New *Early* Zirconium-Sulfido Metallaligands for *Late* Transition Metals; Synthesis and Reactivity of [$Cp^{tt}{}_2Zr(SH)_2$] and [$Cp^{tt}{}_2Zr(SH)(OTf)$]

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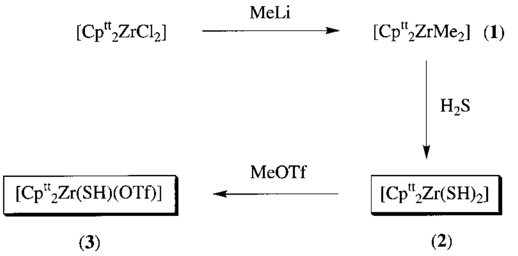
The bishydrosulfido zirconium metallocene compound [$Cp^{tt}{}_2Zr(SH)_2$] (**2**) containing the bulky η^5-1,3-di-*tert*-butylcyclopentadienyl (Cp^{tt}) ligand is readily accessible from [$Cp^{tt}{}_2Zr(CH_3)_2$] (**1**) upon treatment with H_2S. Reaction of **2** with methyltriflate gives the monohydrosulfido complex [$Cp^{tt}{}_2Zr(SH)(OSO_2CF_3)$] (**3**) which exists as two isomers in solution, and has been characterized by X-ray diffraction methods. Complex **2** is an effective metallaligand for the controlled synthesis of new trinuclear *early-late* heterobimetallic complexes (ELHB) with a $ZrRh_2$ core such as [$Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$] (**4**).

Interest in *early-late* heterobimetallic complexes (ELHB) stems in part from the potential new reactivity patterns associated with the presence of two widely divergent transition metals.[1] The combination of both an electron-deficient *early* transition metal and an electron-rich *late* transition metal in a single molecule provides a bifunctional environment which should allow the cooperative activation of organic substrates in both catalytic[2] and stoichiometric reactions.[3] A useful synthetic approach for ELHB complexes involves the use of *early* transition metal complexes as metallaligands for *late* transition metal species.[4] Following this approach we have recently described the use of the titanium bishydrosulfido compound $Cp_2Ti(SH)_2$ for the construction of unusual *early-late* titanium-rhodium tetranuclear complexes and hexanuclear clusters such as [$CpTi(\mu_3\text{-}S_3)\{Rh(tfbb)\}_3$][5] and [$\{CpTi\}_2(\mu_4\text{-}O)(\mu_3\text{-}S)_4\{Rh_4(CO)_4(PR_3)_2\}$],[6] respectively.

As part of our general interest in this chemistry we have extended this synthetic methodology to the preparation of zirconium-rhodium ELHB complexes. Mononuclear metallocene zirconium sulfido and hydrosulfido derivatives are rare and usually undergo the loss of H_2S to give sulfido-bridged dimers.[7] Thus, we have attempted to synthesize stable mononuclear zirconium-metallocene hydrosulfido compounds suitable for the synthesis of ELHB complexes. This paper describes the synthesis of such zirconium hydrosulfido complexes containing the bulky Cp^{tt} ligand (Cp^{tt} = η^5-1,3-di-*tert*-butylcyclopentadienyl) and their use as metallaligands for the construction of heterotrinuclear Zr-Rh complexes.

The bishydrosulfido complex [$Cp^{tt}{}_2Zr(SH)_2$] (**2**) is obtained in two steps starting from the corresponding metallocene dichloride (Scheme 1). Thus, reaction of [$Cp^{tt}{}_2ZrCl_2$] with a slight excess of MeLi in diethyl ether at −78 °C gives the dimethyl complex [$Cp^{tt}{}_2Zr(CH_3)_2$] (**1**) which can be isolated as off-white crystals,[8] in 96% yield, after removal of LiCl by extraction of the product with hexane. Reaction of **1** with an excess of H_2S(g), in toluene at 95 °C in a Pyrex bomb under pressure for 14 h, affords a bright yellow solution from which the complex [$Cp^{tt}{}_2Zr(SH)_2$] (**2**) can be obtained as pale yellow crystals, in 87% yield, after recrystallisation from diethyl ether. The ^{1}H NMR spectrum of **2** shows the expected resonances for the protons of the two equivalent Cp^{tt} rings (C_{2v} symmetry) and a singlet at δ = 2.11 ppm for the SH groups. The complex [$Cp^{tt}{}_2Zr(SH)_2$] (**2**) reacts with a threefold excess of methyltriflate (CF_3SO_3Me) in dichloromethane to give the monohydrosulfido complex [$Cp^{tt}{}_2Zr(SH)(OSO_2CF_3)$] (**3**). This complex is isolated as moisture-sensitive yellow crystals in 81% yield after recrystallisation from diethyl ether.



Scheme 1. The synthesis of hydrosulfido zirconium complexes

The crystal structure of **3** consists of discrete monomers (Figure 1). The metal centre exhibits a *pseudo*-tetrahedral geometry with the sulfur atom of the hydrosulfido ligand, the oxygen of the coordinated triflate anion and the two Cp^{tt} ring centroids at the apices. The Zr−Cp^{tt} ring-centroid distances {2.237(4) and 2.239(5) Å} are identical to those observed in the related complex [$Cp^{tt}{}_2ZrI_2$] (2.248 and 2.251 Å)[8a] although the Cp^{tt}−Zr−Cp^{tt} angle is slightly smaller in **3** {129.78(15)°} than in the latter compound (133.0°). The relative disposition of the Cp^{tt} rings along the G(1)···G(2) direction is staggered with a dihedral angle C(2)···G(1)···G(2)···C(15) of 52.4(5)°, thereby reducing the

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steric hindrance of the bulky *tert*-butyl substituents. The Zr−O(1) bond length {2.199(3) Å} is similar to other Zr−O(triflate) bond lengths, such as that reported in $[Cp_2Zr(OSO_2CF_3)(\mu\text{-}H)]_2$ {2.205(2) Å};[9] the rather large Zr−O(1)−S(2) angle, 136.59(15)°, compares well with the values described in other triflate complexes (range: 100−164°).[10]

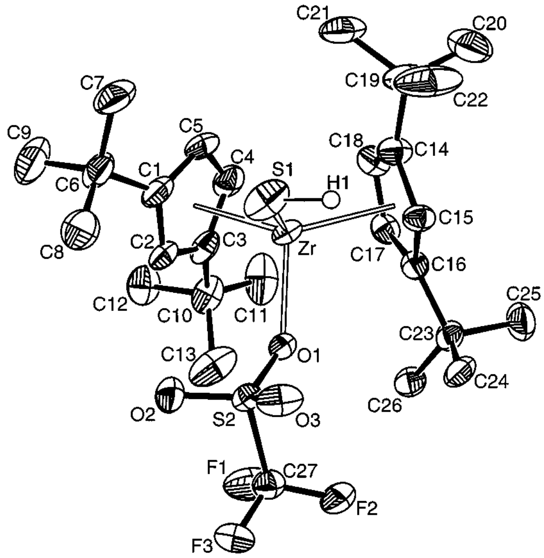
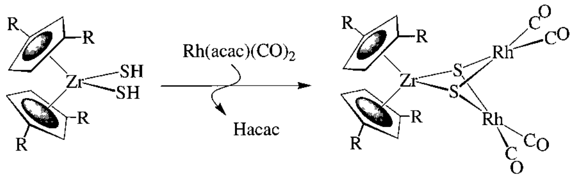


Figure 1. Molecular drawing of $[Cp^{tt}{}_2Zr(SH)(OSO_2CF_3)]$ (**3**) (hydrogen atoms, except H1, have been omitted for clarity); selected bond lengths [Å] and angles [°]: Zr−S(1) 2.4586(15), Zr−O(1) 2.199(3), Zr−G(1) 2.237(4), Zr−G(2) 2.239(5); S(1)−Zr−O(1) 92.61(7), S(1)−Zr−G(1) 106.74(12), S(1)−Zr−G(2) 105.99(12), O(1)−Zr−G(1) 107.69(13), O(1)−Zr−G(2) 107.74(14), G(1)−Zr−G(2) 129.78(15) [G(1) and G(2) represent the midpoints of the C(1)−C(5) and C(14)−C(18) rings, respectively]

The complex $[Cp^{tt}{}_2Zr(SH)(OSO_2CF_3)]$ (**3**) exists in solution as two isomers (3:1 ratio in C_6D_6, isomers **3a** and **3b**) as evidenced by ^1H, ^{19}F and ^{13}C NMR spectroscopy. These isomers do not arise from a dissociation of the triflate ligand nor from association of mononuclear complexes, since **3** is a nonconductor in dichloromethane and the molecular weight measured in chloroform is in agreement with a mononuclear formulation. Both isomers show three triplets for the protons of the two equivalent Cp^{tt} rings in the ^1H NMR spectrum in C_6D_6 in accordance with the lower symmetry of **3** compared to its precursor **2**. The main difference between **3a** and **3b** concerns the SH ligand. The major isomer **3a** possesses the structure found in the solid state, since an NOE effect (10%) is observed between the proton of SH ligand at $\delta = 4.04$ ppm and one of the protons of the Cp^{tt} ring {the H(1)···H(C15) distance is 2.526 Å in the solid state}. The minor isomer **3b** shows an unusually low-field-shifted resonance for the proton of the hydrosulfido ligand at $\delta = 6.27$ ppm. In addition, no NOE effect is observed between the SH group and any of the protons of the Cp^{tt} ligands. A reasonable explanation for these observations in **3b** could be the existence of an intramolecular hydrogen bonding between the SH proton and one of the unbound oxygen atoms of the triflate ligand forming a six-membered metallacycle. In fact, a rotation of the hydrosulfido ligand around the Zr−S bond in a molecular model based on the solid state structure of **3** can bring the hydrogen atom to a distance from O(3) of less than 2.55 Å. It should be noted that a similar intramolecular interaction has been observed in the solid state structure of the aquo-complex $[(CH_3)_2Au(H_2O)(OSO_2CF_3)]$.[11] Interestingly, the related complex $[Cp^*{}_2Zr(OH)(OSO_2CF_3)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$), obtained by reaction of $[Cp^*{}_2Zr(OH)Cl]$ with silver triflate, exits as a single compound in solution.[12]

Additive-deprotonation of $[Cp^{tt}{}_2Zr(SH)_2]$ (**2**) with appropriate rhodium complexes results in the clean formation of trinuclear d^0-d^8 ELHB compounds with a $ZrRh_2$ core. In contrast, additive-deprotonation reactions of $[Cp^{tt}{}_2Zr(SH)(OSO_2CF_3)]$ (**3**) are much more complex since the transfer of the sulfido ligands to the d^8 metal centres is observed. Thus, reaction of **2** with two molar equiv. of $[Rh(acac)(CO)_2]$, in diethyl ether, gives the complex $[Cp^{tt}{}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2]$ (**4**) as a sparingly soluble, emerald-green microcrystalline powder in 93% yield (Scheme 2). The structure of **4** has a triangular $ZrRh_2$ core capped by two symmetrical μ_3-sulfido ligands in accordance with the high symmetry (C_{2v}) observed by NMR spectroscopy. In particular, the ^1H NMR spectrum shows only two resonances for the protons of the Cp^{tt} rings, and a unique doublet for the carbonyl ligands is observed in the $^{13}C\{^1H\}$ NMR spectrum. Reaction of **3** with one molar equiv. of $[Rh(acac)(CO)_2]$ in diethyl ether does not afford the desired *early-late* heterodinuclear complex since a ligand redistribution process takes place. The known anion[13] $[Rh_3(\mu_3\text{-}S)_2(CO)_6]^-$ and the new cation[14] $[Cp^{tt}{}_2Zr(acac)]^+$ are detected in the reaction mixture. Both species are formed by the transference of the sulfido ligands from zirconium to rhodium, probably through a heterobimetallic intermediate. However, the formation of the ion-pair compound $[Cp^{tt}{}_2Zr(acac)][Rh_3(\mu_3\text{-}S)_2(CO)_6]$[15] is not clean since the trinuclear ELHB complex **4** and free HCp^{tt} are also observed spectroscopically.

In conclusion, we have synthesized new zirconium hydrosulfido metallocenes containing the bulky Cp^{tt} ligand and shown the ability of the bishydrosulfido complex **2** to build unusual $ZrRh_2$ ELHB complexes in a controlled way. Further work concerning both the scope of this synthetic methodology and the potential reactivity of the monosulfido complex **3** is in progress.



(2) **(4)**

Scheme 2. The synthesis of a trinuclear *early-late* complex with a $ZrRh_2$ core; R denotes the *tert*-butyl group

Experimental Section

General: All manipulations were performed under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled under argon immediately prior to use. [$Cp^{tt}_2ZrCl_2$][16] and [Rh(acac)(CO)$_2$][17] were prepared according to reported methods. NMR spectra were recorded at 20°C on Varian Gemini 2000 (^{1}H: 300.08, ^{19}F: 282.33 and ^{13}C{^{1}H}: 75.47 MHz) or Varian UNITY 300 (^{1}H cyclenOe experiments) spectrometers. Chemical shifts δ are reported in ppm and referenced to Me_4Si using the signal of the deuterated solvent (^{1}H and ^{13}C). ^{19}F chemical shifts are relative to $CFCl_3$. Coupling constants are given in Hz. IR spectra were recorded on a Nicolet 550 spectrometer. Elemental analyses were performed with a Perkin−Elmer 2400 analyzer. Conductivities were measured in ca. 5×10^{-4} M dichloromethane solutions with a Philips PW 9509 conductimeter. Molecular weights were determined with a Knauer osmometer from chloroform solutions of the complexes. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in both FAB$^+$ and FAB$^-$ modes. Ions were produced with the standard Cs$^+$ gun at ca. 30 kV, 3-nitrobenzyl alcohol (NBA) was used as matrix.

[$Cp^{tt}_2Zr(CH_3)_2$] (1): [$Cp^{tt}_2ZrCl_2$] (5 g, 9.68 mmol) was slurried in 100 mL of diethyl ether at −78°C and reacted with a 1.5 M diethyl ether solution of methyllithium (14 mL, 21 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for a further 12 h. The mixture was again cooled to −78°C and 1 mL of methanol was added to destroy the unchanged methyllithium. Solvents were removed under vacuum and the residue was extracted with 70 mL of n-hexane and filtered over dry celite. The resulting solution was concentrated under reduced pressure to ca. 20 mL and stored at −25°C overnight to give off-white crystals. The crystals were collected by filtration and dried in vacuo. Concentration and cooling of the mother liquor gave a second crop of crystals. Overall yield: 4.4 g (96%). − ^{1}H NMR ($CDCl_3$): δ = 6.47 [t, ^4J(H,H) = 2.7 Hz, 2 H, H_2], 5.38 (d, ^4J(H,H) = 2.7 Hz, 4 H, H_4 and H_5), 1.21 (s, 36 H, CMe_3) (Cp^{tt}), −0.28 (s, 6 H, Zr−CH_3). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 138.6 (C_1 and C_3), 115.7 (C_2), 100.5 (C_4 and C_5), 33.4 (CMe$_3$), 31.4 (CMe_3) (Cp^{tt}), 31.0 (Zr−CH$_3$). − $C_{28}H_{48}Zr$ (475.91): calcd. C 70.67, H 10.17; found C 70.00, H 9.33.

[$Cp^{tt}_2Zr(SH)_2$] (2): A solution of [$Cp^{tt}_2Zr(CH_3)_2$] (**1**) (2 g, 4.202 mmol) in toluene (10 mL) was placed in a Pyrex bomb. The reaction vessel was evacuated and charged to a pressure of *ca.* 2.5 atm. with H_2S. The solution was stirred at 95°C for 14 h. The reaction vessel was depressurised and the resulting bright yellow solution flushed with argon. The volatiles were removed under reduced pressure and the residue was dissolved in 55 mL of diethyl ether. The solution was filtered and concentrated under vaccum to the point of crystallisation. Cooling of the solution to −25°C overnight gave the compound as pale yellow crystals which were collected and dried in vacuo. Concentration and cooling of the mother liquor gave a second crop of crystals. Overall yield: 1.876 g (87%). − ^{1}H NMR ($CDCl_3$): δ = 6.46 [t, ^4J(H,H) = 2.7 Hz, 2 H, H_2], 5.71 [d, ^4J(H,H) = 2.7 Hz, 4 H, H_4 and H_5 of Cp^{tt}], 2.11 (s, 2 H, Zr−SH), 1.31 (s, 36 H, CMe_3). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 140.6 (C_1 and C_3), 119.8 (C_2), 102.2 (C_4 and C_5), 33.8 (CMe$_3$), 31.7 (CMe_3). − MS (CH_2Cl_2, *m*/*z*,%); FAB$^+$: 477 (100) [$Cp^{tt}_2Zr(SH)^+$]; FAB$^-$: 509 (90) [$Cp^{tt}_2Zr(SH)(S)^-$], 331 (100) [$Cp^{tt}Zr{=}S(S)^-$]. − $C_{26}H_{44}S_2Zr$ (511.98): calcd. C 61.00, H 8.66, S 12.53; found C 60.95, H 8.07, S 12.61.

[$Cp^{tt}_2Zr(SH)(OSO_2CF_3)$] (3): A solution of [$Cp^{tt}_2Zr(SH)_2$] (**2**) (0.2 g, 0.391 mmol) in dichloromethane (5 mL) was reacted with methyltriflate (130 µL, 1.185 mmol) to give a bright yellow solution which was stirred for 15 min at room temperature. The volatiles were removed under vacuum and the residue was extracted with 10 mL of diethyl ether. The solution was then filtered and cooled to −25°C to give yellow crystals of the complex which were isolated by filtration and dried under reduced pressure. Yield: 0.1985 g (81%). − ^{1}H NMR ([D$_6$]benzene); isomer **3a**: δ = 6.92, 5.83 and 5.68 [t, J(H,H) = 2.7 Hz, 2 H each, H_2, H_4 and H_5 of Cp^{tt}], 4.04 (s, 1 H, Zr−SH), 1.22 and 1.21 (s, 18 H each, CMe_3); isomer **3b**: δ = 6.49, 5.95 and 5.76 [t, J(H,H) = 2.7 Hz, 2 H each, H_2, H_4 and H_5 of Cp^{tt}], 6.27 (s, 1 H, Zr−SH) 1.21 and 1.13 (s, 18 H each, CMe_3). − ^{19}F ([D$_6$]benzene): δ = −76.1 and −76.7 (Zr−OSO$_2$CF_3, isomers **3a** and **3b**, respectively). − ^{13}C{^{1}H} NMR ([D$_6$]benzene); isomer **3a**: δ = 144.9 and 144.7 (C_1 and C_3 of Cp^{tt}), 120.0 [q, J(C,F) = 320 Hz, Zr−OSO$_2$$CF_3$], 119.1, 105.5 and 104.9 (C_2, C_4 and C_5 of Cp^{tt}), 34.2 and 33.6 (CMe$_3$), 31.3 and 31.1 (CMe_3); isomer **3b**: δ = 148.9 and 147.3 (C_1 and C_3 of Cp^{tt}), 120.2 [q, J(C,F) = 320 Hz, Zr−OSO$_2$$CF_3$], 111.6, 107.1 and 104.2 (C_2, C_4 and C_5 of Cp^{tt}), 33.7 and 33.5 (CMe$_3$), 31.0 and 30.5 (CMe_3). − MS (CH_2Cl_2, *m*/*z*,%); FAB$^+$: 477 (11) [$Cp^{tt}_2Zr(SH)^+$]; FAB$^-$: 149 (100) [$CF_3SO_3^-$]. − Molecular weight ($CHCl_3$, g mol^{-1}): 622 (calcd. 628). − Conductivity Λ_M (CH_2Cl_2, 4.97.10^{-4} M, Ω^{-1} cm^{2}mol^{-1}): 0.22. − $C_{27}H_{43}F_3O_3S_2Zr$ (627.98): calcd. C 51.64, H 6.90, S 10.21; found C 51.55, H 7.17, S 9.14.

[$Cp^{tt}_2Zr(\mu_3\text{-}S)_2\{Rh(CO)_2\}_2$] (4): [Rh(acac)(CO)$_2$] (0.504 g, 1.953 mmol) was added to a yellow solution of [$Cp^{tt}_2Zr(SH)_2$] (**2**) (0.5 g, 0.977 mmol) in diethyl ether (20 mL). The solution immediately turned dark green and a solid crystallized out while stirring for 10 min at room temperature. Filtration of the resulting suspension gave the title compound as an emerald-green microcrystalline powder after washing with n-hexane (2 × 10 mL) and drying in vacuo. Yield: 0.7535 g (93%). − ^{1}H NMR ($CDCl_3$): δ = 6.56 [t, ^4J(H,H) = 2.6 Hz, 2 H, H_2], 6.03 [d, ^4J(H,H) = 2.6 Hz, 4 H, H_4 and H_5 of Cp^{tt}], 1.31 (s, 36 H, CMe_3). − ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 185.3 [d, J(C,Rh) = 73 Hz, Rh−CO], 148.6 (C_1 and C_3), 121.3 (C_2), 109.0 (C_4 and C_5), 34.6 (CMe$_3$), 32.3 (s, CMe_3). − MS (FAB$^+$, CH_2Cl_2, *m*/*z*,%): 826 (29) [M$^+$], 770 (39) [M$^+$ − 2CO], 742 (34) [M$^+$ − 3CO], 714 (100) [M$^+$ − 4CO], 649 (30) [M$^+$ − Cp^{tt}], 565 (29) [M$^+$ − Cp^{tt} − 3CO]. − IR (CH_2Cl_2) $\tilde{\nu}_{(CO)}$: 2066 (s), 2041 (s), 1994 (s) cm^{-1}. − $C_{30}H_{42}O_4Rh_2S_2Zr$ (827.82): calcd. C 43.53, H 5.11, S 7.75; found C 43.60, H 5.12, S 7.82.

X-ray Structure Analysis of 3: X-ray quality crystals were obtained from a satured solution of **3** in diethyl ether at −25°C. Crystal data for **3**: $C_{27}H_{43}F_3O_3S_2Zr$, M = 627.95, monoclinic, space group $P2_1/n$, a = 12.1680(16), b = 16.594(3), c = 15.184(2) Å, β = 91.260(14)°, V = 3065.1(9) Å^3, T = 173 K, Z = 4, D_c = 1.361 g cm^{-3}, μ(Mo-K_α) = 0.538 mm^{-1}, graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). Data collected on a Siemens-Stoe AED-2 diffractometer. 8504 ref. collected, 5491 unique and used in the refinement. A ψ-scan absorption correction was applied (min. and max. transmission factors: 0.773, 0.862). The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares on F^2 (SHELXL97). Anisotropic displacement parameters used for all non-hydrogen atoms. Hydrogens were refined riding on the corresponding atoms and included in the model in calculated positions, except that of the hydrosulfido ligand which has been located in a difference-Fourier map. Final R_1 = 0.0456 (4239 ref., $F_o > 4\sigma(F_o)$) and wR_2 = 0.1110 (all data). Crystallographic data for the reported structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-124105 Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[14] $[\mathrm{Cp^{tt}{}_2Zr(acac)}]^+$: ^{1}H NMR ($\mathrm{CDCl_3}$): δ = 7.07 (d, $^4J(\mathrm{H,H})$ = 2.7 Hz, 4 H, $\mathrm{H_4}$ and $\mathrm{H_5}$ $\mathrm{Cp^{tt}}$), 6.27 (s, 1 H, C*H* acac), 6.01 (t, $^4J(\mathrm{H,H})$ = 2.7 Hz, 2 H, $\mathrm{H_2}$ $\mathrm{Cp^{tt}}$), 2.27 (s, 6 H, $\mathrm{C}H_3$ acac), 1.11 (s, 36 H, $\mathrm{C}Me_3$ $\mathrm{Cp^{tt}}$). − $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$): δ = 195.6 (*C*O acac), 152.8 ($\mathrm{C_1}$ and $\mathrm{C_3}$), 112.9 ($\mathrm{C_2}$), 111.7 ($\mathrm{C_4}$ and $\mathrm{C_5}$) ($\mathrm{Cp^{tt}}$), 106.7 (*C*H acac) 34.1 ($C\mathrm{Me_3}$), 30.6 ($\mathrm{C}Me_3$) ($\mathrm{Cp^{tt}}$), 26.6 ($C\mathrm{H_3}$ acac). − MS ($\mathrm{FAB^+}$, $\mathrm{CH_2Cl_2}$, *m*/*z*,%): 543 (100) $[\mathrm{Cp^{tt}{}_2Zr(acac)^+}]$.

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