# Electronic Supplementary Information

for

# Sterically encumbered pyrrolyl ligands and their incorporation into the cycloheptatrienyl zirconium coordination sphere

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## Contents

# 1. Additional molecular structures

### Molecular structure of the hydroperoxide of 3

Special features: The OH hydrogen was refined freely.

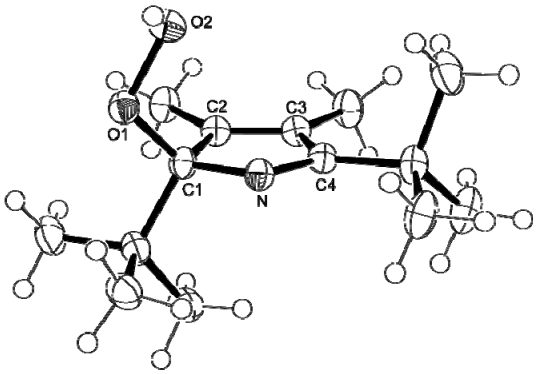


**Figure S1.** ORTEP diagram with thermal displacement parameters drawn at 50% probability.

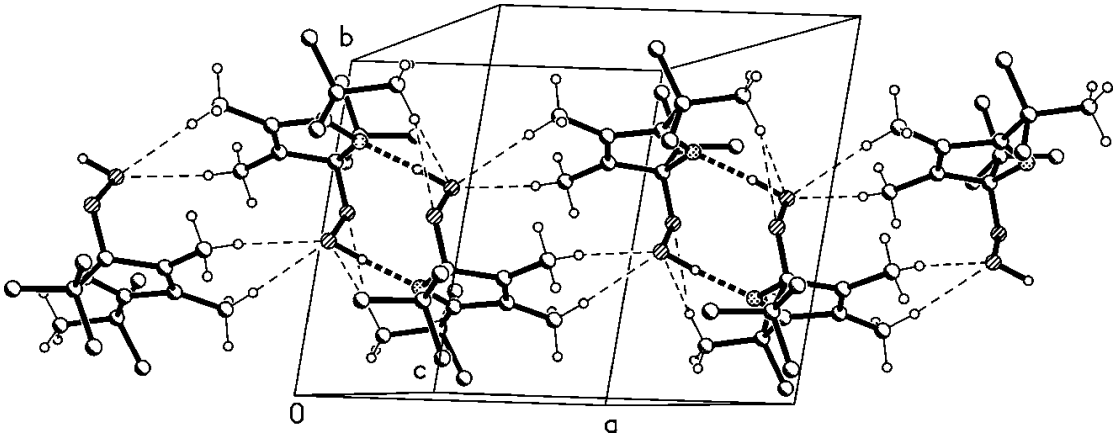


**Figure S2.** Section of the crystal lattice showing classical and "weak" hydrogen bonds (thick and thin dashed lines respectively).

### Crystal data and structure refinement

| | |
|---|---|
| Empirical formula | $C_{14}H_{25}NO_2$ |
| Formula weight | 239.35 |
| Temperature | 100(2) K |
| Wavelength | 1.54184 Å |

| | | |
|---|---|---|
| Crystal system | Triclinic | |
| Space group | $P\bar{1}$ | |
| Unit cell dimensions | a = 8.7383(8) Å | α= 81.310(7)° |
| | b = 9.5314(8) Å | β= 63.418(8)° |
| | c = 9.7570(8) Å | γ = 82.113(7)° |
| Volume | 716.17(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.110 $Mg/m^3$ | |
| Absorption coefficient | 0.574 $mm^{-1}$ | |
| F(000) | 264 | |
| Crystal size | 0.25 x 0.15 x 0.10 $mm^3$ | |
| Theta range for data collection | 4.71 to 76.14° | |
| Index ranges | -10<=h<=10, -11<=k<=11, -12<=l<=12 | |
| Reflections collected | 30721 | |
| Independent reflections | 2965 [R(int) = 0.0284] | |
| Completeness to theta = 75.00° | 99.9 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9448 and 0.8698 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 2965 / 0 / 166 | |
| Goodness-of-fit on $F^2$ | 1.033 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0384, wR2 = 0.1031 | |
| R indices (all data) | R1 = 0.0406, wR2 = 0.1052 | |
| Largest diff. peak and hole | 0.282 and -0.238 $e.Å^{-3}$ | |

**Molecular structure of (tmeda)Li($Pyr^{Ph_4}$)**

A suspension of 2,3,4,5-tetraphenyl-1*H*-pyrrol[1] (3.0 g, 8.08 mmol) in a pentane:toluene mixture (1:1) (40 mL) was cooled to 0°C and *n*-BuLi (5.1 mL, 1.6M in hexane) was added. The reaction mixture was warmed to ambient temperature and TMEDA (1 mL) was added and the suspension

was stirred at room temperature overnight. The solution was filtered and dried under dynamic vacuum to yield a colourless powder (3.89 g, 8.06 mmol, 99%). (tmeda)Li($Pyr^{Ph_4}$) can be crystallized from a saturated toluene solution at -30 °C. The compound displays crystallographic twofold symmetry and crystallizes with two molecules of toluene per molecule, which are each disordered over an inversion centre.

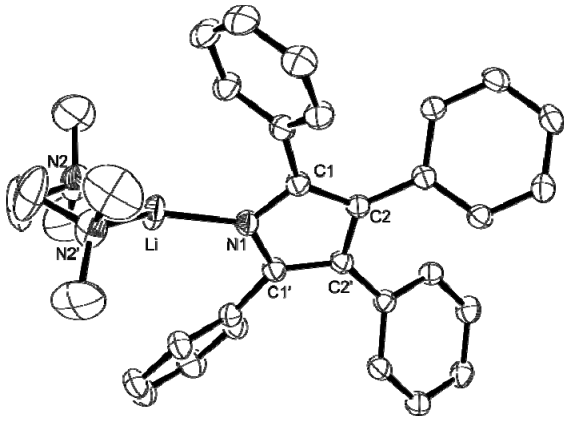


**Figure S3.** ORTEP diagram with thermal displacement parameters drawn at 50% probability, hydrogen atoms and solvent molecules are omitted for clarity.

**Crystal data and structure refinement**

| | | |
|---|---|---|
| Empirical formula | $C_{48}H_{52}LiN_3$ | |
| Formula weight | 677.87 | |
| Temperature | 100(2) K | |
| Wavelength | 1.54184 Å | |
| Crystal system | monoclinic | |
| Space group | *C*2/c | |
| Unit cell dimensions | a = 20.6834(4) Å | α= 90° |
| | b = 17.2623(2) Å | β= 110.377(2)° |
| | c = 11.8317(2) Å | γ = 90° |
| Volume | 3960.07(11) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.137 $Mg/m^3$ | |

| | |
|---|---|
| Absorption coefficient | 0.492 $mm^{-1}$ |
| F(000) | 1456 |
| Crystal size | 0.07 x 0.07 x 0.06 $mm^3$ |
| Theta range for data collection | 3.43 to 76.08° |
| Index ranges | -24<=h<=25, -21<=k<=21, -14<=l<=14 |
| Reflections collected | 26512 |
| Independent reflections | 4114 [R(int) = 0.0250] |
| Completeness to theta = 75.00° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.65569 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4114 / 98 / 277 |
| Goodness-of-fit on $F^2$ | 1.063 |
| Final R indices [I>2sigma(I)] | R1 = 0.0504, wR2 = 0.1309 |
| R indices (all data) | R1 = 0.0540, wR2 = 0.1341 |
| Largest diff. peak and hole | 0.448 and -0.291 $e.Å^{-3}$ |

# 2. Cone angles

The cone angles are measured according to a recent report.[2] Values used for the determination of $\Theta$ or $\Omega$ are highlighted in yellow.

### $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Pyr^{tBu_2})]$ (6)

| Centroid-Zr-H | | | |
|---|---|---|---|
| N | 29.77 | | |
| H9 | 42.70 | Theta: | 111.92 |
| H10 | 42.33 | | |
| | | | |
| *t*Bu on C8 | | | |
| 1. Me | 82.12 | | |
| | 70.65 | | |
| | 66.01 | | |
| 2. Me | 72.10 | | |
| | 63.80 | | |
| | 52.94 | | |
| 3. Me | 45.48 | | |
| | 35.94 | | |
| | 30.82 | | |
| *t*Bu on C11 | | | |
| 1. Me | 82.87 | | |
| | 70.95 | | |
| | 67.03 | | |
| 2. Me | 72.11 | | |
| | 64.86 | | |
| | 53.13 | | |
| 3. Me | 46.35 | | |
| | 36.74 | | |
| | 31.48 | | |

| C(alpha)-C(ipso)-H | | | |
|---|---|---|---|
| *t*Bu on C8 | | | |
| 1. Me | 50.64 | Omega: | 102.65 |
| | 49.52 | | |
| | 25.25 | | |
| 2. Me | 51.07 | | |

| | |
|---|---|
| | 48.66 |
| | 25.20 |
| 3. Me | 52.32 |
| | 51.60 |
| | 27.15 |
| *t*Bu on C11 | |
| 1. Me | 51.64 |
| | 47.77 |
| | 25.10 |
| 2. Me | 52.20 |
| | 51.29 |
| | 26.88 |
| 3. Me | 50.09 |
| | 49.76 |
| | 25.03 |

**[($\eta^7$-$C_7H_7$)Zr($\eta^5$-Pyr$^{tBu_2Me_2}$)] (7)**

| | | | |
|---|---|---|---|
| Centroid-Zr-H | | | |
| N | 30.29 | | |
| | | Theta: | 124.42 |

| | |
|---|---|
| *t*Bu on C8 | |
| 1. Me | 75.96 |
| | 67.92 |
| | 58.10 |
| 2. Me | 79.33 |
| | 69.00 |
| | 61.04 |
| 3. Me | 44.74 |
| | 32.86 |
| | 32.17 |
| Me on C9 | 60.72 |
| | 52.51 |
| | 41.23 |
| Me on C10 | |
| | 61.17 |
| | 49.82 |
| | 41.62 |

| | |
|---|---|
| *t*Bu on C11 | |
| 1. Me | 79.55 |
| | 68.24 |
| | 61.23 |
| 2. Me | 76.30 |
| | 68.26 |
| | 58.49 |
| 3. Me | 45.01 |
| | 33.04 |
| | 32.47 |

C(alpha)-C(ipso)-H

| | | | |
|---|---|---|---|
| *t*Bu on C8 | | For *t*Bu | |
| 1. Me | 49.37 | Omega: | 101.90 |
| | 46.67 | | |
| | 23.31 | For Me | |
| 2. Me | 50.15 | Omega: | 53.44 |
| | 49.73 | | |
| | 25.11 | | |
| 3. Me | 52.95 | | |
| | 51.76 | | |
| | 27.57 | | |
| Me on C9 | | | |
| | 26.73 | | |
| | 26.72 | | |
| | 26.74 | | |
| Me on C10 | | | |
| | 26.71 | | |
| | 26.71 | | |
| | 26.70 | | |
| tBu on C11 | | | |
| 1. Me | 51.27 | | |
| | 48.37 | | |
| | 25.19 | | |
| 2. Me | 49.31 | | |
| | 46.64 | | |
| | 23.32 | | |
| 3. Me | 52.65 | | |
| | 51.68 | | |
| | 27.45 | | |

**[($\eta^7$-$C_7H_7$)Zr($\eta^5$-Pyr$^{tBu_3}$)] (8)**

These values are based on a calculated molecular structure (see below).

| Centroid-Zr-H | | | |
|---|---|---|---|
| N | 29.55 | | |
| H10 | 43.84 | Theta: | 127.75 |
| | | | |
| *t*Bu on C8 | | | |
| 1. Me | 82.58 | | |
| | 69.31 | | |
| | 62.58 | | |
| 2. Me | 77.17 | | |
| | 67.27 | | |
| | 57.74 | | |
| 3.Me | 45.98 | | |
| | 33.64 | | |
| | 31.4 | | |
| *t*Bu on C9 | | | |
| 1. Me | 80.61 | | |
| | 70.99 | | |
| | 68.8 | | |
| 2. Me | 63.23 | | |
| | 56.85 | | |
| | 42.86 | | |
| 3. Me | 44 | | |
| | 40.05 | | |
| | 26.75 | | |
| *t*Bu on C10 | | | |
| 1. Me | 82.8 | | |
| | 69.44 | | |
| | 64.42 | | |
| 2. Me | 74.39 | | |
| | 64.97 | | |
| | 53.65 | | |
| 3.Me | 45.16 | | |
| | 34.73 | | |
| | 29.54 | | |

| C(alpha)-C(ipso)-H |
|---|
| *t*Bu on C8 |

| | | | |
|---|---|---|---|
| 1. Me | 52.84 | Omega: | 104.32 |
| | 50.78 | | |
| | 24.53 | | |
| 2. Me | 48.78 | | |
| | 47.04 | | |
| | 20.71 | | |
| 3.Me | 54.2 | | |
| | 53.02 | | |
| | 26.49 | | |
| *t*Bu on C9 | | | |
| 1. Me | 49.71 | | |
| | 48.2 | | |
| | 21.79 | | |
| 2. Me | 51.58 | | |
| | 51.35 | | |
| | 24.25 | | |
| 3. Me | 53.87 | | |
| | 50.71 | | |
| | 25.31 | | |
| *t*Bu on C11 | | | |
| 1. Me | 51.53 | | |
| | 51.25 | | |
| | 24.02 | | |
| 2. Me | 52.48 | | |
| | 49.65 | | |
| | 23.76 | | |
| 3. Me | 54.46 | | |
| | 53.94 | | |
| | 26.86 | | |

**$[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Im^{tBu_3})]$ (9)**

| **Centroid-Zr-H** | | | |
|---|---|---|---|
| N1 | 29.00 | | |
| N2 | 29.11 | Theta: | 117.91 |
| *t*Bu on C8 | | | |
| 1. Me | 73.41 | | |
| | 63.36 | | |

| | |
|---|---|
| | 54.57 |
| 2. Me | 78 |
| | 66.06 |
| | 61.05 |
| 3.Me | 41.98 |
| | 32.44 |
| | 28.16 |
| *t*Bu on C9 | |
| 1. Me | 80.9 |
| | 69.73 |
| | 69.08 |
| 2. Me | 65.98 |
| | 59.53 |
| | 46.73 |
| 3. Me | 44.21 |
| | 38.15 |
| | 28.59 |
| *t*Bu on C10 | |
| 1. Me | 77.77 |
| | 66.48 |
| | 60.84 |
| 2. Me | 72.32 |
| | 63.46 |
| | 54.81 |
| 3.Me | 42.29 |
| | 31.32 |
| | 29.6 |

| C(alpha)-C(ipso)-H | | | |
|---|---|---|---|
| *t*Bu on C8 | | | |
| 1. Me | 50.91 | Omega: | 101.88 |
| | 47.59 | | |
| | 24.51 | | |
| 2. Me | 50.78 | | |
| | 49.05 | | |
| | 25.03 | | |
| 3.Me | 54.01 | | |
| | 52.01 | | |
| | 28.2 | | |
| *t*Bu on C9 | | | |
| 1. Me | 48.14 | | |

| | |
|---|---|
| | 46.65 |
| | 22.74 |
| 2. Me | 50.61 |
| | 50.39 |
| | 25.79 |
| 3. Me | 51.87 |
| | 50.31 |
| | 26.45 |
| *t*Bu on C10 | |
| 1. Me | 47.3 |
| | 46.47 |
| | 22.08 |
| 2. Me | 51.5 |
| | 48.88 |
| | 25.59 |
| 3. Me | 53.36 |
| | 51.41 |
| | 27.71 |

# 3. Computational details

All computations were performed using the density functional method M06 as implemented in the Gaussian09 program.[3] For all main-group elements (C, H and N) the all-electron triple-z basis set (6-311G**) was used,[4] whereas for zirconium a small-core relativistic ECP together with the corresponding double-z valence basis set was employed (Stuttgart RSC 1997 ECP).[5]

**Energies of the optimized structures**

| Compound | E(0 K)[a] [Ha] | H(298 K)[b] [Ha] | G(298 K)[b] [Ha] |
|---|---|---|---|
| $[Cp^{tBu2}]^-$ | -507.457974 | -507.442228 | -507.498594 |
| $[Pyr^{tBu2}]^-$ | -523.541060 | -523.525492 | -523.581666 |
| $[Cp^{tBu3}]^-$ | -664.504258 | -664.483676 | -664.548774 |
| $[Pyr^{tBu3}]^-$ | -680.588493 | -680.567830 | -680.634315 |
| $[Im^{tBu3}]^-$ | -696.672281 | -696.651709 | -696.717735 |
| $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Cp^{tBu2})]$ | -825.219538 | -825.196222 | -825.269813 |
| $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Pyr^{tBu2})]$ (**6**) | -841.283342 | -841.260272 | -841.332909 |
| $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Cp^{tBu3})]$ | -982.262952 | -982.234451 | -982.318294 |
| $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Pyr^{tBu3})]$ (**8**) | -998.331440 | -998.302969 | -998.385832 |
| $[(\eta^7\text{-}C_7H_7)Zr(\eta^5\text{-}Im^{tBu3})]$ (**9**) | -1014.395807 | -1014.367815 | -1014.449099 |

[a]DFT energy incl. ZPE. [b]standard conditions T = 298.15 K and p = 1 atm.

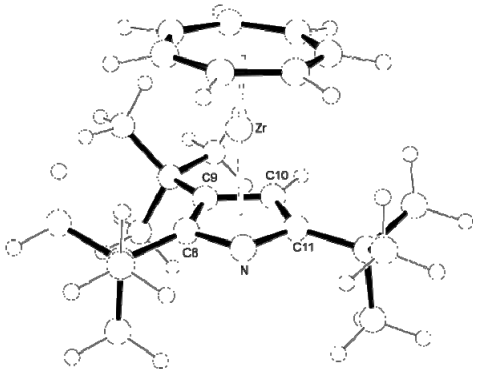


**Figure S4.** Calculated molecular structure of **8.** Selected bond lengths (Å): Zr-N 2.390, Zr-C8 2.476, Zr-C9 2.615, Zr-C10 2.580, Zr-C11 2.481.

# 4. References

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[3] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. J. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, E. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, (2009) Gaussian, Inc., Wallington CT.

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