New Synthon in the Design of *ansa*-Cyclopentadienyl Ligands with Variable Substitution at the Bridging Atom

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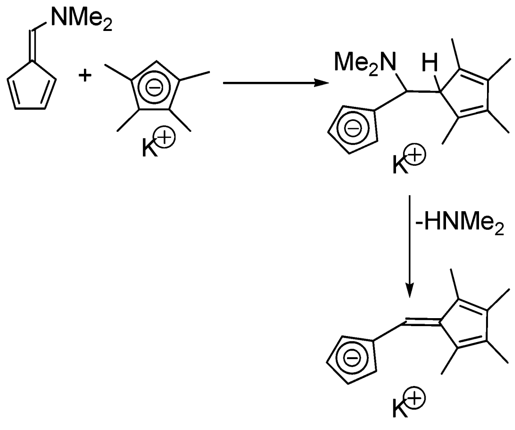
Summary: This communication describes the synthesis and structural characterization of a potassium fulvene-substituted cyclopentadienyl compound which acts as a synthon in the facile preparation of ansa-metallocene complexes with variable substitution at the bridging atom.

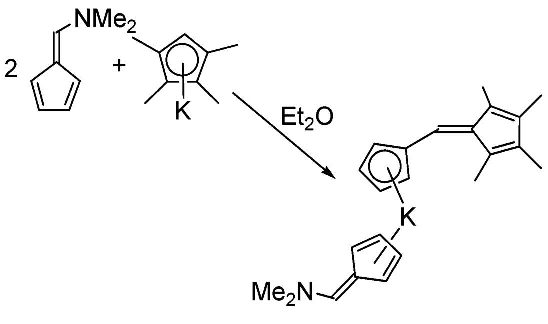
In the world of single-site metallocene catalysis there is a growing emphasis in ligand design toward the goal of "made to measure" *ansa*-metallocene catalysts for the preparation of polyolefins with defined properties[1] and the immobilization of the catalyst on distinct substrates by the prefunctionalization of the *ansa* ligand of the metallocene complex.[2] Here we report the synthesis and characterization of a potassium fulvene-substituted cyclopentadienyl compound and its use in the introduction of specific substituents at the bridging atom of the *ansa* ligand.

The reaction of 6-(dimethylamino)fulvene with $(C_5Me_4H)K$ in THF gave, after $HNMe_2$ elimination, $(C_5Me_4){=}CH(\{C_5H_4\}K)$ (**1**).[3] This type of amine elimination has previously been observed, although not explained, by Alt and co-workers.[4] The reaction of alkali-metal organic derivatives with aminofulvenes does not always give the same result. For example, for $(C_5H_4){=}C(Me)NMe_2$ the reaction with methyllithium in THF gave $Me_2N(CH_2{=})C(\{C_5H_4\}Li)$ and methane.[5] The same reaction in Et_2O gave the addition product $Me_2N(Me_2)C(\{C_5H_4\}Li)$.[5] The proposed mechanism for the formation of **1** is given in Scheme 1. The first step involves nucleophilic addition of tetramethylcyclopentadienyl to the aminofulvene molecule followed by the intramolecular elimination of $HNMe_2$. The potassium cation is now the counterion to the C_5H_4 anionic moiety.

Scheme 1. Proposed Mechanism in the Synthesis of 1



Scheme 2. Synthesis of 2



When the same reaction was carried out in Et_2O, $(C_5Me_4){=}CH(\{C_5H_4\}K\{(C_5H_4){=}C(H)NMe_2\})$ (**2**) was isolated as the crystalline product in a somewhat reduced yield. The second addition of excess $(C_5Me_4H)K$ to the exocyclic double bond of **2** was not observed. The yield of **2** was greatly improved when the reaction was repeated using 2 molar equiv of the aminofulvene reagent (Scheme 2). The presence of a 6-(dimethyl-

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(1) See for example: (a) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (b) Coates, G. W. *Chem. Rev.* **2000**, *100*, 1223. (c) Resconi, L.; Cavallo, L.; Fait, A.; Piemontesi, F. *Chem. Rev.* **2000**, *100*, 1253. (d) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) (a) Hlatky, G. C. *Chem. Rev.* **2000**, *100*, 1347. (b) Lee, B. Y.; Oh, J. S. *Macromolecules* **2000**, *33*, 3194. (c) Galan-Fereres, M.; Koch, T.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1999**, *580*, 145. (d) Lee, B. Y.; Oh, J. S. *J. Organomet. Chem.* **1998**, *552*, 313.

(3) Preparation of **1**: 6-(dimethylamino)fulvene (1.50 g, 12.5 mmol) in THF (50 mL) was added slowly to $(C_5Me_4H)K$ (2.00 g, 12.5 mmol) in THF (100 mL) at −40 °C. The mixture was warmed to room temperature and stirred for 16 h, and filtered. Solvent was removed from the filtrate under reduced pressure to give the title complex as a red solid (2.41 g, 82%). ^1H NMR (400 MHz, C_6D_6/d_8-THF): δ 2.04 (3H), 2.06 (3H), 2.31 (3H), 2.52 (3H) (s, $C_5\mathit{Me}_4$), 6.20 (1H), 6.42 (1H), 7.31 (2H) (m, $C_5Me_4CH{=}C_5\mathit{H}_4$), 6.53 (s, 1H, $C_5Me_4C\mathit{H}{=}C_5H_4$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6/d_8-THF): δ 11.9, 11.6, 11.8, 16.2 ($C_5\mathit{Me}_4$), 111.7, 114.4, 119.1, 131.2, 135.0 (C_5H_4), 119.8, 125.5, 128.7, 133.7, 134.1 (C_5Me_4), not observed ($C_5Me_4\mathit{C}H{=}C_5H_4$). Anal. Calcd for $C_{15}H_{17}K$: C, 76.21; H, 7.25. Found: C, 76.00; H, 7.18.

(4) Alt, H. G.; Zenk, R. *J. Organomet. Chem.* **1996**, *526*, 295.

(5) Venne-Dunker, S.; Kehr, G.; Fröhlich, R.; Erker, G. *Organometallics* **2003**, *22*, 948.

10.1021/om049425a CCC: $27.50

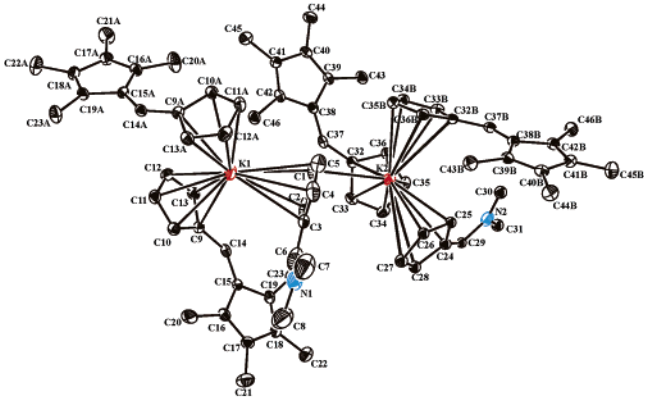

Figure 1. Molecular structure of **2** with thermal ellipsoids at the 30% probability level. Selected distances (Å) and angles (deg): K(1)−Ct(1) = 2.88(3), K(1)−Ct(2) = 2.97(4), K(2)−Ct(3) = 2.88(3), K(2)−Ct(4) = 2.94(3), average K(1)−C(Ct(1)) = 3.085, average K(1)−C(Ct(2)) = 3.215, average K(2)−C(Ct(3)) = 3.108, average K(2)−C(Ct(4)) = 3.20, K(2)−C(1) = 3.186(4), C(9)−C(14) = 1.438(5), C(14)−C(15) = 1.371(5), C(32)−C(37) = 1.430(5), C(37)−C(38) = 1.377(5), C(3)−C(6) = 1.416(8), C(6)−N(1) = 1.384(8), C(24)−C(29) = 1.36(1), C(29)−N(2) = 1.400(7), 1.44(1); Ct(1)−K(1)−Ct(1)′ = 119.39(6), Ct(1)−K(1)−Ct(2) = 127.33(3), Ct(3)−K(2)−Ct(3)′ = 114.0(1), Ct(3)−K(2)−Ct(4) = 110.18(2), Ct(3)−K(2)−C(1) = 107.58(9), Ct(4)−K(2)−C(1) = 111.38(9), C(9)−C(14)−C(15) = 137.7(3), C(32)−C(37)−C(38) = 137.5(3), K(1)−C(1)−K(2) = 168.4(2), C(3)−C(6)−N(1) = 126.4(5), C(24)−C(29)−N(2) = 126.7(6), 122.0(7). Ct(1) corresponds to the centroid of C(9)−C(13); Ct(2) corresponds to the centroid of C(1)−C(5); Ct(3) corresponds to the centroid of C(32)−C(36); Ct(4) corresponds to the centroid of C(24)−C(28).

amino)fulvene molecule coordinated to the metal was revealed by NMR spectroscopy[6] and single-crystal X-ray diffraction studies.

The 6-(dimethylamino)fulvene on reaction with $(C_5Me_4H)K$ has two possible courses of action open to it: addition and coordination. When the reaction is carried out in THF, the coordination of the aminofulvene is probably disfavored by the presence of the strongly Lewis basic solvent. However, the reaction in Et_2O occurs, most probably, with the initial coordination of aminofulvene to the potassium atom and the subsequent addition to the exocyclic double bond of a second aminofulvene molecule. To support this theory, we have observed that there was no reaction when 6-(dimethylamino)fulvene was added to a suspension of **1** in Et_2O and the mixture stirred at room temperature for several hours. The conclusion drawn from this fact is that, if aminofulvene coordination is to take place, then this must occur in the first step of the reaction. The further possible reaction of **1** and **2** with 6-(dimethylamino)fulvene, to give compounds with three or more C_5 rings, can also be ruled out, and the presence of such products was not detected in the final isolated yields of **1** and **2**.

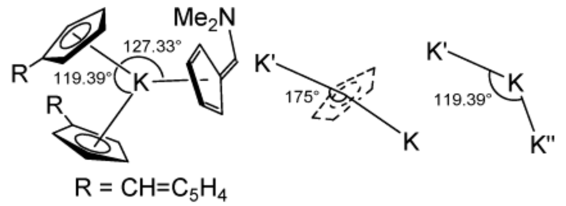

Figure 2. Coordination environment of K(1).

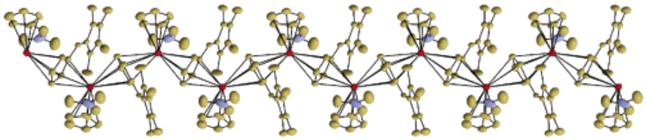

Figure 3. Polymeric chain **P1**.

Few structural determinations have been carried out for potassium cyclopentadienyl systems, and any new contributions to this field are of importance.[7] With this aim in mind, we have determined the molecular structure of **2** by single-crystal X-ray diffraction studies.[8] An ORTEP representation of **2** is given in Figure 1. The molecular structure is made up of laminas which contain interlinked polymeric chains. There is no apparent interaction between laminas. The polymeric structure consists of cyclopentadienyl and aminofulvene moieties bridging the potassium atoms. The fulvene substituents of the cyclopentadienyl ligands do not interact with the potassium atoms. There are two distinct potassium environments in the unit cell, which lead to the formation of two different and alternating ring−metal−ring−metal chains (**P1** and **P2**).

In the first chain, **P1** (Figures 2 and 3), the potassium atom adopts a distorted-trigonal-planar conformation. The cyclopentadienyl units are situated in an η^5 bent-metallocene arrangement (Ct(1)−K(1)−Ct(1)′ = 119.39(6)°) and bridge adjacent potassium atoms in the polymeric chain. The K(1)−Ct(1)−K(1)′ angle is slightly deviated from linear (175(1)°), in accordance with that previously described for other potassium cyclopenta-

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(6) Preparation of **2**: $(C_5Me_4H)K$ (2.00 g, 12.5 mmol) in Et_2O (50 mL) was added slowly to 6-(dimethylamino)fulvene (3.02 g, 25.0 mmol) in Et_2O (100 mL) at −40 °C. The mixture was warmed to room temperature and stirred for 16 h. The suspension was filtered and solvent removed from the filtrate under reduced pressure to give the title complex as a red solid (2.81 g, 63%). ^1H NMR (400 MHz, C_6D_6/d_8-THF): δ 1.85 (3H), 1.87 (3H), 2.11 (3H), 2.32 (3H) (s, C_5Me_4), 2.20 (s, 6H, NMe_2), 5.94 (2H), 6.20 (2H) (m, 2H, $C_5Me_4CH{=}C_5H_4$), 6.35 (1H), 6.40 (1H), 6.42 (1H), 6.63 (1H) (m, $Me_2NCH{=}C_5H_4$), 6.41 (s, 1H, $C_5Me_4CH{=}C_5H_4$), 6.41 (s, 1H, $Me_2NCH{=}C_5H_4$). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6/d_8-THF): δ 11.3, 12.0, 12.1, 16.6 (C_5Me_4), 42.7 (NMe_2), 111.8, 114.6, 119.3, 132.2, 132.8 (C_5H_4), 114.7, 120.0, 125.6, 128.7, 133.7 (C_5Me_4), not observed ($C_5Me_4CH{=}C_5H_4$), 114.6, 120.1, 125.0, 125.8, 132.4 ($Me_2NCH{=}C_5H_4$), 147.5 ($Me_2NCH{=}C_5H_4$). Anal. Calcd for $C_{23}H_{28}KN$: C, 77.26; H, 7.89; N, 3.92. Found: C, 77.03; H, 7.18; N, 3.94.

(7) (a) Dinnebier, R. E.; Behrens, U.; Olbrich, F. *Organometallics* **1997**, *16*, 3855. (b) Jordan, V.; Behrens, U.; Olbrich, F.; Weiss, E. *J. Organomet. Chem.* **1996**, *517*, 81. (c) Cole, M. L.; Jones, C.; Junk, P. C. *Dalton* **2002**, 896. (d) Jutzi, P.; Leffers, W.; Hampel, B.; Pohl, S.; Saak, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 583. (e) Evans, W. J.; Brady, J. C.; Fujimoto, C. H.; Giarikos, D. G.; Ziller, J. W. *J. Organomet. Chem.* **2002**, *649*, 252. (f) Rabe, G.; Roesky, H. W.; Stalke, D.; Pauer, F.; Sheldrick, G. M. *J. Organomet. Chem.* **1991**, *403*, 11. (g) Bercaw, J. E.; Schaefer, W. D.; *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1993**, *49*, 1489. (h) Harvey, M. J.; Hanusa, T. P.; Pink, M. *Dalton* **2001**, 1128. (i) Leung, W.-P.; Song, F.-Q.; Xue, F.; Mak, T. C. W. *J. Chem. Soc., Dalton Trans.* **1997**, 4307.

(8) Crystal data for **2**: $C_{54}H_{66}K_2N_3$, $M_r = 835.3$, crystal size 0.32 × 0.21 × 0.19 mm^3, $Z = 4$, monoclinic, space group $P2_1/c$, $a = 16.710(2)$ Å, $b = 9.8370(10)$ Å, $c = 29.408(2)$ Å, $\beta = 92.080(3)°$, $V = 4830.8(8)$ Å^3, $\rho = 1.149$ Mg/m^3, $T = 170(2)$ K, $\theta_{min} = 1.81°$, $\theta_{max} = 28.35°$, $\lambda = 0.710\,73$ Å. Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 30 mA, using the $\omega/2\theta$ scan technique. The crystal used for the diffraction studies showed no decomposition during data collection. The integration process yielded a total of 30 197 reflections, of which 11 548 were independent (R(int) = 0.0737). The structure was solved using direct methods (SIR97) and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined in the riding mode. Final R1 = 0.0736 and wR2 = 0.1746 (5348 reflections with $I > 2\sigma(I)$). Residual electron density $\rho_{max} = 1.108$ e Å^{-3} and $\rho_{min} = -0.430$ e Å^{-3}.

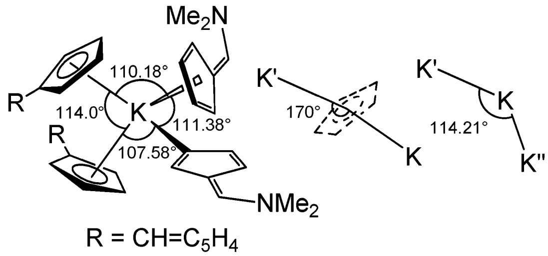


Figure 4. Coordination environment of K(2).

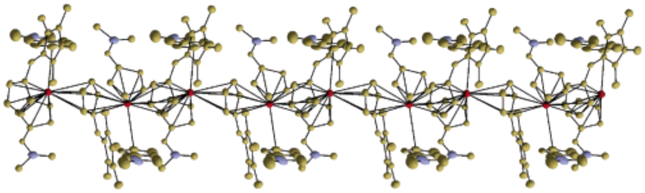


Figure 5. Polymeric chain **P2**.

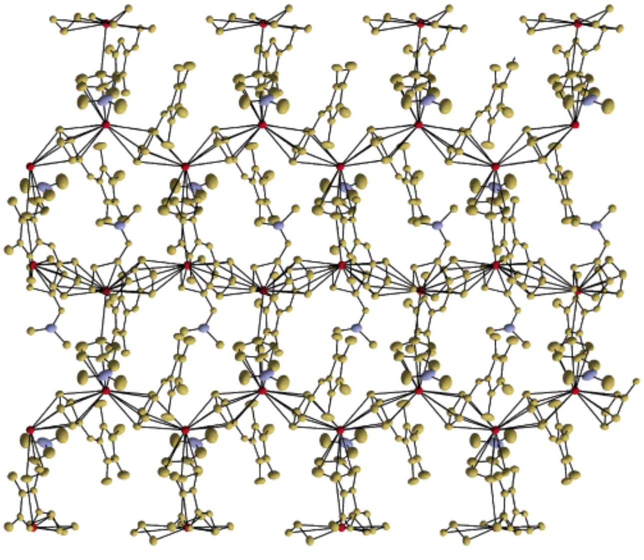
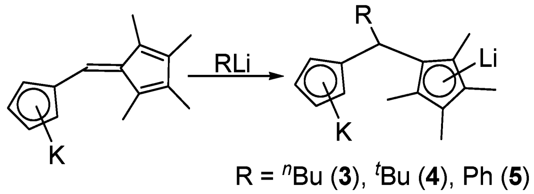


Figure 6. Extended structure of **2**.

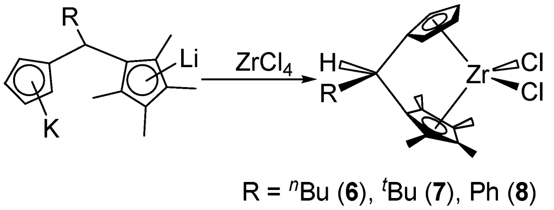
dienyl compounds with extended structures.[7] The coordination sphere of the potassium atom is completed by an aminofulvene molecule via a proposed η^5 bonding interaction instead of an η^6 interaction, on the grounds that the K(1)−C(6) distance (3.964(7) Å) is significantly greater than those observed for the atoms of the C_5 ring C(1)−C(5) (between 3.144 and 3.300 Å). However, it is important to highlight the planarity of the aminofulvene moiety, which maintains the fulvene six-electron delocalized system. The polymeric chain adopts a zigzag conformation (K(1)′−K(1)−K(1)″ = 119.39(3)°).

The potassium atoms in the second polymeric chain, **P2** (Figures 4 and 5), adopt a distorted-tetrahedral geometry and are arranged in a zigzag conformation with respect to each other (K(2)′−K(2)−K(2)″ = 114.21(3)°). The cyclopentadienyl units form an η^5 bent metallocene substructure (Ct(3)−K(2)−Ct(3)′ = 114.0(1)°) and bridge the potassium atoms of **P2**. The K(2)−Ct(3)−K(2)′ angle (170(1)°) is slightly smaller than that observed in the first polymeric chain **P1**. In addition, the coordination sphere of the potassium atom contains a planar π-coordinated aminofulvene ligand. This moiety presents disorder in the structural determination, and two positions were assigned. The first possibility indicates an η^5 rather than an η^6 interaction, as in the case of **P1**, considering the greater distance observed for K(2)−C(29) (3.914(7) Å) compared with those corresponding to C(24)−C(28) (between 2.977 and 3.43 Å). In the alternative position the distance K(2)−C(29) (3.57(1) Å) is somewhat shorter and makes the election of an η^5 or η^6 interaction unclear. The potassium atom of **P2** is also linked to an aminofulvene of an adjacent **P1** chain via a proposed η^1 interaction (K(2)−C(1) = 3.186(4) Å). An η^2 interaction may be ruled out on considering the greater distances observed for K(2)−C(2) (3.582(5) Å) and K(2)−C(5) (3.827(6) Å). Interchain associations, similar to those observed in **2**, have also been reported for the compounds $(C_5H_5)K$, $(C_5H_5)K(OEt_2)$, $(C_5H_5)K(DME)_{0.5}$, and $(C_5H_4SiMe_3)K$.[7a−d] In **P1** the potassium atoms are slightly more exposed than in **P2**, but surprisingly, no interactions with the neighboring chains were observed. This may be due to crystal-packing forces, which oblige the potassium atoms to sit in hexagonal rings with respect to each other (Figure 6).

Scheme 3. Synthesis of 3−5



Scheme 4. Synthesis of 6−8



The alkyllithium reagents, RLi (R = ^{n}Bu, ^{t}Bu, Ph), react with **1** with nucleophilic addition at the exocyclic double bond to give the lithium−potassium *ansa*-biscyclopentadienyl compounds $K\{(C_5H_4)CH(R)(C_5Me_4)\}Li$ (R = ^{n}Bu (**3**), ^{t}Bu (**4**), Ph (**5**); Scheme 3).[9] Using the synthon **1**, we have devised a method for the facile synthesis of *ansa*-metallocene precursors with variable substitution at the bridging atom.

The reaction of **3**−**5** with $ZrCl_4$ gave the corresponding zirconocene(IV) complexes $[(R)HC(\eta^5\text{-}C_5Me_4)(\eta^5\text{-}C_5H_4)]ZrCl_2$ (R = ^{n}Bu (**6**), ^{t}Bu (**7**), Ph (**8**)) (Scheme 4), which were characterized by NMR spectroscopy.[10] In the ^{1}H NMR spectra of the chiral complexes **6**−**8**, eight signals were observed corresponding to the four protons of the unsubstituted cyclopentadienyl moiety and to the four methyl groups of the tetramethylcyclopentadienyl fragment. For **6**, the proton at the *ansa* bridge gave a triplet signal; in **7** and **8** this signal was observed as a singlet.

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(9) Preparation of **3**: ^{n}BuLi (1.6 M in hexane; 1.27 mL, 2.0 mmol) was added dropwise to a solution of **1** (0.48 g, 2.0 mmol) in Et_2O (50 mL) at −78 °C. The mixture was warmed to 25 °C and stirred for 15 h. Solvent was removed in vacuo, and the resulting solid was washed with hexane (2 × 50 mL) and dried under vacuum to yield, as an orange powder, the title complex (0.56 g, 95%). Anal. Calcd for $C_{19}H_{26}KLi$: C, 75.95; H, 8.72. Found: C, 75.68; H, 8.66. **4** and **5** were prepared in a similar manner. Anal. Calcd for $C_{19}H_{26}KLi$ (**4**): C, 75.95; H, 8.72. Found: C, 75.75; H, 8.71. Anal. Calcd for $C_{21}H_{22}KLi$ (**5**): C, 78.71; H, 6.92. Found: C, 78.36; H, 6.84.

The signals associated with the alkyl or aryl substituent of the *ansa* bridge were also present. The $^{13}C\{^1H\}$ NMR spectra were as expected, with the carbon *ansa* bridgehead atom giving a signal at ca. δ 45.

In addition, the molecular structure of **8** was determined by single-crystal X-ray diffraction studies (Figure 7).[11] This is the first reported X-ray structure of an *ansa*-bis(cyclopentadienyl) group 4 complex with an alkyl- or aryl/hydride-substituted *ansa* methylene bridge. The only similar example encountered in the literature is that of a cyclopentadienyl−indenyl *ansa* system.[12] The usual bent-metallocene conformation is observed in **8**, with the geometry around the zirconium atom being pseudo-tetrahedral. The *ansa* ligand chelates the zirconium atom, and both C_5 rings are bound to the metal in an η^5 mode. The centroids of the cyclopentadienyl rings form an angle with the zirconium atom of 116.99(4)°, typical for dichloride *ansa*-zirconocene complexes (compare, for example, with $[Me_2C(\eta^5\text{-}C_5H_4)_2]ZrCl_2$ with a Ct−Zr−Ct angle of 116.6(1)°).[13]

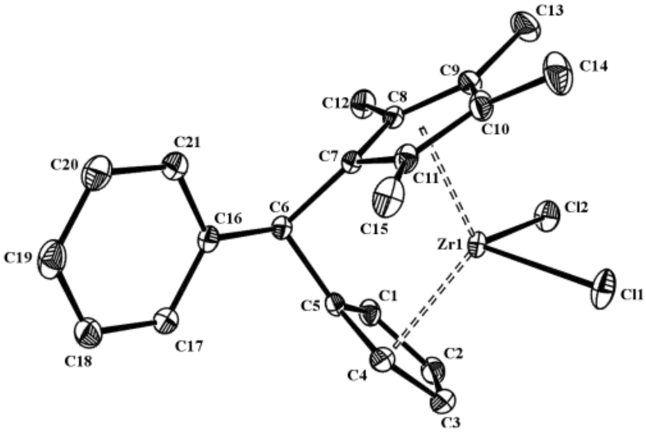

Figure 7. Molecular structure of **8** with thermal ellipsoids at the 30% probability level. Selected distances (Å) and angles (deg): Zr(1)−Cl(1) = 2.436(7), Zr(1)−Cl(2) = 2.432(7), Zr(1)−Ct(1) = 2.495(5), Zr(1)−Ct(2) = 2.502(6), average Zr(1)−C(Ct(1)) = 2.495, average Zr(1)−C(Ct(2)) = 2.502; Ct(1)−Zr(1)−Ct(2) = 117.1(1), Ct(1)−Zr(1)−Cl(1) = 110.4(1), Ct(1)−Zr(1)−Cl(2) = 109.3(3), Ct(2)−Zr(1)−Cl(1) = 110.1(3), Ct(2)−Zr(1)−Cl(2) = 109.1(3), Cl(1)−Zr(1)−Cl(2) = 99.40(2), C(5)−C(6)−C(7) = 100.9(2), Ct(1)−C(5)−C(6) = 163(2), Ct(2)−C(7)−C(6) = 165(1), C(5)−C(6)−C(16) = 117.3(2), C(7)−C(6)−C(16) = 115.9(2). Ct(1) corresponds to the centroid of C(1)−C(5); Ct(2) corresponds to the centroid of C(7)−C(11).

In conclusion, we report here the synthesis and molecular structure of a potassium cyclopentadienyl−fulvene compound, which acts as a synthon in the preparation of *ansa*-metallocene precursors with variable substitution at the bridging atom. This novel synthetic method should be of great utility in the design of tailored single-site catalysts.

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Supporting Information Available: Crystallographic data and data collection details, atom coordinates, anisotropic displacement parameters, and bond distances and angles for complexes **2** and **8** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org

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(10) (a) Preparation of **6**: $ZrCl_4(THF)_2$ (0.64 g, 1.7 mmol) in toluene (50 mL) was added to a solution of **3** (0.48 g, 1.7 mmol) in Et_2O (100 mL). The reaction mixture was stirred for 12 h. Solvent was removed under reduced pressure and hexane (100 mL) added to the resulting solid. The mixture was filtered and the filtrate concentrated (10 mL) and cooled to −30 °C to yield crystals of the title complex (0.41 g, 59%). ^1H NMR (400 MHz, C_6D_6): δ 1.52 (3H), 1.68 (3H), 1.87 (3H), 1.88 (3H) (s, C_5Me_4), 0.84 (3H), 1.26 (2H), 1.40−2.10 (4H) (m, $CH_2CH_2CH_2CH_3$), 3.81 (t, 1H, ^{n}BuC*H*), 5.06 (1H), 5.22 (1H), 6.40 (1H), 6.49 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.4, 11.7, 14.2, 14.3 (C_5Me_4), 12.5, 22.8, 29.9, 30.7 (^{n}*Bu*), 39.4 (^{n}Bu*C*H), 104.4, 104.5, 107.3, 119.7, 121.9 (C_5H_4), 114.9, 117.7, 120.4, 128.9, 129.9 (C_5Me_4). MS electron impact (*m*/*e* (relative intensity)): 416 (100) [M^+]. Anal. Calcd for $C_{19}H_{26}Cl_2Zr$: C, 54.79; H, 6.29. Found: C, 54.64; H, 6.23. (b) Preparation of **7** was carried out in a manner identical with that for **6**. ^1H NMR (400 MHz, C_6D_6): δ 1.54 (3H), 1.71 (3H), 1.88 (6H), (s, C_5Me_4), 1.04 (s, 9H, ^{t}*Bu*), 3.81 (s, 1H, ^{t}BuC*H*), 5.04 (1H), 5.18 (1H), 6.31 (1H), 6.52 (1H) (m, C_5H_4). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.7, 11.8, 12.6, 16.5 (C_5Me_4), 30.0, 31.8 (^{t}*Bu*), 51.7 (^{t}Bu*C*H), 105.6, 106.2, 110.6, 117.8, 124.1 (C_5H_4), 113.4, 116.4, 128.4, 130.8 (C_5Me_4). MS electron impact (*m*/*e* (relative intensity)): 416 (50) [M^+]. Anal. Calcd for $C_{19}H_{26}Cl_2Zr$: C, 54.79; H, 6.29. Found: C, 54.53; H, 6.26. (c) Preparation of **8** was carried in a manner identical with that for **6**. ^1H NMR (400 MHz, C_6D_6): δ 1.18, 1.51, 1.79, 1.89 (4s, each 3H, C_5Me_4), 5.15 (s, 1H, PhC*H*), 5.10, 5.19, 6.37, 6.47 (4m, each 1H, C_5H_4), 7.00−7.25 (m, 5H, *Ph*). $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6): δ 11.4, 11.5, 12.4, 14.8 (C_5Me_4), 43.0 (Ph*C*H), 105.4, 108.6, 119.2, 120.3, 123.0 (C_5H_4), 104.5, 109.8, 112.8, 118.2, 120.9 (C_5Me_4), 127.8, 129.4, 130.7, 140.0 (*Ph*). EI-MS (*m*/*z* (%)): 436 (38) [M^+]. Anal. Calcd for $C_{21}H_{22}Cl_2Zr$: C, 57.78; H, 5.08. Found: C, 57.55; H, 5.10.

(11) Crystal data for **8**: $C_{21}H_{22}Cl_2Zr$, $M_r = 436.51$, crystal size 0.30 × 0.19 × 0.12 mm^3, $Z = 4$, monoclinic, space group $P2_1/n$, $a = 9.7472(11)$ Å, $b = 16.924(2)$ Å, $c = 11.9315(14)$ Å, $\beta = 100.747(2)°$, $V = 1933.7(4)$ Å^3, $\rho = 1.499$ Mg/m^3, $T = 170(2)$ K, $\theta_{min} = 2.11°$, $\theta_{max} = 26.38°$, $\lambda = 0.710\,73$ Å. Data were collected on a Bruker SMART CCD-based diffractometer operating at 50 kV and 30 mA, using the $\omega/2\theta$ scan technique. The crystal used for the diffraction studies showed no decomposition during data collection. The integration process yielded a total of 11 166 reflections, of which 3949 were independent (R(int) = 0.0329) for **8**. Absorption corrections were applied using the SADABS program (maximum and minimum transmission coefficients 0.9055 and 0.7858). The structure was solved using the Bruker SHELXTL-PC software by direct methods and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined in the riding mode. Final R1 = 0.0299 (3143 reflections with $I > 2\sigma(I)$) and wR2 = 0.0722 (all data). Residual electron density $\rho_{max} = 0.352$ e Å^{-3} and $\rho_{min} = -0.333$ e Å^{-3}.

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