups. The bond distances Zr–T(1) and Zr–T(2) are 2.2450(11) and 2.2391(10) Å respectively, which are comparable to those observed in other zirconium(IV) complexes such as $[Cp^{tt}_2Zr(SH)(OSO_2CF_3)]$ (2.237(4) and 2.239(5) Å)[11b] or $[Cp^{tt}_2ZrI_2]$ (2.248 and 2.251 Å).[21] The Zr–N bond distance, 2.1642(19) Å, is similar to that found in zirconium complexes such as $[(^tBu–NH–o–C_6H_4)_2Zr(NMe_2)Cl]$ (2.102(3) and 2.098(3) Å)[22] or $[HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Zr(S_2C)Fe(CO)_2Cp]$ (2.060(8)-2.124(8) Å),[23a] or $[Cp_2Zr(dipicolinato)]$ (2.199(2) Å).[23b] However, the Zr–S(1) (2.8319(7) Å) and Zr–S(2) (2.8685(6) Å) bond distances are significantly longer than those observed in the majority of mononuclear complexes of Zr(IV), which lie within the range 2.39-2.80 Å,[24] although they are comparable with those found in complex $[Cp^*ZrCl_2\{Ph_4P_2N_4S(SMe)\}]$ (2.8010(6) and 2.919(6) Å).[25] Therefore, while the Zr–N bond reflects a normal interaction, those formed between the zirconium and sulfur atoms seems to be rather weak.

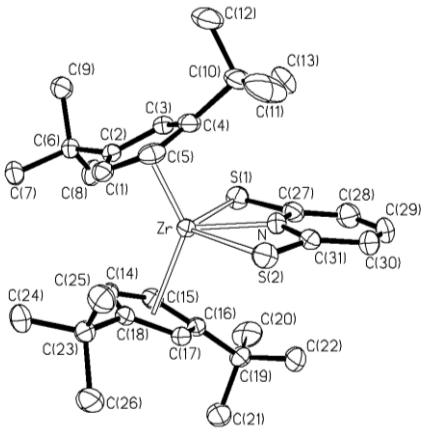


Figure 1. Molecular structure of complex **4**.

On the other hand, the 2,6-pyridinedithiolate ligand is nearly planar, with sulfur deviations below 0.023(1) Å (for S(2)). The bond separations C(27)–S(1) (1.730(3) Å) and C(31)–S(2) (1.732(3) Å) are comparable to those observed in complex $[Rh_4(\mu\text{-}pyS_2)_2(cod)_4]$ (cod = 1,5-cyclooctadiene) in which both sulfur atoms are coordinated solely to a rhodium atom (C–S: 1.739(4) Å).[20] However, the structural arrangement of the pyridinic ligand in complex **3** is very different, since in this case the three donor atoms are coordinated to one metal center. This disposition makes the N-C(31)-S(2) (108.24(18)º) and N-C(27)-S(1) (107.41(18)º) angles to be more acute then those corresponding to the tetranuclear rhodium complex mentioned above (119.8(3) and 117.0(3)º). These differences are specially relevant in the angles centered at the sulfur atoms, which are Zr-S(1)-C(27) (78.32(9)º) and Zr-S(2)-C(31) (77.36(8)º), considerably smaller than those observed in the tetranuclear rhodium complex (116.1(1), 105.6(1) and 108.8(1)º). These values strongly indicate that in complex **4** there exists a high degree of tension due to the chelate coordination of the pyridinic ligand, and it suggests, in principle, that complex **4** should be highly reactive, as the long Zr–S distances observed also indicate.

Table 1. Selected bond distances (Å) and angles (º) of complex **4**.*

Zr–T(1)	2.2450 (11)	N–C(31)	1.329 (3)
Zr–T(2)	2.2391 (10)	N–C(27)	1.339 (3)
Zr–S(1)	2.8319 (7)	C(27)–C(28)	1.391 (4)
Zr–S(2)	2.8685 (6)	C(28)–C(29)	1.377 (4)

T(1)–Zr–T(2)	132.84 (4)	Zr–S(1)–C(27)	78.30 (8)
S(1)–Zr–T(1)	104.31 (3)	Zr–S(2)–C(31)	77.38 (8)
S(1)–Zr–T(2)	100.12 (3)	C(31)–N–C(27)	126.4 (2)
S(2)–Zr–T(1)	99.71 (3)	N–C(27)–C(28)	117.4 (2)
S(2)–Zr–T(2)	105.47 (3)	C(29)–C(28)–C(27)	117.7 (3)
N–Zr–T(1)	112.70 (6)	C(28)–C(29)–C(30)	123.1 (3)
N–Zr–T(2)	114.46 (6)	C(29)–C(30)–C(31)	117.3 (3)
S(1)–Zr–S(2)	115.12 (2)	C(30)–C(31)–N	118.0 (2)

* T(1) and T(2) represent the centroids of both Cp^{tt} ligands.

The high yield synthesis of complex **4** allowed us attempting some reactivity with complexes based on late transition metals. In principle, the coordination mode of the pyridine ligand to zirconium in **4** could have an effect in its reactivity towards metallic fragments, since there are no coordination sites available. However, reactions with naked metallic ions could lead to a structural reorganization which could form metallomacrocycles, as it was reported earlier in the reaction of the tetranuclear $[Rh_4(\mu\text{-}pyS_2)_2(cod)_4]$[20] in its reaction with thallium salts, producing a metallomacrocycle in which the thallium center is coordinated through the nitrogen pyridine atoms.[26] Disappointingly, the result of the reaction of **4** with $TlPF_6$ (or $TlCF_3SO_3$) led to the isolation of insoluble solids, which were not further characterized. On the contrary, treatment of complex **4** with the solvate complex $[Rh(cod)(Me_2CO)][BF_4]$ in a 1:1 molar ratio formed the aforementioned tetranuclear complex $[Rh_4(\mu\text{-}pyS_2)_2(cod)_4]$, which was identified by comparison of their NMR spectra. Additionally, a fraction of colorless crystals were obtained as a sub-product. The ^1H NMR spectrum of the crystals showed a pattern characteristic of the moiety "Cp^{tt}_2Zr". Additionally, spectrometric measurements showed two intense peaks at *m/z*: 483 and 463 corresponding to the molecular ions $[Cp^{tt}_2ZrF_2]^+$ and $[Cp^{tt}_2ZrF]^+$, respectively, an information that indicates that the "Cp^{tt}_2Zr" fragments resulting from the ligand transfer to rhodium most probably abstract fluorine atoms from the BF_4^- anion.

The formation of ELHB complexes usually competes with transfer processes of ligands with intrinsic ability to act as bridges within late metal centres,[27] a situation particularly observed in the case of thiolate-based ligands. As a matter of

fact, ligand transfer reactions from thiolate titanocene and zircocene complexes have been used to prepare the corresponding late transition metal thiolate complexes of Co,[28] Rh,[10a,29] Pd[30] and Pt.[31]

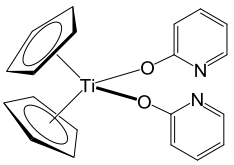
Conclusions

We have prepared some mononuclear titanium and zirconium complexes functionalized with pyridine-based bifunctional ligands. The metathetical approach starting from $[Cp_2TiCl_2]$ and pyO^- salts allowed preparing a titanium complex functionalized with two pyridonate ligands. On the other hand, the use of the zirconium complex $[Cp^{tt}{}_2ZrMe_2]$ allowed applying a different synthetic strategy based on the ability of the methyl groups to be protonated with acidic ligands. In this way, methanol and 2-hydroxopyridine protonated only one of the methyl groups in $[Cp^{tt}{}_2ZrMe_2]$ affording the corresponding alkoxo methyl complexes. The use of 2,6-dimercaptipyridine allowed protonating both methyl ligands in $[Cp^{tt}{}_2ZrMe_2]$ forming a mononuclear complex with the 2,6-pyridinedithiolate ligand exhibiting an unusual κ*S*,κ*S*,κ*N* tridentate coordination mode.

Experimental Section

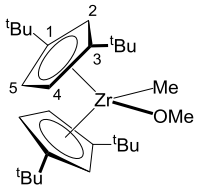
All manipulations were performed under a dry argon atmosphere using Schlenk-tube techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. Carbon and hydrogen analyses were performed in a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded in a VG Autospec double-focusing mass spectrometer operating in the FAB^+ mode. Ions were produced with the standard Cs^+ gun at ca. 30 kV; 3-nitrobenzyl alcohol (NBA) was used as matrix. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ spectra were recorded on Varian UNITY, Bruker ARX 300, and Varian Gemini 300 spectrometers operating at 299.95, 75.47 and 121.49 MHz; 300.13, 75.47 and 121.49 MHz; and 300.08, 75.46 and 121.47 MHz, respectively. Chemical shifts are reported in ppm and referenced to Me_4Si using the signal of the deuterated solvent (^1H and ^{13}C) as external references. Complex $[Cp^{tt}{}_2ZrMe_2]$[32] and compound $py(SH)_2$[19] were prepared according to published procedures. The compounds $[Cp_2MCl_2]$ (M = Ti, Zr) were purchased from Aldrich and used as received.

Preparation of $[Cp_2Ti(Opy)_2]$ (1). *Method (a)*: To a solution of pyOH (0.39 g, 4.02 mmol) in thf (20 mL), NEt_3 (0.56 ml, 4.036 mmol) was added *via* syringe. After stirring the solution for 5 min., solid $[Cp_2TiCl_2]$ (0.50 g, 2.01 mmol) was added. The resulting mixture turned orange gradually and a white solid precipitated ($HNEt_3Cl$). After 16 h of stirring, the orange solution was filtered through a cannula, and then the solvent was evaporated under vacuum, rendering an oily material. This was washed with hexanes, affording an orange solid, which was then vacuum-dried. Yield: 0.52 g (70%). *Method (b)*: To a solution of pyOH (0.17 g, 1.69 mmol) in thf (10 mL) at 0 ºC, ^{n}BuLi (1.1 mL, 1.6 M in hexane, 1.76 mmol) was added *via* syringe, forming a pale yellow solution. Further addition of solid of $[Cp_2TiCl_2]$ (0.20 g, 0.80 mmol) formed a dark brown solution that was stirred for 2 h from which a yellow solid crystallized out. This was isolated by filtration, washed with diethyl ether and then vacuum-dried. Yield: 0.09 g (30%).



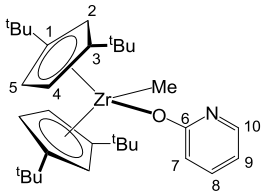
^1H NMR (C_6D_6, 293 K): δ 8.15 (m, 2H), 7.48 (m, 2H), 6.70 (m, 2H), 6.60 (m, 2H) (pyO), 6.41 (s, 10H, Cp^{tt}). EI(+, CH_2Cl_2): *m/z* (%): 301 (M^+–Cp, 24), 272 (M^+–pyO, 42), 207 (M^+–Cp–pyO, 75), 142 (M^+–2 Cp–pyO, 6), 113 (M^+–Cp^{tt}–2 pyO, 6). Anal. Calcd for $C_{20}H_{18}N_2O_2Ti$: C, 65.58; H, 4.95; N, 7.65. Found: C, 65.49; H, 4.82; N, 7.58.

Preparation of $[Cp^{tt}{}_2ZrMe(OMe)]$ (2). To a yellowish solution of $[Cp^{tt}{}_2ZrMe_2]$ (0.05 g, 0.11 mmol) in hexane (5 mL), CH_3OH (93 µL, 1.05 mmol, 10 equiv) was added *via* microsyringe. The solution was heated at 60 °C for 30 min to give a cloudy solution. The solvent was removed under vacuum to give a microcrystalline white powder.



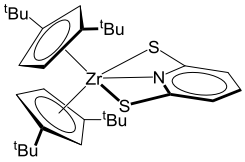
^1H NMR ($CDCl_3$, 293 K): δ 6.14 (t, 2H, J_{H-H} = 2.4 Hz), 5.63 (t, 2H, J_{H-H} = 2.7 Hz), 5.53 (t, 2H, J_{H-H} = 2.4 Hz) (Cp^{tt}), 3.64 (s, 3H, OMe), 1.19 (s, 18H, ^{t}Bu), 1.18 (s, 18H, ^{t}Bu), 0.01 (s, 3H, Me). $^{13}C\{^1H\}$ RMN ($CDCl_3$, 293 K): δ 138.1, 137.0 (C1 and C3), 112.2 (C2), 102.7, 100.8 (C4 and C5), 61.3 (OMe), 33.2, 32.7 (*C*Me_3), 31.3, 30.9 (C*Me*$_3$), 19.3 (Zr–Me).

Preparation of $[Cp^{tt}{}_2ZrMe(Opy)]$ (3). Complex $[Cp^{tt}{}_2ZrMe_2]$ (0.20 g, 0.42 mmol) and pyOH (0.412 g, 0.420 mmol) were dissolved in toluene (15 mL) and the solution was transferred to a Kontes tube. The mixture was stirred for 5 h at 85 ºC and the resulting solution was allowed to reach room temperature. The solvent was removed under vacuum affording a colorless oil, which solidified after two days at 4 °C. Yield: 0.21 g (92%).



^1H NMR (C_6D_6, 293 K): δ 8.04 (m, 1H), 7.15 (m, 1 H), 6.42 (t, 2H, J_{H-H} = 2.52 Hz), 6.33 (m, 1H), 6.28 (m, 1H), 6.00 (t, 2H, J_{H-H} = 2.98 Hz), 5.80 (t, 2H, J_{H-H} = 2.75 Hz), 1.40 (s, 18H, ^{t}Bu), 1.30 (s, 18H, ^{t}Bu), 0.75 (s, 3H, Me). $^{13}C\{^1H\}$ RMN (C_6D_6, 293 K): δ 172.3 (s, N-*C*$_6$-O), 146.7 (s, *C*$_{10}$-N), 139.4 (s, *C*H pyO), 138.6, 138.4 (C_1 and C_3), 112.8, 112.4 (s, CH pyO), 114.4, 103.6, 102.6 (C_2, C_4, C_5), 33.7, 33.3 (*C*(Me_3)), 31.4, 31.3 (C*Me*$_3$), 27.3 (s, Zr–Me). (FAB+, THF): *m/z* (%): 538 (M^+–CH_3, 17), 443 (M^+–CH_3–pyO, 35).

Preparation of $[Cp^{tt}{}_2Zr(pyS_2)]$ (4). To a solution of complex $[Cp^{tt}{}_2ZrMe_2]$ (0.30 g, 0.63 mmol) in toluene (20 mL), solid $py(SH)_2$ (0.09 g, 0.63 mmol) was added, giving a yellow solution which was stirred for 30 min. At this point the solvent was removed under vacuum yielding an oily residue. This was washed with hexane, which afforded a yellow solid which was isolated by filtration and then it was vacuum-dried. Yield: 0.30 g (82%).



^1H NMR (C_6D_6, 293 K): δ 7.07 (t, 2H, $^4J_{H-H}$ = 2.5 Hz, Cp^{tt}), 7.01 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, H$_p$ pyS$_2$), 6.21 (d, 2H, $^3J_{H-H}$ = 8.0 Hz, H$_o$ pyS$_2$),

5.99 (d, 4H, $^4J_{H–H}$ = 2.5 Hz, Cp^{tt}), 1.12 (s, 36H, ^{t}Bu). $^{13}C\{^1H\}$ RMN ($CDCl_3$, 293 K): δ 172.7 (s, C–S pyS_2), 138.8 (s, Cp^{tt}), 120.5 (s, pyS_2), 115.5 (s, Cp^{tt}), 105.9 (s, pyS_2), 104.2 (s, Cp^{tt}), 339 (s, *C*Me$_3$), 31.1 (s, C*Me$_3$*). Anal. Calcd for $C_{31}H_{45}NS_2Zr$: C, 63.43; H, 7.33; N, 2.39. Found: C, 63.28; H, 7.55; N, 2.28.

Crystal Structure Determination of Complex [Cp$^{tt}_2$Zr(pyS_2)] (4). Single crystals for the X-ray diffraction study were grown from a saturated solution of **4** in hexane at –15 °C. X-ray diffraction data were collected at 173(2) K with graphite monochromated Mo Kα radiation (λ = 0.71073 Å), using narrow ω rotation (0.3º) on a Bruker SMART APEX CCD diffractometer. Intensities were integrated and corrected for absorption effects with the SAINT-PLUS program.[33] The structure was solved by direct methods with SHELXS-97.[34] Refinement, by full matrix least squares on F^2, was performed with SHELXL-97.[35] All atoms were refined first with isotropic and then with anisotropic displacement parameters. Hydrogen atoms were included from observed positions and refined as free isotropic atoms.

Crystal data: $C_{31}H_{45}NS_2Zr$, M = 587.02 g·mol^{-1}; yellow irregular block, 0.366 × 0.275 × 0.250 mm^3; monoclinic, $P2_1/c$; a = 15.1041(12), b = 10.2311(8), c = 19.3472 (15) Å; β = 99.1460(10)º; Z = 4; V = 2951.7(4) Å^3; ρ_{calc} = 1.321 Mg·m^{-3}; μ = 0.534 mm^{-1}, min. and max. absorption correction factors 0.600 and 0.906; $2\theta_{max}$ = 57.53º; 19016 collected reflections, 7009 unique (R_{int} = 0.039); number of data/restrains/parameters 7009/0/496; final *GOF* 0.921; R_1 = 0.0397 (5366 reflections, $I > 2\sigma(I)$); wR_2 = 0.0777 for all data; largest difference peak 0.742 e/Å^3. Crystallographic data (including structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1408667 (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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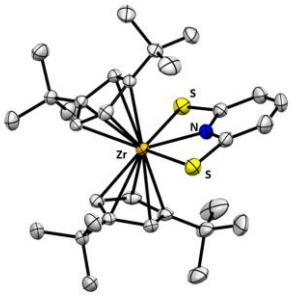

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Synthesis of Titanium and Zirconium Complexes with 2-Pyridonate and 2,6-Pyridinedithiolate Ligands