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Four Homologous Zirconium 2,2′-Biphenyldiyls: Synthesis, Structure, and Reactivity

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Summary: A homologous family of zirconohydrocarbons bearing the 2,2′-biphenyldiyl ligand (biphe) has been prepared. One of the homologues is a tetraanionic zirconate, two are examples of homoleptic σ-bound zirconohydrocarbons, and three are anionic "ate" complexes.

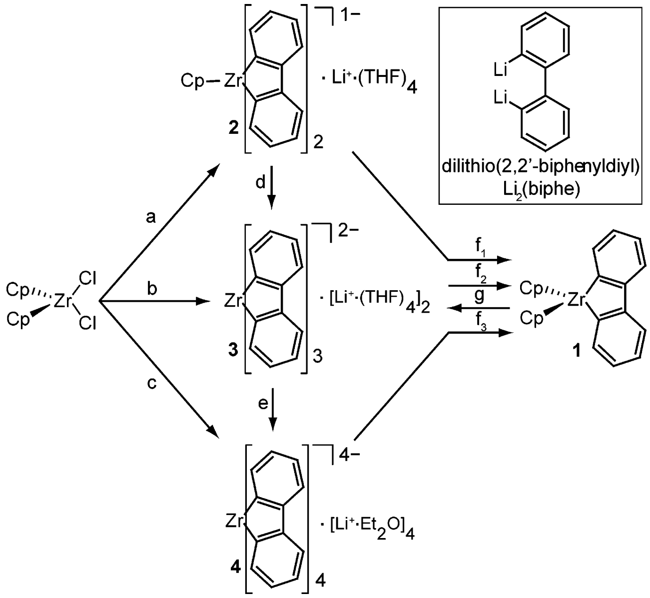
We report the preparation, characterization, and preliminary reactivity studies of a homologous family of zirconohydrocarbons bearing one, two, three, or four 2,2′-biphenyldiyl (biphe) ligands. In all cases, the biphe ligands are bidentate, forming doubly benzannulated zirconacyclopentadienes. One of the homologues is a tetraanionic zirconate, two are examples of homoleptic σ-bound zirconohydrocarbons, three are anionic "ate" complexes, and all four are easily prepared on a 0.5 g scale. Perhaps most importantly, members of this family exhibit unusual aryl−aryl bond forming reactivity that may provide new routes to aryl−aryl bond formation.

The organometallic chemistry of zirconium has been studied for more than 50 years[1] and is dominated by zirconocenes,[2] which are widely used as catalysts for olefin polymerization[3] and in organic synthesis.[4] The ability of alkyl or aryl zirconocenes to transmetalate stoichiometrically (Cu, Hg, Sn, B, and Al) or catalytically (Ni and Pd) is synthetically useful.[2] In particular, the formal [4 + 2] cycloaddition of zirconacyclopentadienes via their transmetalated derivatives with acetylenes is an increasingly popular route to highly substituted benzenes[5] and heterocycles.[6] Sharp has extended this concept to the formal [3 + 2] cycloaddition of polycyclic aromatic hydrocarbons with acetylenes.[7]

Our initial motivation was to use the hitherto unreported bis(cyclopentadienyl)zirconium 2,2′-biphenyldiyl (Cp_2Zr(biphe), **1**) in a [4 + 2] route to phenanthrene derivatives, by a path similar to that of Eisch.[8] In 1971, Rausch and co-workers prepared the titanium analogue of **1**, Cp_2Ti(biphe), in 12% yield by treating Cp_2TiCl_2 with Li_2(biphe);[9] the crystal structure has been reported.[10]

Treatment of Cp_2ZrCl_2 with Li_2(biphe), even in substoichiometric amounts, did not produce the expected product **1** but instead produced [Li·$(THF)_4$][CpZr$(biphe)_2$] (**2**) by loss of a Cp^- ligand (Scheme 1a). The reactivity of Cp_2ZrCl_2 with Li_2(biphe) continued to surprise us. Treatment of Cp_2ZrCl_2 with excess Li_2(biphe) in THF gave the homoleptic complex [Li·$(THF)_4$]$_2$[Zr$(biphe)_3$] (**3**) in 87% yield. An identical reaction, except using Et_2O in place of THF, gave [Li·Et_2O]$_4$[Zr$(biphe)_4$] (**4**) in 56% yield.

Scheme 1. Synthesis and Interconversions of Complexes 1−4[a]



[a] Legend: (a) 1.0 Li_2(biphe), THF, −30 °C, 76%; (b) 4.0 Li_2(biphe), THF, −30 °C, 87%; (c) 4.0 Li_2(biphe), Et_2O, −30 °C, 56%; (d) 2.0 Li_2(biphe), THF, −30 °C; (e) 1.0 Li_2(biphe), Et_2O, −30 °C, 93%; (f) excess CpH, f_1 67%, f_2 86%, f_3 10%; (g) 2.0 Li_2(biphe), THF, −30 °C, 92%.

These reactions involve loss of Cp^- ligands. Few examples of the loss of a single Cp^- from a zirconocene have been reported: transfer to Ir,[11] transfer to Mo or W,[12] and displacement by alkyllithium reagents.[13] Excluding exhaustive protonolysis or oxidation, only one example of the loss of both Cp^- ligands from a zirconocene has been reported: treatment of Cp_2ZrMe_2 with MeLi was reported to afford 2 equiv of CpLi, but the resulting zirconium species was not characterized.[14]

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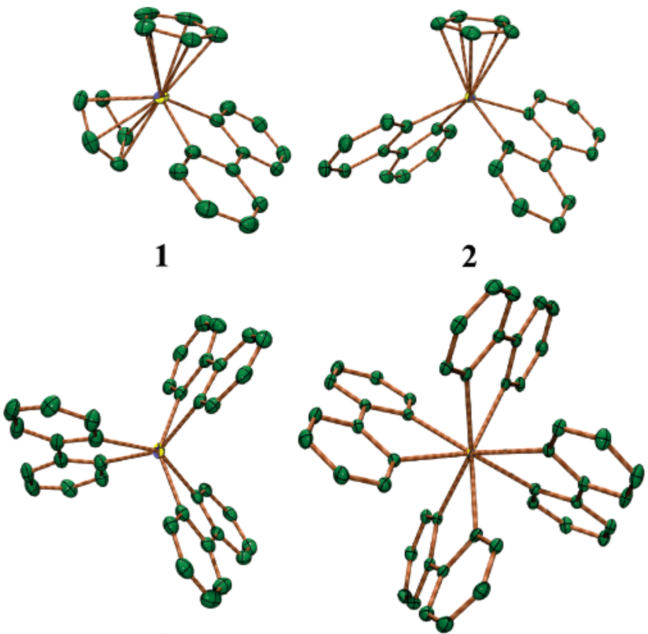

Figure 1. Single-crystal X-ray diffraction analysis structures of **1**−**4**. Hydrogens, counterions, and solvate molecules are omitted for clarity.

Table 1. X-ray Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{22}H_{18}Zr$	$C_{47}H_{53}LiO_4Zr$	$C_{68}H_{86}Li_2O_8Zr$	$C_{64}H_{72}Li_4O_4Zr$
fw	373.58	788.05	1136.47	1024.20
cryst syst	rhombohedral	monoclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P2_1/c$	$C2/c$	$P2_1/n$
a, Å	19.1732(16)	19.2821(17)	28.632(10)	12.9268(5)
b, Å	19.1732(16)	14.6363(13)	13.128(5)	17.6970(6)
c, Å	24.043(4)	15.0442(13)	21.206(7)	23.7283(8)
α, deg	90.00	90.00	90.00	90.00
β, deg	90.00	106.650	131.001(8)	95.9130
γ, deg	120.00	90.00	90.00	90.00
V, Å^3	7653.6	4067.7(6)	6015(4)	5399.3
Z	18	4	4	4
temp, K	100(2)	100(2)	100(2)	100(2)
total no. of rflns	33 084	69 947	38 854	69 988
no. of unique rflns (R_{int})	3919 (0.1915)	14 180 (0.0217)	6914 (0.0660)	12 393 (0.0411)
2*θ* max (deg)	55	65.08	55	55
R1, wR2 ($I > 2\sigma(I)$)	0.0398, 0.0865	0.0339, 0.0937	0.0559, 0.1253	0.0350, 0.0887

The complex we initially sought, **1**, could not be prepared by the direct reaction of Cp_2ZrCl_2 with Li_2(biphe), even when using substiochiometric Li_2(biphe)—only **2**−**4** were obtained. The elusive complex **1** was ultimately prepared by protonolysis of biphe ligands from **2**−**4** using the mild acid CpH with concomitant interception of a Zr intermediate by the conjugate base, Cp^-, a method reported by Scott et al.[15] Thus, all homologous zirconium 2,2′-biphenyldiyls, **1**−**4**, have been prepared.

The structures of complexes **1**−**4** were determined by single-crystal X-ray diffraction analysis (Figure 1 and Table 1; see the Supporting Information for figures showing the counterions and solvent). Complex **1** is similar to other zirconacyclopentadienes, except that the C(α)−C(*β*) bonds, which are common to both the five- and six-membered rings, are longer (1.42 Å; cf. $Cp_2Zr(C_4Ph_4)$, 1.36 Å).[16] This difference, also observed in **2**−**4**, is similar to that between furan[17] (1.32 Å) and dibenzofuran[18] (1.38 Å).

Table 2. Geometric Measures of 1−4

	r(C−Zr)/Å (av, std dev)	Σ∠(C(α))/deg (av, std dev)	*r*(Cp centroid−Zr)/Å
1	2.27, 0.01	360, 0.0	2.20, 2.21
2	2.34, 0.02	359.6, 0.4	2.27
3	2.36, 0.02	359.6, 0.2	
4	2.49, 0.02	358.5, 1.5	

In the crystal structure of **2**, the Li•$(THF)_4$ cation is separated (7.27 Å) from the formally anionic zirconium atom. A disordered THF molecule fills a void. This zirconate possesses a four-legged piano-stool geometry. In the crystal structure of **3**, the two Li•$(THF)_4$ cations are separated (8.02 Å) from the formally dianionic zirconium atom. The three biphe ligands are disposed about the Zr atom with a geometry closer to prismatic than octahedral ($\theta = 22.4°$, where θ is the angle between the medians of the triangles formed by the C atoms bound to Zr; $\theta = 0°$ for a prism and $\theta = 60°$ for an octahedron). Similar structures with bisphosphinine or 2,2′-bipyridyl ligands have been reported.[19] In the crystal structure of **4**, a single Li•Et_2O cation nests in each of the four clefts defined by the biphe ligands. The Li cations are in van der Waals contact with roughly six C atoms (average, 2.33 Å, standard deviation 0.13 Å). The C atoms remain essentially planar, as demonstrated by the sum of the angles around C(α) exceeding 358° in all cases (cf. sp^3 328.5° and sp^2 360°). Hence, the Li−C interactions are ionic, not covalent. The four biphe ligands are disposed about Zr with a geometry closer to square antiprismatic than square prismatic ($\theta = 32.2°$, where θ is the angle of offset between the squares formed by the C atoms bound to Zr; $\theta = 45°$ for a square antiprism and $\theta = 0°$ for a square prism). The distance between the C atoms of the biphe ligands and the Zr atom increases with the number of biphe ligands (Table 2).

The inability to prepare **1** from the direct reaction of Cp_2ZrCl_2 with Li_2(biphe) demonstrates that the addition of the second biphe and loss of Cp^- is faster than the addition of the first biphe.[20] Indeed, the stepwise addition of biphe ligands is effective. Both complexes **1** and **2** can be converted to **3** by treatment with Li_2(biphe) in THF in >90% yield. Likewise, complex **3** is converted to **4** by treatment with excess Li_2(biphe) in Et_2O in 97% yield. The conversion of **1** to **2** has not been realized.

Compounds **1**−**4** can all be prepared on a greater than 500 mg scale as crystalline solids. The simplest to prepare is **3**, which immediately precipitates as a pure, crystalline solid. Treatment of **3** with Li_2(biphe) in Et_2O is our preferred method to prepare **4**, which crystallizes from the reaction mixture at −30 °C.

The reactivity of **1**−**4** varies drastically with the number of biphe ligands. Both the neutral species **1** and monoanion **2** are indefinitely stable at 25 °C as a solid or in Et_2O or THF solution. The dianion **3**, which is poorly soluble, is indefinitely stable at −35 °C but decomposes at room temperature over 12 h in THF under an Ar atmosphere. In benzene, a good solvent for **3**, the decomposition occurs within 1 h. The tetraanion **4** is extraordinarily reactive—it decomposes rapidly at room temperature as a solid or in solution but can be stored for days at −35 °C under Et_2O.

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Thermolysis of **2** (70 °C, toluene) provided biphenyl, biphenylene, and quaterphenyl as the only detectable organic products. Thermolysis of **3** (70 °C, toluene) provided biphenylene as the main organic product. Thermolysis of **4** (20 °C, Et$_2$O) provided biphenyl and biphenylene. Decomposition over 10 days at −35 °C provided quaterphenyl as well. The inorganic or organometallic products from these reactions were intractable and were not characterized.

These compounds are sensitive to acids and oxidants. Complex **1** was quantitatively converted to zirconocene dichloride by protonolysis with ethereal HCl. Oxidation of **4** with CoCl$_2$ in Et$_2$O provides *o*-quaterphenyl, *o*-sexiphenyl, quaterphenylene, and sexiphenylene (GC-MS), as well as traces of higher oligophenyls (LD-TOF). The products of these thermolysis and oxidation reactions suggest that these complexes may provide new methods to form aryl−aryl bonds.

A new family of zirconium complexes has been prepared and characterized. All members are metallohydrocarbons. Compounds **3** and **4** are homoleptic. The Zr fragment, assuming a full positive charge on Li, varies from neutral to a remarkable tetraanion. In all cases, the Zr atom is electronically unsaturated: in complex **1**, it carries 16e, in complexes **2** and **4**, it carries 14e, and in complex **3**, it carries 12e. Our original intent, the use of dibenzozirconacyclopentadienes as substrates for formal [4 + 2] cycloaddition reactions, was realized. The reaction of **3** with (PPh$_3$)$_2$NiBr$_2$ followed by diphenylacetylene gave 9,10-diphenylphenanthrene (47%); when followed by 3-hexyne, it gave 9,10-diethylphenanthrene. The [4 + 2] cycloaddition chemistry of this family of molecules may, however, be the least interesting outcome of this work. We expect the aryl−aryl bond forming reactivity of these complexes to be especially interesting, especially for the dianion **3** and the reactive tetraanion **4**.

Experimental Section. (Biphenyl-2,2′-diyl)zirconocene (1). The complex **2** or **3** (∼0.5 g) or **4** (∼30 mg) and neat cyclopentadiene (ca. 8 mL) were stirred for 2 h. Precipitated CpLi was removed by filtration. Removal of cyclopentadiene under reduced pressure followed by two crystallizations from hexanes gave (biphenyl-2,2′-diyl)zirconocene (from **2**, 67%; from **3**, 86%; from **4**, 2%). Anal. Calcd (found) for $C_{22}H_{18}Zr$: C, 70.96 (70.68); H, 4.88 (4.99). ^{1}H NMR (500 MHz, d_8-THF): δ 7.56 (d, $J = 7.0$ Hz, 1.9H, Ar *H*), 6.86 (t, $J = 8.0$ Hz, 2.0H, Ar *H*), 6.72 (t, $J = 7.1$ Hz, 1.8H, Ar *H*), 6.49 (d, $J = 6.1$ Hz, 1.6H, Ar *H*), 6.36 (s, 9.8 H, Cp *H*), 3.56 (s, solvent), 1.71 (s, solvent). ^{13}C NMR (125 MHz, C_6D_6): δ 186.6, 148.0, 136.3, 126.7, 125.3, 122.4, 113.6.

Bis(biphenyl-2,2′-diyl)cyclopentadienylzirconate, Li Salt (2). *n*-Butyllithium (1.76 M in hexane, 6.8 mL, 12 mmol) was added to a solution of 2,2′-dibromobiphenyl (1.807 g, 5.8 mmol) in THF (20 mL) at −80 °C. After the mixture was warmed to −30 °C, Cp$_2$ZrCl$_2$ (1.693 g, 5.8 mmol) was added. This temperature was maintained for 1 h and then the reaction mixture was warmed to 25 °C. Solvent was removed under vacuum, and the residue was washed with hexane and then dissolved in THF (20 mL). The volume of the THF was reduced by half, and the solution was placed in the freezer. Yellow crystals (1.736 g, 76%) formed overnight. ^{1}H NMR (500 MHz, C_6D_6): δ 7.85 (t, $J = 7.0$ Hz, 8H, Ar *H*), 7.21 (t, $J = 7.5$ Hz, 4H, Ar *H*), 7.12 (t, $J = 7.5$ Hz, 4H, Ar *H*), 6.32 (s, 5H, Cp *H*), 3.10 (m, 16H, THF), 1.13 (m, 16H, THF). ^{13}C NMR (125 MHz, C_6D_6): δ 190.6, 155.6, 139.7, 128.7, 127.5, 125.9, 121.8, 114.0, 68.5, 25.8.

Tris(biphenyl-2,2′-diyl)zirconate(2−), Li Salt (3). *n*-Butyllithium (2.9 M in hexane, 6.9 mL, 20.0 mmol) was added to a solution of 2,2′-dibromobiphenyl (3.120 g, 10.0 mmol) in 100 mL of THF at −80 °C. After the mixture was warmed to −30 °C, Cp$_2$ZrCl$_2$ (0.730 g, 2.5 mmol) was added. The temperature was maintained for 18 h, and fine yellow crystals (2.47 g, 87%) precipitated from solution. ^{1}H NMR (500 MHz, C_6D_6): δ 8.41 (m, $J = 6.5$ Hz, 6H, Ar *H*), 7.75 (m, $J = 7.5$ Hz, 6H, Ar *H*), 7.21 (m, $J = 7$ Hz, 6H, Ar *H*), 7.15 (m, $J = 7$ Hz, 6H, Ar *H*), 3.34 (m, 48H, THF), 1.31 (m, 44H, THF). ^{13}C NMR (125 MHz) (C_6D_6): δ 190.9, 157.7, 140.7, 128.9, 125.9, 121.0, 67.8, 25.6.

Tetrakis(biphenyl-2,2′-diyl)zirconate(4−), Li Salt (4). The reaction sequence was identical with that used to prepare **3**, except that Et$_2$O replaced THF and the reaction was scaled by 0.57. Blocklike crystals (0.825 g, 56%) were formed. ^{1}H NMR (500 MHz, d_8-toluene): δ 7.98 (m, $J = 8$ Hz, 16H, Ar *H*), 7.13 (m, $J = 7.5$ Hz, 8H, Ar *H*), 6.88 (m, $J = 7.5$ Hz, 8H, Ar *H*), 3.38 (q, 7 Hz, 138H, Et$_2$O), 1.12 (t, 7 Hz, 208H, Et$_2$O). ^{13}C NMR (125 MHz, C_6D_6): δ 153.7, 144.8, 128.7, 126.4, 126.0, 122.8, 66.1, 15.7.

3 from 2. *n*-Butyllithium (1.62 M in hexane, 0.4 mL, 0.66 mmol) was added to a solution of 2,2′-dibromobiphenyl (0.103 g, 0.33 mmol) in THF (10 mL) at −78 °C. The solution was warmed to −30 °C and then added to a solution of **2** (0.250 g, 0.33 mmol) in THF (5 mL), also at −30 °C. The resulting yellow precipitate was collected by filtration and rinsed with THF (0.360 g, 96%). The ^{1}H NMR spectrum and crystal unit cell were identical with those of **3** prepared from Cp$_2$ZrCl$_2$.

4 from 3. *n*-Butyllithium (1.62 M in hexane, 0.26 mL, 0.44 mmol) was added to a stirred solution of dibromobiphenyl (0.137 g, 0.44 mmol) in Et$_2$O (20 mL) at −40 °C. After 0.5 h, **3** (0.500 g, 0.44 mmol) was added as a solid. The temperature was maintained at −40 °C for 16 h. The reaction volume was reduced by half, and crystals formed overnight (0.4191 g, 93%), which gave ^{1}H and ^{13}C NMR spectra identical with those of **4** prepared from Cp$_2$ZrCl$_2$.

3 from 1. A solution of 2,2′-dilithiobiphenyl (0.0442 g, 0.266 mmol) in THF (10 mL) was added over 5 min to **1** (0.050 g, 0.133 mmol) dissolved in THF (10 mL) at −35 °C. After 1 h, the reaction mixture was warmed to 25 °C. The precipitate was collected by filtration and rinsed with hexane and THF to yield **3** (0.139 g, 92%), which gave^{1}H and ^{13}C NMR spectra identical with those of **3** prepared from Cp$_2$ZrCl$_2$.

Thermolysis of 2 and 3. The complex **2** or **3** (200 mg) was dissolved in toluene (50 mL) in a Schlenk flask under Ar and then heated to 70 °C for 3 h. Solvent was removed under vacuum, and the hexane-soluble fraction was analyzed by GC-MS. Compound **2** yielded biphenyl, biphenylene, and quaterphenyl, and **3** yielded primarily biphenylene with trace amounts of biphenyl and quaterphenyl.

Thermolysis of 4. Complex **4** in Et$_2$O was thermolyzed at 25 °C under Ar for 24 h. The solvent was removed under vacuum, and the hexane-soluble fraction was analyzed by GC-MS, which revealed biphenyl and biphenylene.

Hydrochlorolysis of 1. Complex **1** (150 mg, 0.40 mmol) was dissolved in 1 M HCl in diethyl ether (∼15 mL), and the yellow solution immediately turned clear. After evaporation the residue was triturated with hexane to isolate biphenyl (60.3 mg, 100%, GC-MS). The insoluble material was recrystallized from THF to yield Cp$_2$ZrCl$_2$ (117 mg, 100%, ^{1}H NMR).

Oxidation of 3. Complex **3** (0.250 g, 0.22 mmol), suspended in Et$_2$O, was mixed with CoCl$_2$ (0.058 g, 0.22 mmol) for 6 h at 25 °C. The solvent was removed under vacuum and the toluene-soluble fraction analyzed by GC-MS, which revealed quaterphenyl, quaterphenylene, hexaphenyl, and hexaphenylene.

LDTOF-MS analysis showed hexaphenyl and hexaphenylene and traces of octaphenyl, octaphenylene, and decaphenylene.

Reaction of 3 with Diphenylacetylene and $Ni(PPh_3)_2Br_2$. Complex **3** (0.125 g, 0.11 mmol) and diphenylacetylene (0.066 g, 0.33 mmol) were suspended in THF (10 mL), and $Ni(PPh_3)_2Br_2$ (0.275 g 0.33 mmol) was added. After 12 h, aqueous HCl (6 M, 50 mL) was added. Extraction with toluene, chromatography, and PPh_3 removal with CuCl afforded diphenylphenanthrene (0.052 g, 48%, GC-MS, ^1H NMR).

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Supporting Information Available: Figures giving ^{13}C and ^1H NMR spectra and thermal ellipsoid plots of **1**−**4** showing counterions and solvent and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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