

## Zwitterionic 18-Electron $d^0$ -Anionic Metallocene Complexes

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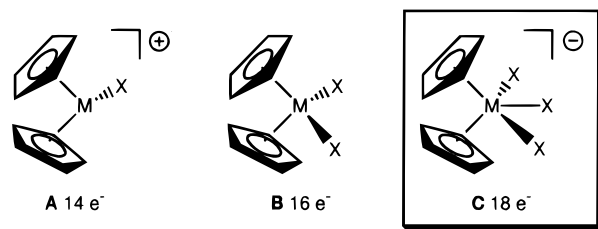
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Formal [3+2] cycloaddition reactions between the  $\alpha$ -phosphino zirconaindene **1** and various cumulenes [CO<sub>2</sub>, CS<sub>2</sub>, Cy–N=C=N–Cy (Cy = cyclohexyl), R–N=C=S (R = Me, Ph), R–N=C=O (R = Ph, <sup>t</sup>Bu)] afford stable zwitterionic monomeric five-coordinated anionic bis(cyclopentadienyl) zirconium complexes **2–6**. Single-crystal X-ray structures of two of these compounds (**3**, **6b**) are reported. A related biszwitterionic zirconocene complex **9** is prepared through the reaction of carbon disulfide with the tricyclic  $\alpha$ -phospholane zirconaindan **7**; in this case cycloaddition reactions take place on the two carbon sulfur double bonds of CS<sub>2</sub>.

### Introduction

Group 4  $d^0$ -bis(cyclopentadienyl)complexes Cp<sub>2</sub>MX<sub>n</sub> (M = Ti, Zr, Hf; **A**,  $n = 1$ , **B**,  $n = 2$ , **C**,  $n = 3$ ), with metal–ligand M–X bonds, can exhibit metal centers with 14 to 18 electrons and valence coordination number from 3 to 5 (Figure 1). For nearly 20 years, bent cationic bis(cyclopentadienyl) complexes **A** have received considerable attention, as those compounds have been identified as the active catalytic species in the homogeneous metallocene Ziegler–Natta process for the polymerization of olefins.<sup>1</sup> The chemistry of **B** complexes has been extensively explored, these compounds being used as reagents for the preparation of a number of original organic and organometallic derivatives.<sup>2</sup> Many structural studies have been carried out on **B** complexes.<sup>2,3</sup> An examination of the known chemistry of anionic **C** metallocene chemistry shows that these five-coordinated compounds are postulated as intermediates in a number of stoichiometric and catalytic reactions.<sup>4</sup> Only very few of these metal **C** species have been spectroscopically<sup>5</sup> and structurally characterized.<sup>6</sup> Most



**Figure 1.** Group 4  $d^0$ -metallocene complexes Cp<sub>2</sub>MX<sub>n</sub> (**A**,  $n = 1$ ; **B**,  $n = 2$ ; **C**,  $n = 3$ ).

of the reported **C** compounds exhibit electrostatic anion–cation pairing resulting in dimer, trimer, oligomer, or polymeric structures.<sup>6,7</sup>

In this paper we describe the preparation and structural characterization of stable zwitterionic monomeric five-coordinated anionic bis(cyclopentadienyl) zirconium complexes **C** with one Zr–heteroelement  $\sigma$ -bond and of a related biszwitterionic zirconocene complex.<sup>8</sup>

### Results and Discussion

The metallocene zwitterionic species **2–6** were obtained in toluene at room temperature in good isolated yield (53–84%) by treatment of **1**<sup>9</sup> with an equimolar amount of the corresponding heterocumulenes (CO<sub>2</sub>, CS<sub>2</sub>, Cy–N=C=N–Cy, R–N=C=S, R–N=C=O) (Scheme 1). Complexes **2–6** were characterized by NMR spectroscopy (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C) (Table 1) and mass spectrometry.

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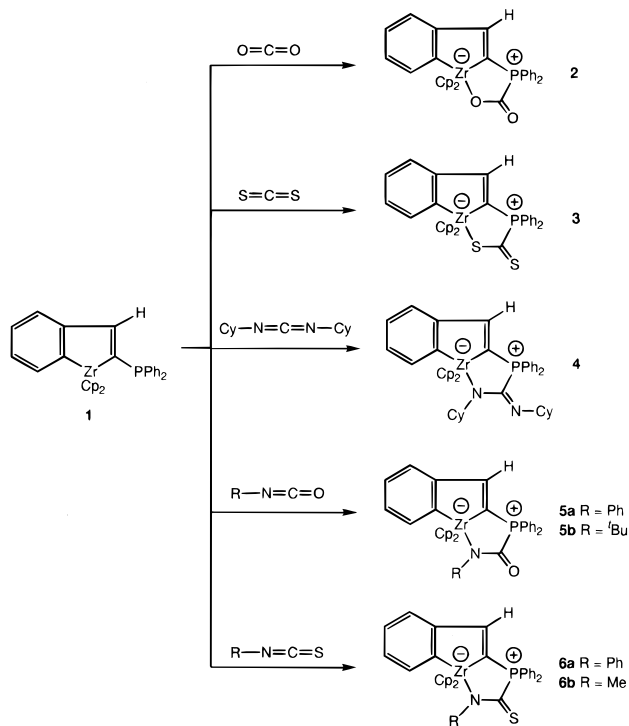
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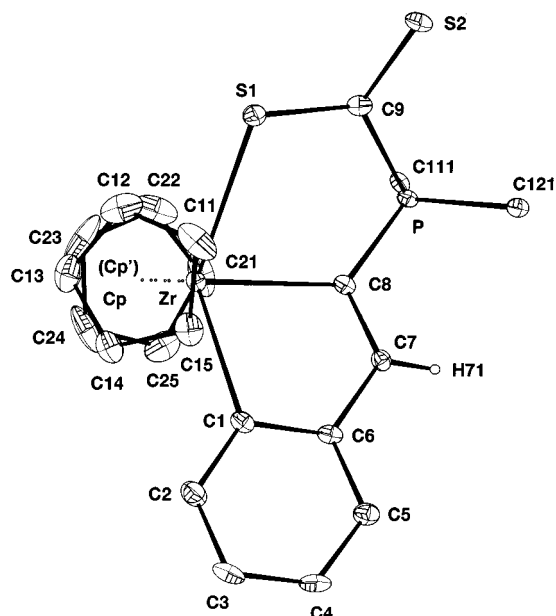
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## Scheme 1. Synthesis of Five-Coordinated Anionic Zirconocene Complexes 2–6

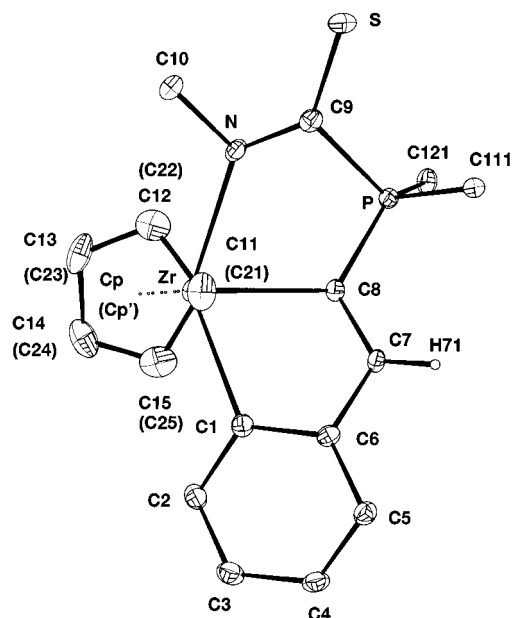


<sup>31</sup>P NMR spectra showed the clean formation of a unique phosphorus product. <sup>1</sup>H NMR signals revealed the presence in the final product of the two η<sup>5</sup>-cyclopentadienyl ligands of the initial zirconium fragment and the presence of the C(7)–H(71) proton of the indene skeleton. The deshielded chemical shift at 192–201 ppm observed in <sup>13</sup>C NMR<sup>10</sup> is indicative of the lateral Zr–C bond ( $\delta = 184.9$  ppm for ZrC<sub>arom</sub> in **1**). In marked contrast, the signal of the central carbon atom linked to zirconium and phosphorus is shifted to high field with an unexpectedly low carbon–phosphorus coupling constant ( $\delta$  from 151.3 to 157.7 ppm with  $0 \leq {}^1J_{C-P} < 11.2$  Hz for **2–6**, to be compared with  $\delta = 191.5$  ppm and  ${}^1J_{C-P} = 49.0$  Hz for **1**).

To confirm the proposed structure of these complexes, X-ray diffraction studies were carried out on **3** and **6b** (Figures 2 and 3, Tables 2 and 3). The cyclopentadienyl rings are bonded to the zirconium atom in a nearly symmetric η<sup>5</sup>-fashion.<sup>11</sup> The atoms of the metallacycle skeleton are practically coplanar and lie roughly in the equatorial plane which bisects the dihedral angle formed by the Cp ligands. The large C(1)–Zr–X angle in **3** and **6b** (Table 2) is typical for five-coordinated Cp<sub>2</sub>Zr(IV) complexes.<sup>12</sup> The Zr–C(sp<sup>2</sup>) bond lengths in **3** and **6b** are halfway from typical neutral Cp<sub>2</sub>Zr(IV)–C σ-bonds and Zr–C distances in Cp<sub>2</sub>Zr(IV)–olefin π-type interaction.<sup>8,13</sup> The other outstanding structural feature of **3** and **6b** is the unusual long Zr–η<sup>1</sup>-X (X = S, N) bond lengths. The Zr–S distance of 2.8261(7) Å in **3** is longer



**Figure 2.** CAMERON view of the structure of **3** along the axis Cp,Cp'-centroids. Ph groups of the phosphonium fragment are omitted for clarity.



**Figure 3.** CAMERON view of the structure of **6b** along the axis Cp,Cp'-centroids. Ph groups of the phosphonium fragment are omitted for clarity.

than any known Zr–S single bond, which typically range from 2.42 to 2.50 Å.<sup>14</sup> However, this unusual long Zr–S bond is close to those observed in five-coordinated dithiocarbamate zirconium(IV) complexes (lateral Zr–S 2.723 Å).<sup>15,16</sup> The Zr–N distance of 2.405(2) Å in **6b** is longer than any known Zr–N single bond,<sup>17</sup> and Zr–N

(10) <sup>13</sup>C NMR assignments were deduced by inverse gradient δ<sup>1</sup>H–δ<sup>13</sup>C{<sup>13</sup>C,<sup>31</sup>P} HMQC and <sup>31</sup>P–<sup>1</sup>H INEPT NMR experiments.

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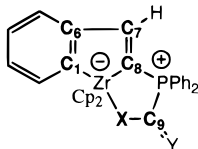
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**Table 1. Selected NMR Spectroscopic Data<sup>a</sup> for Five-Coordinate Anionic Zirconocene Complexes 2–6<sup>b</sup>**

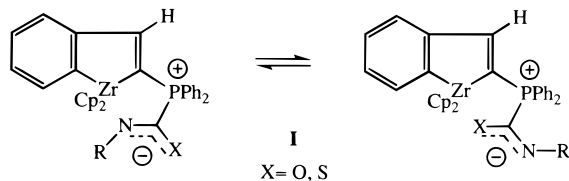
	<sup>31</sup> P	C <sub>1</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>
<b>1</b>	6.9	184.9	165.7	142.7 (13.0)	191.5 (49.0)	
X = Y = O <b>2</b>	-7.1	196.1	154.4 (34.2)	171.5 (3.1)	157.4 (4.1)	153.9 (87.5)
X = Y = S <b>3</b>	38.4	192.4	153.7 (31.7)	171.2	155.5 (8.8)	235.9 (66.9)
X = Y = N-Cy <b>4</b>	1.0	200.9	141.5 (28.3)	170.6	157.7	186.2 (87.2)
X = N-Ph, Y = O <b>5a</b>	7.5	194.9	154.2 (33.5)	169.7	155.3 (11.2)	163.4 (148.5)
X = N-tBu, Y = O <b>5b</b>	3.6	195.3	154.6 (32.4)	169.2	157.5 (10.9)	161.6 (145.4)
X = N-Ph, Y = S <b>6a</b>	26.4	192.9	153.0 (30.8)	171.6	151.3	173.0 (122.3)
X = N-Me, Y = S <b>6b</b>	24.7	193.9	154.7 (30.4)	170.7	154.1	191.9 (112.9)

<sup>a</sup> Chemical shifts in ppm and couplings (between parentheses) in Hz. <sup>b</sup> The numbering system is as follows:

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Anionic Zirconocene Complexes 3 and 6b**

	<b>3</b> (X = S)	<b>6b</b> (X = N)
Distances		
Zr–C(1)	2.376(3)	2.372(3)
Zr–C(8)	2.371(3)	2.341(2)
Zr–X	2.8261(7)	2.405(2)
P–C(8)	1.753(3)	1.742(3)
P–C(9)	1.827(3)	1.817(3)
X–C(9)	1.649(3)	1.314(4)
Angles		
C(1)–Zr–C(8)	70.49(9)	69.31(9)
C(1)–Zr–X	142.54(7)	141.91(8)

distances of 2.45–2.50 Å suggest dative interaction in zirconocene(IV) complexes.<sup>18</sup>



Indeed the Zr–X (X = S, N) bond distances observed for **3**<sup>16</sup> and **6b** are halfway from Zr–X single-bond distances in four-coordinate mononuclear Cp<sub>2</sub>Zr(IV) complexes<sup>19</sup> and Zr–X bond distances in neutral five-coordinate Cp<sub>2</sub>Zr(IV) complexes.<sup>20</sup> Interestingly, the ligand with the heteroatom (S, N) linked to zirconium showed a delocalized π-bonding indicated by the C(9)–X (X = S, N) distances, which are intermediate between single-bond and double-bond distances.<sup>21</sup>

It is reasonable to propose that the first step for the formation of **2–6** is a nucleophilic attack of the phosphane at the electrophilic center of the organic substrate.<sup>22</sup> In the second step, cyclization reaction on the coordinatively unsaturated metal center occurs to form

**Table 3. Crystallographic Data for Zirconocene Complexes 3 and 6b**

	<b>3</b>	<b>6b</b>
chem formula	C <sub>31</sub> H <sub>25</sub> PS <sub>2</sub> Zr	C <sub>32</sub> H <sub>28</sub> NPSZr
fw	583.87	580.84
cryst syst	monoclinic	monoclinic
space group	P2 <sub>1</sub> /n (14)	P2 <sub>1</sub> /n (14)
Z	4	4
a, Å	12.448(2)	11.103(2)
b, Å	15.290(2)	15.844(2)
c, Å	13.962(3)	15.481(2)
β, deg	104.08	106.03(2)
V, Å <sup>3</sup>	2579(4)	2626(2)
F(000)	1181.40	1180.96
D <sub>calc</sub> , g cm <sup>-3</sup>	1.51	1.47
μ (Mo Kα) m cm <sup>-1</sup>	5.71	5.71
2θ range, deg	2.9–48.4	2.9–48.4
no. data collected	18 563	20 698
no. of unique data	2874	3111
R <sub>av</sub>	0.04	0.05
no. of params varied	321	342
S	1.06	1.2
R(F <sub>o</sub> )	0.29	0.025
R <sub>w</sub> (F <sub>o</sub> )	0.027	0.028
(Δρ) <sub>max</sub>	0.59	0.37
(Δρ) <sub>min</sub> , e Å <sup>-3</sup>	-0.34	-0.26

the stable pentavalent anionic zirconocene products. With isocyanates and isothiocyanates, the anionic charge is delocalized over the carbamoyl skeleton in **I**, but the preferred coordination site in these systems is the nitrogen atom. The η<sup>1</sup>-bonding mode of the carbamoyl group in complexes **5** and **6** is very strong since no competition between nitrogen and oxygen or between nitrogen and sulfur was observed either in the solid state or in solution.

This methodology of chemo- and regioselective cycloaddition for the preparation of stable anionic zirconocene species can be extended to other metallocene derivatives such as **7**. Indeed addition of phenylisothiocyanate to **7**<sup>23</sup> in toluene at -40 °C leads to the expected complex **8** isolated in 91% yield after workup (Scheme 2). Surprisingly the same reaction performed with **7** (1 equiv) and carbon disulfide (0.5 equiv) affords unique "dimeric" species **9** (72% yield) arising from successive (or concomitant) cycloaddition reactions on the two carbon sulfur double bonds of CS<sub>2</sub> (Scheme 2). It can be noted that in stoichiometric conditions, only half of the neutral complex **7** is transformed into the biszwitterionic complex **9**. The <sup>31</sup>P NMR spectrum of **9** reveals the presence of two inequivalent phosphorus atoms (δ = 66.1 and 72.9 ppm, J<sub>PP</sub> = 20.5 Hz).<sup>24</sup> <sup>1</sup>H and <sup>13</sup>C NMR

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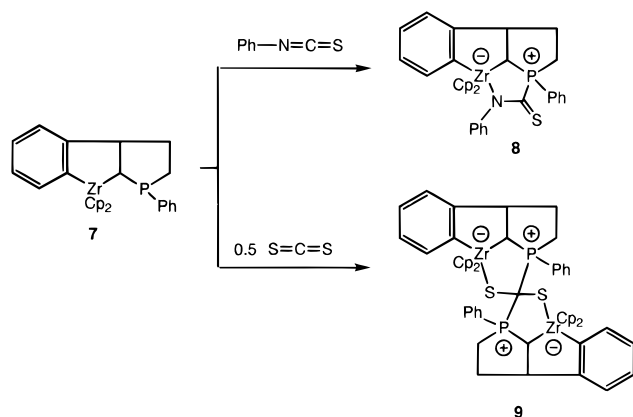
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**Scheme 2. Synthesis of Mono- and Biszwitterionic Anionic Zirconocene Complexes 8 and 9**


show resonances that can be attributed to each inequivalent atom constituting this spirocyclic system. In addition the  $^{13}\text{C}$  signal of the central spiro carbon atom appears at 64.0 ppm (dd,  $J_{\text{CP}} = 49.6$  and 49.9 Hz). Finally mass spectrometry (FAB) ( $m/z$  994 [ $\text{M}^+$ ]) corroborates the structure assigned to **9**.

The scope and limitations of this methodology of synthesis of anionic zirconocene species as well as studies of the chemical properties and reactivity of these zwitterionic complexes are currently under active investigation.

**Experimental Section**

**General Procedures.** All manipulations were conducted under an argon atmosphere with standard Schlenk techniques. Nuclear magnetic resonance (NMR) spectra were recorded on Bruker MSL 400, AM-250, AC-200, and AC-80 Fourier transform spectrometers. Positive chemical shifts are given downfield relative to  $\text{Me}_4\text{Si}$  ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{29}\text{Si}$ ) or  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), respectively. Mass spectrum analyses and elemental analyses were performed by the analytical service of the Laboratoire de Chimie de Coordination (LCC) of the CNRS. Solvents were freshly distilled from sodium/benzophenone ketyl (THF) or lithium aluminum hydride (pentane).  $\text{C}_6\text{D}_6$ ,  $\text{CD}_2\text{Cl}_2$ , and  $\text{CDCl}_3$  were treated with  $\text{CaH}_2$ , distilled, and stored under argon.  $\text{CO}_2$ ,  $\text{CS}_2$ ,  $\text{PhNCS}$ ,  $\text{MeNCS}$ ,  $\text{PhNCO}$ , and  $t\text{-BuNCO}$  were purchased from Aldrich and used without further purification.

**Preparation of Complex 2.** A solution of **1** (0.136 g, 0.268 mmol) in  $\text{C}_6\text{D}_6$  (4 mL) was placed under 1 atm of  $\text{CO}_2$  at room temperature. The resulting solution was stirred at room temperature for 1 h, leading to the formation of complex **2** in almost quantitative yield as monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. Attempts to isolate **2** resulted in its decomposition.  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 32.4 MHz):  $\delta$  -7.1 (s) ppm.  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ , 200.1 MHz):  $\delta$  5.77 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.94–7.97 (m, 14H,  $\text{CH}_{\text{arom}}$ ), 8.25 (d, 1H,  $^3J_{\text{H-P}} = 26.7$  Hz, PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 62.9 MHz):  $\delta$  110.4 (s,  $\text{CH}_{\text{Cp}}$ ), 123.7, 126.7, 127.6 (s,  $\text{CH}_{\text{arom}}$ ), 125.8 (d,  $^1J_{\text{C-P}} = 63.2$  Hz,  $i\text{-PPh}_2$ ), 129.9 (d,  $^2J_{\text{C-P}} = 11.3$  Hz,  $o\text{-PPh}_2$ ), 133.0 (s,  $p\text{-PPh}_2$ ), 133.4 (d,  $^3J_{\text{C-P}} = 9.1$  Hz,  $m\text{-PPh}_2$ ), 140.9 (s,  $\text{CH}_{\text{arom}}$ ), 153.9 (d,  $^1J_{\text{C-P}} = 87.5$  Hz, C=O) 154.4 (d,  $^3J_{\text{C-P}} = 34.2$  Hz, ZrC), 157.4 (d,  $^1J_{\text{C-P}} = 4.1$  Hz, ZrCP), 171.5 (d,  $^3J_{\text{C-P}} = 3.1$  Hz, ZrCCH), 196.1 (s, ZrC) ppm.

**Preparation of Complex 4.** To a solution of **1** (0.194 g, 0.383 mmol) in  $\text{C}_6\text{D}_6$  (5 mL) was added 1,3-dicyclohexylcarbodiimide (0.079 g, 0.383 mmol) at room temperature. The resulting solution was refluxed for 14 h, leading to the

formation of complex **4** in almost quantitative yield as monitored by  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy. The final product **4** was characterized as formed in the solution mixture. Attempts to isolate **4** resulted in its decomposition.  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 32.4 MHz):  $\delta$  1.0 (s) ppm.  $^1\text{H}$  ( $\text{C}_6\text{D}_6$ , 200.1 MHz):  $\delta$  0.87–1.95 (m, 20H,  $\text{CH}_2$ ) 2.82 (m, 1H, NCH), 3.11 (m, 1H, NCH), 5.87 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.74–8.06 (m, 15H,  $\text{CH}_{\text{arom}}$  and PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{C}_6\text{D}_6$ , 62.9 MHz):  $\delta$  25.3, 26.2, 27.0, 34.6, 35.8, 36.3 (s,  $\text{CH}_2$ ), 59.5 (d,  $^3J_{\text{C-P}} = 21.0$  Hz, NCH), 65.9 (s, NCH), 112.5 (s,  $\text{CH}_{\text{Cp}}$ ), 125.5, 127.0 (s,  $\text{CH}_{\text{arom}}$ ), 138.0 (d,  $^1J_{\text{C-P}} = 48.0$  Hz,  $i\text{-PPh}_2$ ), 139.5 (s,  $\text{CH}_{\text{arom}}$ ), 141.5 (d,  $^3J_{\text{C-P}} = 28.3$  Hz, ZrC), 157.7 (s, ZrCP), 170.6 (s, ZrCCH), 186.2 (d,  $^1J_{\text{C-P}} = 87.2$  Hz, C=N), 200.9 (s, ZrC) ppm. MS (FAB):  $m/z$  713 [ $\text{M}^+ + 1$ ].

**Typical Procedure for the Preparation of Complexes 3, 5a, 5b, 6a, and 6b.** To a solution of **1** in toluene (10 mL) was added a stoichiometric amount of the corresponding reagent ( $\text{CS}_2$  (**3**),  $\text{PhNCO}$  (**5a**),  $t\text{-BuNCO}$  (**5b**),  $\text{PhNCS}$  (**6a**), and  $\text{MeNCS}$  (**6b**)) at room temperature. The mixture was stirred for 30 min and then evaporated to dryness. The solid residue was extracted with a mixture of THF (10 mL)/pentane (30 mL) and filtered. The volatiles were removed from the solution, and the resulting solid was washed with pentane (5 mL) to give the corresponding complexes **3**, **5a**, **5b**, **6a**, and **6b**.

**3:** red powder, 0.386 g (0.661 mmol, 84%) prepared with 0.400 g of **1** (0.788 mmol) and 47  $\mu\text{L}$  of  $\text{CS}_2$  (0.788 mmol). Mp: 182–183  $^\circ\text{C}$  (decomp).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 32.4 MHz):  $\delta$  38.4 (s) ppm.  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ , 200.1 MHz):  $\delta$  5.83 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.99–7.21 (m, 3H,  $\text{CH}_{\text{arom}}$ ), 7.44–7.90 (m, 12H,  $\text{CH}_{\text{arom}}$  and PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 62.9 MHz):  $\delta$  108.7 (s,  $\text{CH}_{\text{Cp}}$ ), 123.1, 125.9, 126.5 (s,  $\text{CH}_{\text{arom}}$ ), 126.3 (d,  $^1J_{\text{C-P}} = 75.2$  Hz,  $i\text{-PPh}_2$ ), 129.0 (d,  $^2J_{\text{C-P}} = 11.2$  Hz,  $o\text{-PPh}_2$ ), 132.7 (s,  $p\text{-PPh}_2$ ), 133.2 (d,  $^3J_{\text{C-P}} = 8.8$  Hz,  $m\text{-PPh}_2$ ), 141.2 (s,  $\text{CH}_{\text{arom}}$ ), 153.7 (d,  $^3J_{\text{C-P}} = 31.7$  Hz, ZrC), 155.5 (d,  $^1J_{\text{C-P}} = 8.8$  Hz, ZrCP), 171.2 (s, ZrCCH), 192.4 (s, ZrC), 235.9 (d,  $^1J_{\text{C-P}} = 66.9$  Hz, C=S) ppm. Anal. Calcd for  $\text{C}_{31}\text{H}_{25}\text{S}_2\text{PZr}$ : C 63.77, H 4.31. Found: C 63.87, H 3.65.

**5a:** brown powder, 0.412 g (0.657 mmol, 68%) prepared with 0.490 g of **1** (0.966 mmol) and 105  $\mu\text{L}$  of  $\text{PhNCO}$  (0.966 mmol).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CDCl}_3$ , 32.4 MHz):  $\delta$  7.5 (s) ppm.  $^1\text{H}$  ( $\text{CDCl}_3$ , 200.1 MHz):  $\delta$  5.82 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.99–7.89 (m, 19H,  $\text{CH}_{\text{arom}}$ ), 8.12 (d,  $^3J_{\text{H-P}} = 26.3$  Hz, 1H, PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  109.5 (s,  $\text{CH}_{\text{Cp}}$ ), 122.7, 123.6, 124.4, 125.5, 126.2, 128.4 (s,  $\text{CH}_{\text{arom}}$ ), 129.2 (d,  $^2J_{\text{C-P}} = 10.9$  Hz,  $o\text{-PPh}_2$ ), 132.4 (s,  $p\text{-PPh}_2$ ), 132.9 (d,  $^3J_{\text{C-P}} = 9.1$  Hz,  $m\text{-PPh}_2$ ), 140.0 (s,  $\text{CH}_{\text{arom}}$ ), 148.3 (d,  $^3J_{\text{C-P}} = 21.6$  Hz,  $i\text{-Ph}$ ), 154.2 (d,  $^3J_{\text{C-P}} = 33.5$  Hz, ZrC), 155.3 (d,  $^1J_{\text{C-P}} = 11.1$  Hz, ZrCP), 163.4 (d,  $^1J_{\text{C-P}} = 148.5$  Hz, C=O), 169.7 (s, ZrCCH), 194.9 (s, ZrC) ppm.  $i\text{-PPh}_2$  not observed. MS (FAB):  $m/z$  626 [ $\text{M}^+ + 1$ ]. Anal. Calcd for  $\text{C}_{37}\text{H}_{30}\text{NOPZr}$ : C 70.89, H 4.82, N 2.23. Found: C 70.69, H 4.65, N 2.15.

**5b:** brown powder, 0.414 g (0.694 mmol, 59%) prepared with 0.597 g of **1** (1.176 mmol) and 134  $\mu\text{L}$  of  $t\text{-BuNCO}$  (1.176 mmol).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 32.4 MHz):  $\delta$  3.6 (s) ppm.  $^1\text{H}$  ( $\text{CD}_2\text{Cl}_2$ , 200.1 MHz):  $\delta$  1.5 (d, 9H,  $^5J(\text{H,P}) = 0.6$  Hz,  $\text{CH}_3$ ), 5.92 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.70–7.94 (m, 14H,  $\text{CH}_{\text{arom}}$ ), 8.13 (d,  $^3J_{\text{H-P}} = 25.5$  Hz, 1H, PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CD}_2\text{Cl}_2$ , 62.9 MHz):  $\delta$  30.5 (s,  $\text{CH}_3$ ), 54.5 (d,  $^3J_{\text{C-P}} = 19.5$  Hz, C( $\text{CH}_3$ )), 109.4 (s,  $\text{CH}_{\text{Cp}}$ ), 122.7, 125.3, 126.1 (s,  $\text{CH}_{\text{arom}}$ ), 129.1 (d,  $^2J_{\text{C-P}} = 11.2$  Hz,  $o\text{-PPh}_2$ ), 132.2 (s,  $p\text{-PPh}_2$ ), 132.9 (d,  $^3J_{\text{C-P}} = 9.0$  Hz,  $m\text{-PPh}_2$ ), 140.3 (s,  $\text{CH}_{\text{arom}}$ ), 154.6 (d,  $^3J_{\text{C-P}} = 32.4$  Hz, ZrC), 157.5 (d,  $^1J_{\text{C-P}} = 10.9$  Hz, ZrCP), 161.6 (d,  $^1J_{\text{C-P}} = 145.4$  Hz, C=O), 169.2 (s, ZrCCH), 195.3 (s, ZrC) ppm.  $i\text{-PPh}_2$  not observed. MS (FAB):  $m/z$  606 [ $\text{M}^+ + 1$ ]. Anal. Calcd for  $\text{C}_{35}\text{H}_{34}\text{NOPZr}$ : C 69.27, H 5.46, N 2.30. Found: C 69.09, H 5.32, N 2.25.

**6a:** brown powder, 0.468 g (0.728 mmol, 73%) prepared with 0.506 g of **1** (0.998 mmol) and 119  $\mu\text{L}$  of  $\text{PhNCS}$  (0.998 mmol).  $^{31}\text{P}\{^1\text{H}\}$  ( $\text{CDCl}_3$ , 32.4 MHz):  $\delta$  26.4 (s) ppm.  $^1\text{H}$  ( $\text{CDCl}_3$ , 200.1 MHz):  $\delta$  5.77 (s, 10H,  $\text{CH}_{\text{Cp}}$ ), 6.99–7.71 (m, 19H,  $\text{CH}_{\text{arom}}$ ), 7.87 (d,  $^3J_{\text{H-P}} = 28.8$  Hz, 1H, PCCH) ppm.  $^{13}\text{C}\{^1\text{H}\}$  ( $\text{CDCl}_3$ , 62.9 MHz):  $\delta$  108.7 (s,  $\text{CH}_{\text{Cp}}$ ), 121.3, 123.0, 124.5, 125.9, 126.1, 128.8 (s,  $\text{CH}_{\text{arom}}$ ), 129.1 (d,  $^3J_{\text{C-P}} = 9.6$  Hz,  $m\text{-PPh}_2$ ), 132.4 (s,

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(24) Nonequivalence can be due to some distortions present in the structure of this strained spiro-polycyclic molecule.

*p*-PPh<sub>2</sub>), 133.2 (d, <sup>2</sup>J<sub>C-P</sub> = 10.6 Hz, *o*-PPh<sub>2</sub>), 141.2 (s, CH<sub>arom</sub>), 151.3 (s, ZrCP), 151.8 (d, <sup>3</sup>J<sub>C-P</sub> = 13.7 Hz, *i*-Ph), 153.0 (d, <sup>3</sup>J<sub>C-P</sub> = 30.8 Hz, ZrCC), 171.6 (s, ZrCCH), 173.0 (d, <sup>1</sup>J<sub>C-P</sub> = 122.3 Hz, C=S), 192.9 (s, ZrC) ppm, *i*-PPh<sub>2</sub> not observed. MS (FAB): *m/z* 642 [M<sup>+</sup> + 1]. Anal. Calcd for C<sub>37</sub>H<sub>30</sub>NPSZr: C 69.12, H 4.70, N 2.17. Found: C 69.09, H 4.52, N 2.15.

**6b**: brown powder, 0.273 g (0.470 mmol, 53%) prepared with 0.451 g of **1** (0.890 mmol) and 61 μL of MeNCS (0.890 mmol). Mp: 196–197 °C (decomp). <sup>31</sup>P{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 32.4 MHz): δ 24.7 (s) ppm. <sup>1</sup>H (CD<sub>2</sub>Cl<sub>2</sub>, 200.1 MHz): δ 3.40 (d, <sup>4</sup>J<sub>H-P</sub> = 2.8 Hz, 3H CH<sub>3</sub>), 5.83 (s, 10H, CH<sub>Cp</sub>), 6.95–7.95 (m, 15H, CH<sub>arom</sub> and PCCH) ppm. <sup>13</sup>C{<sup>1</sup>H} (CD<sub>2</sub>Cl<sub>2</sub>, 62.9 MHz): δ 46.6 (d, <sup>3</sup>J<sub>C-P</sub> = 15.0 Hz, CH<sub>3</sub>), 108.5 (s, CH<sub>Cp</sub>), 122.7, 125.5, 126.3 (s, CH<sub>arom</sub>), 126.4 (d, <sup>1</sup>J<sub>C-P</sub> = 79.0 Hz, *i*-PPh<sub>2</sub>), 129.0 (d, <sup>2</sup>J<sub>C-P</sub> = 10.7 Hz, *o*-PPh<sub>2</sub>), 132.6 (s, *p*-PPh<sub>2</sub>), 133.6 (d, <sup>3</sup>J<sub>C-P</sub> = 9.0 Hz, *m*-PPh<sub>2</sub>), 141.0 (s, CH<sub>arom</sub>), 154.2 (s, ZrCP), 154.7 (d, <sup>3</sup>J<sub>C-P</sub> = 30.4 Hz, ZrCC), 170.7 (s, ZrCCH), 191.9 (d, <sup>1</sup>J<sub>C-P</sub> = 112.9 Hz, C=S), 193.9 (s, ZrC) ppm. MS (FAB): *m/z* 580 [M<sup>+</sup> + 1]. Anal. Calcd for C<sub>32</sub>H<sub>28</sub>NPSZr: C 66.17, H 4.85, N 2.41. Found: C 66.09, H 4.72, N 2.35.

**Preparation of Complexes 8.** To a magnetically stirred solution of **7** (0.230 g, 0.50 mmol) in toluene (5 mL) was added PhN=C=S (0.067 g, 0.50 mmol) at –40 °C. The resulting brown mixture was warmed to room temperature, stirred for 1 h, and then evaporated to dryness. The solid residue was extracted with a mixture of THF (5 mL)/pentane (40 mL) and filtered. The volatiles were removed from the solution, and the resulting solid was washed with pentane (5 mL) to give **8** as a yellow solid in 91% yield (0.270 g). <sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 32.4 MHz): δ 50.5 (s) ppm. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 200.1 MHz): δ 2.05–2.80 (m, 4H, CH<sub>2</sub>), 3.14 (m, 1H, CHP), 4.12 (dt, 1H, <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz, <sup>7</sup>J<sub>H-H</sub> = 7.4 Hz, PCCH), 5.69 (s, 5H, CH<sub>Cp</sub>), 5.96 (s, 5H, CH<sub>Cp</sub>), 7.11–7.90 (m, 14H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 62.9 MHz): δ 24.6 (d, <sup>1</sup>J<sub>C-P</sub> = 45.7 Hz, CH<sub>2</sub>P), 26.4 (d, <sup>1</sup>J<sub>C-P</sub> = 50.0 Hz, CHCHP), 33.7 (d, <sup>1</sup>J<sub>C-P</sub> = 5.5 Hz, CH<sub>2</sub>CH<sub>2</sub>P), 58.0 (d, <sup>1</sup>J<sub>C-P</sub> = 15.7 Hz, ZrCHP), 109.1, 109.4 (s, CH<sub>Cp</sub>), 121.7, 122.9, 123.4, 124.3, 124.8, 128.7, 132.0, 141.1 (s, CH<sub>arom</sub>), 129.1.0 (d, <sup>3</sup>J<sub>C-P</sub> = 10.2 Hz, *o*-PPh), 130.2 (d, <sup>2</sup>J<sub>C-P</sub> = 7.4 Hz, *m*-PPh), 150.0 (d, <sup>1</sup>J<sub>C-P</sub> = 28.3 Hz, *i*-PPh), 155.5 (s, *i*-NPh), 155.2 (d, <sup>3</sup>J<sub>C-P</sub> = 20.9 Hz, CCHCHP), 170.8 (d, <sup>1</sup>J<sub>C-P</sub> = 119.8 Hz, C=S), 181.0 (d, <sup>1</sup>J<sub>C-P</sub> = 2.9 Hz, ZrC) ppm. MS (FAB): *m/z* 595 [M<sup>+</sup> + 1]. Anal. Calcd for C<sub>33</sub>H<sub>30</sub>NPSZr: C 66.63, H 5.08, N 2.35. Found: C 66.49, H 5.02, N 2.25.

**Preparation of Complexes 9.** To a magnetically stirred solution of **7** (0.221 g, 0.48 mmol) in toluene (15 mL) was added CS<sub>2</sub> (0.018 g, 0.24 mmol) at –40 °C. The resulting brown mixture was stirred for 1 h at room temperature and then evaporated to dryness. The solid residue was extracted with a mixture of THF (5 mL)/pentane (40 mL) and filtered. The volatiles were removed from the solution, and the resulting solid was washed with pentane (5 mL) to give **9** as a brown solid in 72% yield (0.343 g).

<sup>31</sup>P{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 32.4 MHz): δ 66.1 (d, <sup>1</sup>J<sub>P-P</sub> = 20.5 Hz, P<sub>B</sub>), 72.9 (d, <sup>1</sup>J<sub>P-P</sub> = 20.5 Hz, P<sub>A</sub>) ppm. <sup>1</sup>H (C<sub>6</sub>D<sub>6</sub>, 200.1 MHz): δ 1.95–2.80 (m, 8H, CH<sub>2</sub>), 3.30 (m, 2H, CHP), 3.55 (m, 2H, PCCH), 5.85, 5.91, 5.92, 5.96 (s, 5H each, CH<sub>Cp</sub>), 7.00–7.70 (m, 18H, CH<sub>arom</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} (C<sub>6</sub>D<sub>6</sub>, 62.9 MHz): δ 21.4 (d, <sup>1</sup>J<sub>C-P</sub> = 66.5 Hz, CH<sub>2</sub>P<sub>A</sub>), 23.0 (d, <sup>1</sup>J<sub>C-P</sub> = 48.8 Hz, CH<sub>2</sub>P<sub>B</sub>), 27.8 (d, <sup>1</sup>J<sub>C-P</sub> = 5.7 Hz, CH<sub>2</sub>CH<sub>2</sub>P<sub>A</sub>), 30.4 (br s, CH<sub>2</sub>CH<sub>2</sub>P<sub>B</sub>), 33.3 (d, <sup>1</sup>J<sub>C-P</sub> = 39.7 Hz, CHCHP<sub>A</sub>), 37.1 (d, <sup>1</sup>J<sub>C-P</sub> = 45.0 Hz, CHCHP<sub>B</sub>), 53.7 (d, <sup>1</sup>J<sub>C-P</sub> = 16.6 Hz, ZrCHP<sub>B</sub>), 57.5 (d, <sup>1</sup>J<sub>C-P</sub> = 24.2 Hz, ZrCHP<sub>A</sub>), 64.0 (dd, <sup>1</sup>J<sub>C-PA</sub> = 49.9 Hz, <sup>1</sup>J<sub>C-PB</sub> = 49.6 Hz, PCS), 110.1, 110.7, 111.1, 111.5 (s, CH<sub>Cp</sub>), 122.6, 122.7, 123.7, 124.5, 127.6, 129.1, 132.2, 132.4, 141.1, 141.6 (s, CH<sub>arom</sub>), 130.4 (d, <sup>1</sup>J<sub>C-P</sub> = 28.3 Hz, *i*-P<sub>B</sub>Ph), 132.0 (d, <sup>1</sup>J<sub>C-P</sub> = 59.8 Hz, *i*-P<sub>A</sub>Ph),

159.1 (d, <sup>3</sup>J<sub>C-P</sub> = 22.9 Hz, CCHCHP<sub>B</sub>), 160.2 (d, <sup>3</sup>J<sub>C-P</sub> = 19.6 Hz, CCHCHP<sub>A</sub>), 182.2 (d, <sup>1</sup>J<sub>C-P</sub> = 4.8 Hz, CZrCP<sub>B</sub>), 182.5 (d, <sup>1</sup>J<sub>C-P</sub> = 5.5 Hz, CZrCP<sub>A</sub>) ppm. MS (FAB): *m/z* 994 [M<sup>+</sup>]. Anal. Calcd for C<sub>53</sub>H<sub>50</sub>P<sub>2</sub>S<sub>2</sub>Zr<sub>2</sub>: C 63.94, H 5.06. Found: C 63.79, H 5.02.

**X-ray Analyses of 3 and 6b.** Single crystals of **3** and **6b** were obtained by layering pentane on top of a saturated dichloromethane solution of the corresponding complexes. X-ray diffraction analyses were carried out at 160 K on a STOE IPDS (Imaging plate Diffraction System) equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 80 mm with the crystal oscillated in  $\varphi$ . For the two structures coverage of the unique set was close to 98% complete to at least  $2\theta = 48.4^\circ$ . Crystal decay was monitored by measuring 200 reflections per image. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections using a Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. Numerical absorption corrections<sup>25</sup> were applied. Relevant crystal data are given in Table 3. The structures were solved by direct methods SIR92<sup>26</sup> and refined by least-squares procedures on  $F_{\text{obs}}$ . H atoms were located on a difference Fourier map, but they were introduced in the calculation in idealized positions ( $d(\text{C-H}) = 0.96 \text{ \AA}$ ), and their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the carbon to which they are connected. Concerning the specific hydrogen atoms H(71) for the two structures and H(91) for **6b**, these atoms were isotropically refined. All non-hydrogen atoms were refined anisotropically. Least-squares refinements were carried out by minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , where  $F_o$  and  $F_c$  are the observed and calculated structure factors. A weighting scheme was used.<sup>27</sup> Models reached convergence with  $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ ,  $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ . The calculations were carried out with the aid of the CRYSTALS programs<sup>28</sup> running on the PC. The drawing of the molecule was realized with CAMERON<sup>29</sup> with thermal ellipsoids at the 50% probability level. The atomic scattering factors were taken from *International Tables for X-Ray Crystallography*.<sup>30</sup>

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**Supporting Information Available:** Tables giving atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **3** and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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