Organometallics **1999,** *18,* 3976−3980

Fulvene to Cyclopentadienyl Conversion with Homoleptic Complexes of Zirconium and Hafnium

Jonathan S. Rogers,† Rene J. Lachicotte,† and Guillermo C. Bazan*,‡

Departments of Chemistry, University of California, Santa Barbara, California 93106, and University of Rochester, Rochester, New York 14627-0216

Received May 26, 1999

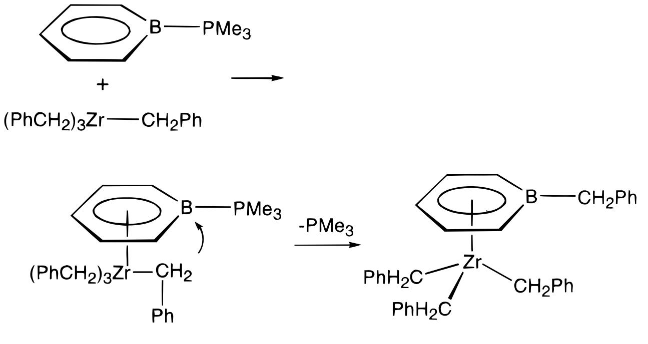
The reaction of 6,6-dimethylfulvene with $M(CH_2Ph)_4$ (M = Zr, Hf) in benzene gives $[\eta^5\text{-}C_5H_4(CMe_2CH_2Ph)]M(CH_2Ph)_3$ (**1,** M = Zr; **2**, M = Hf) without any observable byproducts. A similar reaction for M = Ti is not observed. The single-crystal X-ray study of **1** shows a three-legged piano-stool geometry with an η^2-bound benzyl ligand. A second equivalent of 6,6-dimethylfulvene does not react with either **1** or **2**. The bulkier 6,6-diphenyfulvene only reacts cleanly with the more Lewis acidic $Hf(CH_2Ph)_4$ to give $[\eta^5\text{-}C_5H_4(CPh_2CH_2Ph)]Hf(CH_2Ph)_3$ (**3**). Using the tetraamido complexes $M(NMe_2)_4$ and 6,6-dimethylfulvene, one obtains dimethylamine and $[\eta^5\text{-}C_5H_4(CMeCH_2)]M(NMe_2)_3$ (**4** for M = Zr) in good yield. These products are formally derived from the deprotonation of a fulvene methyl group and subsequent coordination of the resulting 2-propenylcyclopentadienyl fragment. Reaction of **4** and 6,6-dimethylfulvene affords the bent metallocene $[\eta^5\text{-}C_5H_4(CMeCH_2)]_2Zr(NMe_2)_2$ (**5**). Excess 8,8-dimethylbenzofulvene and $M(NMe_2)_4$ provides exclusively the product with only one coordinated indene.

Introduction

Group 4 complexes containing one or two cyclopentadienyl (Cp) ligands are versatile reagents which find use in catalytic and stoichiometric reactions. Compounds of this type are effective catalysts for the polymerization of olefins,[1] the asymmetric cyclopolymerization of dienes,[2] Diels−Alder cycloaddition reactions,[3] enantioselective carbomagnesations,[4] Pauson−Khand type cyclocarbonylations,[5] and the hydrogenation[6] and hydrosilation[7] of olefins, among others.[8] New preparative methods for Cp−group 4 metal complexes therefore make an impact in diverse areas of chemical synthesis.

The most widely used approach for coordination of Cp, as well as the many variations of this ligand, requires use of salts containing the ligand anion (i.e. LiCp, NaCp, $MgCp_2$, etc.). Disadvantages of these procedures include the need to prepare moisture- and air-sensitive ligand anions and the sometimes difficult removal of metal halide byproducts. Several reports are now available which circumvent these difficulties. A recent report by Jordan and co-workers describes the use of neutral reagents for the preparation of racemic bis(indenyl) and bis(cyclopentadienyl) group 4 complexes.[9] Another example is the reaction of trimethylsilyl-substituted cyclopentadienyls with transition-metal halides.[10]

In connection to our work with boratabenzene-supported catalysts,[11] we recently reported that the reaction of homoleptic group 4 tetraalkyls and tetraamides with borabenzene−Lewis base adducts provides a means to synthesize boratabenzene complexes.[12] For example, as shown by the reaction of tetrabenzylzirconium with 1 equiv of borabenzene−PMe_3 ($C_5H_5B-PMe_3$) gives $[\eta^6\text{-}C_5H_5B-CH_2Ph]Zr(CH_2Ph)_3$ in excellent yield. It is likely that the reaction proceeds via coordination of boraben-



---

† University of Rochester.

‡ University of California.

(1) (a) *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*; Kaminsky, W., Sinn, H., Eds.; Springer-Verlag: Berlin, 1988. (b) *Ziegler Catalysts*; Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds.; Springer-Verlag: Berlin, 1995. (c) Brintzinger, H.-H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.

(2) (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (b) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1993**, *115*, 91. (c) Habaue, S.; Sakamoto, H.; Okamoto, Y. *Polym. J.* **1997**, *29*, 384.

(3) (a) Hong, Y.; Kuntz, B. A.; Collins, S. *Organometallics* **1993**, *12*, 964. (b) Hong, Y.; Norris, D. J.; Collins, S. *J. Org. Chem.* **1993**, *58*, 3591. (c) Jaquith, J. B.; Guan, J.; Wang, S.; Collins, S. *Organometallics* **1995**, *14*, 1079 and references therein.

(4) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262.

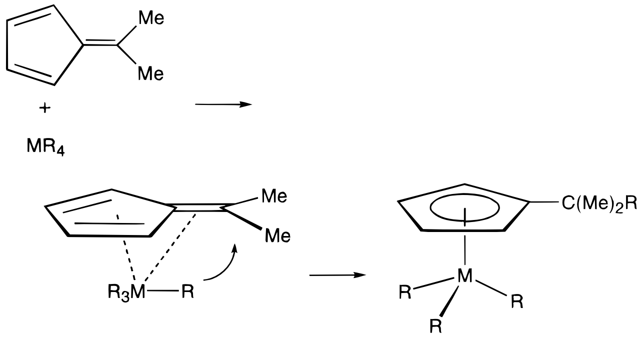
(5) (a) Negishi, E.; Holmes, S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2568. (b) Hicks, F. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 11688 and references therein.

(6) For examples see: (a) Couturier, S.; Goutheron, B. *J. Organomet. Chem.* **1978**, *157*, C61. (b) Waymouth, R.; Pino, P. *J. Am. Chem. Soc.* **1990**, *112*, 4911. (c) Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12569.

(7) (a) Takahashi, T.; Hasegawa, M.; Suzuki, N.; Saburi, M.; Rousset, C. J.; Fanwick, P. E.; Negishi, E. *J. Am. Chem. Soc.* **1991**, *113*, 8564. (b) Kesti, M. R.; Waymouth, R. M. *Organometallics* **1992**, *11*, 1095.

10.1021/om990402j CCC: $15.00

Scheme 1

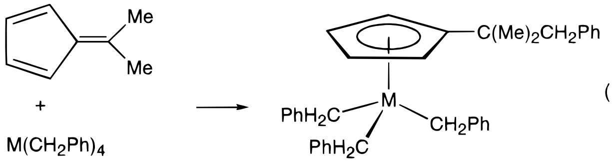


zene-PMe$_3$ to zirconium, followed by intramolecular nucleophilic attack by one of the metal-bound ligands onto the boron atom. In the case of zirconium tetraamides the resulting products contain aminoboratabenzene ligands.

A similar type of reaction can be envisioned by starting with group 4 homoleptic compounds and fulvene derivatives. Coordination of the *cis*-diene functionality to the metal should encourage transfer of the metal ligands to the exocyclic carbon and give the desired Cp ligand, as shown in Scheme 1. Such a sequence should be encouraged with increased electron deficiency at the metal center and by polarized metal−ligand bonds. In this contribution we study the scope of the reactivity in Scheme 1 and focus on the effect of metal, ligand, and substitution patterns on the periphery of the fulvene framework.

Results and Discussion

Tetrabenzylzirconium reacts with 6,6-dimethylfulvene at 65 °C in C_6D_6 to give the desired "insertion" product [η^5-$C_5H_4(CMe_2CH_2Ph)$]$Zr(CH_2Ph)_3$ (**1**), as shown in eq 1. The reaction is easily monitored by ^{1}H NMR spectroscopy and proceeds in excellent yield. As the reaction progresses, two sets of pseudotriplets in a 1:1 ratio grow at 5.28 and 5.53 ppm at the expense of the methylene signal of tetrabenzylzirconium (1.52 ppm). A signal, attributed to the metal-bound benzylic protons, is also observed at 1.64 ppm for the final product. Formation of **1** occurs within 22 h, and subsequent crystallization from pentane provides a bright yellow crystalline solid. Heating solutions of 6,6-dimethylfulvene and $Ti(CH_2Ph)_4$ only gave noncharacterizable decomposition products. Use of tetrabenzylhafnium proceeds to give [η^5-$C_5H_4(CMe_2CH_2Ph)$]$Hf(CH_2Ph)_3$ (**2**), as a pale yellow solid. Neither **1** nor **2** reacts with a second equivalent of 6,6-dimethylfulvene to provide the bis(cyclopentadienyl) product.



(1)

1, M = Zr
2, M = Hf

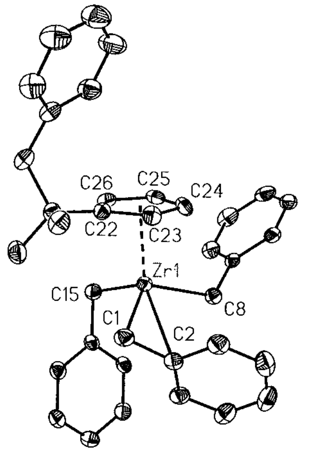
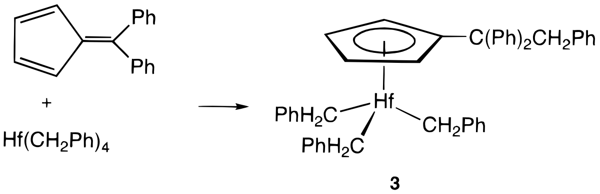


Figure 1. ORTEP view of **1**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. Selected bond distances (Å): Zr(1)−C(1), 2.302(5); Zr(1)−C(2), 2.659(5); Zr(1)−C(8), 2.289(5); Zr(1)−C(15), 2.258(5); Zr(1)−C(22), 2.507(5); Zr(1)−C(23), 2.447(5); Zr(1)−C(24), 2.449(5); Zr(1)−C(25), 2.511(5); Zr(1)−C(26), 2.575(5). Selected bond angles (deg): Zr(1)−C(1)−C(2), 87.0(3); Zr(1)−C(8)−C(9), 123.1(3); Zr(1)−C(15)−C(16), 101.5(3).

Single crystals of **1** suitable for X-ray diffraction studies were grown from pentane, and the results are shown in Figure 1. The overall molecular structure of **1** resembles a three-legged piano stool in which the five carbons of the cyclopentadienyl core form the base of the seat. The Cp ring is slightly slip distorted such that the bulky exocyclic substituent is pushed away from the metal, with Zr−C distances ranging from 2.447(5) Å (Zr−C(23)) to 2.511(5) Å (Zr−C(25)). The two benzyl ligands adjacent to the exocyclic 1,1-dimethyl-2-phenylethane fragment are rotated away from the five-membered ring, and one is η^2-bound. This ligand exhibits a $Zr-CH_2-C(2)$ angle of 87.0(3)° and a Zr−C(2) distance of 2.659(5) Å. In solution at 25 °C the three benzyl ligands are equivalent by ^{1}H NMR spectroscopy.

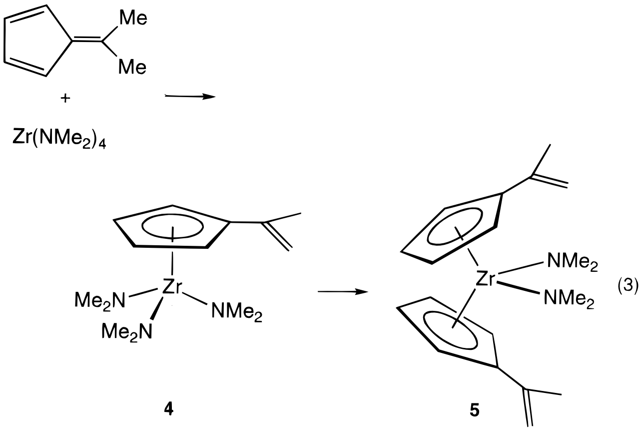
With the bulkier 6,6-diphenylfulvene a clean reaction is only observed with tetrabenzylhafnium. The product of the reaction, [η^5-$C_5H_4(CPh_2CH_2Ph)$]$Hf(CH_2Ph)_3$ (**3** in eq 2), can be purified by trituration in pentane to give a nearly colorless, microcrystalline solid. Attempts to repeat the process using $Zr(CH_2Ph)_4$ resulted in the formation of unidentified decomposition products. We suspect that, since $Zr(CH_2Ph)_4$ is a weaker Lewis acid, the requisite fulvene adduct is less favored.



(2)

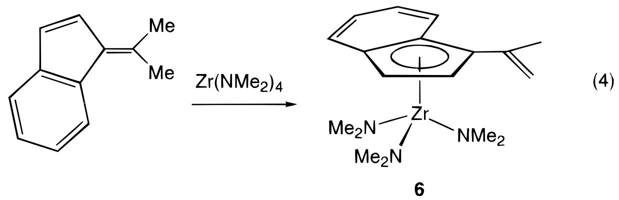
3

When the reaction of $Zr(NMe)_4$ with 6,6-dimethylfulvene at 80 °C is followed by ^{1}H NMR spectroscopy, one observes a rapid consumption of both starting materials, together with the appearance of resonances due to cyclopentadienyl proton resonances. However, in contrast to the reactions with the benzyl derivatives, a pair of *olefinic* resonances appear at 4.85 and 5.23 ppm. Integration shows that three dimethylamido ligands remain coordinated to zirconium. Free dimethylamine is also observed. These data are consistent with the



formation of [η^5-$C_5H_4(CMeCH_2)$]Zr(NMe_2)$_3$ (**4** in eq 3), which contains a cyclopentadienyl ligand with an exocyclic 2-propenyl group. Further reaction of **4** with an additional 1 equiv of 6,6-dimethylfulvene gives bis(2-propenylcyclopentadienyl)bis(dimethylamido)zirconium (**5** in eq 3). ^{1}H NMR spectroscopy shows that reactions starting with Hf(NMe_2)$_4$ give similar results. Compounds **4** and **5**, as well as their hafnium analogues, are isolated as highly air- and moisture-sensitive yellow oils. Related to compound **5** is the work by Erker and co-workers, who studied complexes of the type (alkenyl-Cp)$_2$MCl_2 (M = Zr, Hf) and their intramolecular [2 + 2] cycloaddition chemistry.[13]

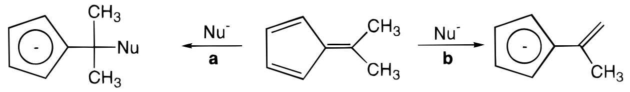
Only 1 equiv of 8,8-dimethylbenzofulvene reacts with Zr(NMe_2)$_4$ to give the (2-propenyl)indene complex **6** in eq 4 as an air-sensitive yellow oil. Compound **6** is stable to further reaction with 8,8-dimethylbenzofulvene, even when heated to 80 °C for 2 days. No reaction is observed with Zr(NMe_2)$_4$ and 6,6-diphenylfulvene, which lacks acidic hydrogens.



Summary and Conclusion

In summary, reactions 1−4 show that it is possible to obtain transition-metal complexes containing cyclopentadienyl-based ligands directly from fulvene and a suitable homoleptic complex. The M(CH_2Ph)$_4$ complexes give products that can be thought as originating from nucleophilic attack of a benzyl ligand onto the exocyclic carbon of the coordinated fulvene. Formally, this sequence amounts to an insertion step. We note that a direct insertion should be disfavored, since the reactive olefin is tetrasubstituted. For the tetraamides the resulting cyclopentadienyl ligands contain an exocycylic propenyl group. Such a process is easily understood by invoking deprotonation of the methyl group by an amido ligand followed by coordination of the resulting cyclopentadienyl core. It is an open question at this stage whether coordination is required prior to deprotonation.

The exact mechanistic details responsible for determining the reaction outcome are not understood at this stage. We point out that there is ample precedence for both the Brønsted acidity and the Lewis acidity of 6,6-dimethylfulvene. In fact, the two competing paths provide a sensitive probe for the electronic structure of reactive organic anions in the gas phase.[14] More relevant to the reactivity reported here is the fact that different products are observed by reaction of 6,6-dimethylfulvene with different lithium reagents:



Nucleophilic addition (path **a**) is observed with LiAlH_4,[15] MeLi,[15] PhLi,[15] C_9H_7Li,[16] and $C_{13}H_9Li$.[17] The closely related amide reagents NaNH_2[15] and LiN^{i}Pr$_2$[18] serve as deprotonating agents (path **b**). The dual function of Ph$_2$PCH_2Li (path **a** or **b**), depending on choice of solvent, has also been discussed.[19] Also relevant to this discussion is the recent report that Bu_2ZrCl_2 reacts with 6,6-dimethylfulvene to give bis(isopropylcyclopentadienyl)zirconium dichloride.[20] While the exact reaction sequence with Bu_2ZrCl_2 remains to be resolved, the overall process reduces to path **a**, where hydride plays the role of the nucleophile.

Experimental Section

General Remarks. All manipulations were performed an under inert atmosphere using standard glovebox and Schlenk techniques.[21] Tetrabenzylzirconium,[22] tetrabenzylhafnium,[23]

---

(8) (a) *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH Verlag: Weinheim, Germany, 1998. (b) *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Hegedus, L. S., Vol. Ed.; Elsevier: Oxford, U.K., 1995; Vol. 12.

(9) (a) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4030. (c) Christopher, J. N.; Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4038. (d) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045.

(10) For examples see: (a) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156. (b) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426. (c) Winter, C. H.; Zhou, X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210.

(11) (a) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Müller, C. *J. Am. Chem. Soc.* **1996**, *118*, 2291. (b) Bazan, G. C.; Rodriguez, G.; Ashe, A. J., III; Al-Ahmad, S.; Kampf, J. W. *Organometallics* **1997**, *16*, 2492. (c) Rogers, J. S.; Bazan, G. C.; Sperry, C. K. *J. Am. Chem. Soc.* **1997**, *119*, 9305. (d) Barnhart, R. W.; Bazan, G. C.; Mourey, T. *J. Am. Chem. Soc.* **1998,** *120***,** 1082. (e) Rogers, J. D.; Lachicotte, R. J., Bazan, G. C. *J. Am. Chem. Soc.* **1999**, *121*, 1288.

(12) Putzer, M. A.; Rogers, J. S.; Bazan. G. C. *J. Am. Chem. Soc.*, in press.

(13) (a) Erker, G.; Aul, R. *Chem. Ber.* **1991**, *124*, 1301 and references therein. (b) Erker, G.; Wilker, S.; Kruger, C.; Nolte, M. *Organometallics* **1993**, *12*, 2140.

(14) Brickhouse, M. D.; Squires, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 2706.

(15) Knox, G. R.; Pauson, P. L. *J. Chem. Soc.* **1961**, 4610.

(16) Mallin, D. T.; Rausch, M. D.; Lin, Y.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030.

(17) (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Razavi, A.; Ferrara, J. *J. Organomet. Chem.* **1992**, *435*, 299. (c) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117.

(18) Macomber, D. W.; Hart, W. P.; Rausch, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 884.

(19) Schore, N. E.; LaBelle, B. E. *J. Org. Chem.* **1981**, *46*, 2306.

(20) Eisch, J. J.; Owuor, F. A.; Shi, X. *Organometallics* **1999**, *18*, 1583.

(21) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987.

(22) Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357.

6,6-dimethylfulvene,[24] 6,6-diphenylfulvene,[24] 8,8-dimethylbenzofulvene,[25] and $Zr(NMe_2)_4$[9a] were prepared according to literature methods. Benzene, pentane, and diethyl ether were distilled from sodium benzophenone ketyl. NMR spectra were obtained using a Varian Unity 400 or 500 spectrometer. ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated using signals from the solvent and are reported downfield from $SiMe_4$. Elemental Analyses were performed by Desert Analytics, Inc., Tucson, AZ. Mass spectroscopic analyses were obtained using a VG-70E double-focusing magnetic sector instrument operated with an OPUS/SIOS data system with an electron ionization source.

$[\eta^5\text{-}C_5H_4(CMe_2CH_2Ph)]Zr(CH_2Ph)_3$ (1). 6,6-Dimethylfulvene (33 mg, 0.31 mmol) and tetrabenzylzirconium (125 mg, 0.275 mmol) were placed in a 100 mL round-bottom flask with 4 mL of benzene and a stir bar. The resulting mixture was heated to 65 °C for 22 h. The excess fulvene and benzene were removed in vacuo. The product was extracted with pentane, and the extracts were filtered. Cooling to −35 °C overnight gave bright yellow crystals of **1** (90 mg, 0.16 mmol, 58% isolated yield). ^1H NMR (C_6D_6, 400 MHz): δ 1.09 (s, 6H, $C_5H_4C(C\mathit{H}_3)_2$), 1.64 (s, 6H, $Zr(C\mathit{H}_2Ph)_3$), 2.61 (s, 2H, $C_5H_4CMe_2(C\mathit{H}_2Ph)$), 5.28 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 5.54 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 6.55 (d, 6H, $Zr(CH_2CC\mathit{H}CHCH)_3$, $^3J_{HH} = 7$ Hz), 6.77 (dd, 2H, $^4J_{HH} = 2$ Hz, $^3J_{HH} = 8$ Hz), 6.95 (t, 6H, $^3J_{HH} = 8$ Hz), 7.05−7.12 (m, 6H, Ph-H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 27.8 ($C_5H_4C(\mathit{C}H_3)_2(CH_2Ph)$), 37.3 ($C_5H_4\mathit{C}Me_2(CH_2Ph)$), 53.2 ($C_5H_4CMe_2(\mathit{C}H_2Ph)$), 67.0 ($Zr(\mathit{C}H_2Ph)_3$), 110.0, 111.9, 123.4, 126.4, 128.5, 129.8, 130.9, 138.6, 140.2, 144.1, 145.6. Anal. Calcd ($C_{36}H_{38}Zr$): C, 76.95; H, 6.82. Found: C, 77.02; H, 7.09.

$[\eta^5\text{-}C_5H_4(CMe_2CH_2Ph)]Hf(CH_2Ph)_3$ (2). 6,6-Dimethylfulvene (57 mg, 0.54 mmol) and tetrabenzylhafnium (242 mg, 0.446 mmol) were placed in a 100 mL round-bottom flask with 4 mL of benzene and a stir bar. The resulting mixture was heated to 65 °C for 20 h. Benzene and the excess fulvene were removed in vacuo. Pentane was added and removed in vacuo twice, giving a pale yellow microcrystalline powder. The product was extracted with 4 mL of diethyl ether, and the extracts were filtered and cooled to −35 °C overnight. Pale yellow plates were isolated and dried under vacuum (187 mg, 0.288 mmol, 64% isolated yield). ^1H NMR (C_6D_6, 400 MHz): δ 1.06 (s, 6H, $C_5H_4C(C\mathit{H}_3)_2$), 1.69 (s, 6H, $Hf(C\mathit{H}_2Ph)_3$), 2.54 (s, 2H, $C_5H_4CMe_2(C\mathit{H}_2Ph)$), 5.36 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 5.51 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 6.71 (dd, 6H, $Hf(CH_2CC\mathit{H}CHCH)_3$, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 8$ Hz), 6.72 (d, 2H, under 6.71 ppm peak), 6.92 (tt, 3H, Ph H, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 7$ Hz), 7.07−7.17 (m, 9H, Ph H). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 27.7 ($C_5H_4C(\mathit{C}H_3)_2CH_2Ph$), 53.0 ($C_5H_4CMe_2\mathit{C}H_2Ph$), 65.9 ($C_5H_4\mathit{C}Me_2CH_2Ph$), 79.4 ($Hf(\mathit{C}H_2Ph)_3$), 110.2, 112.9, 123.3, 124.6, 126.5, 129.2, 130.9, 137.3, 138.3, 141.8, 144.7. Anal. Calcd ($C_{36}H_{38}Hf$): C, 66.61; H, 5.90. Found: C, 65.90; H, 5.86.

$[\eta^5\text{-}C_5H_4(CPh_2CH_2Ph)]Hf(CH_2Ph)_3$ (3). 6,6-Diphenylfulvene (133 mg, 0.577 mmol) and tetrabenzylhafnium (313 mg, 0.577 mmol) were placed in a 100 mL round-bottom flask with 4 mL of benzene and a stir bar. The resulting mixture was heated to 65 °C for 29 h. Volatiles were removed in vacuo, yielding a pale yellow microcrystalline powder (371 mg, 0.479 mmol, 83% isolated yield). Purification by trituration in pentane for 5 h and filtration gave the product as a tan powder. ^1H NMR (C_6D_6, 400 MHz): δ 1.46 (s, 6H, $Hf(C\mathit{H}_2Ph)_3$), 3.81 (s, 2H, $C_5H_4CPh_2(C\mathit{H}_2Ph)$), 5.36 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 5.90 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 6.66 (dd, 6H, $Hf(CH_2CC\mathit{H}CHCH)_3$, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 7$ Hz), 6.74 (dd, 2H, Ph H, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 7$ Hz), 6.90−7.18 (m, 22H, Ph H). $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 45.3 ($C_5H_4CPh_2(\mathit{C}H_2Ph)$), 55.7 ($C_5H_4\mathit{C}Ph_2(CH_2Ph)$), 80.3 ($Hf(\mathit{C}H_2Ph)_3$), 111.5, 113.7, 123.2, 126.6, 127.0, 128.0 (under solvent peak, corresponds to a methine resonance in APT spectra), 128.1, 128.3, 129.0, 130.4, 131.8, 138.0, 141.5, 144.9,146.4. Anal. Calcd. ($C_{46}H_{42}Hf$): C, 71.45; H, 5.47. Found: C, 69.99; H, 5.30.

Table 1. Summary of Crystallographic Data for 1

Crystal Parameters	
chem formula	$C_{41}H_{48}Zr$
fw	632.01
cryst syst	monoclinic
space group	$P2_1/c$
Z	4
a, Å[a]	10.9433(2)
b, Å	10.7916(2)
c, Å	26.9377(3)
β, deg	97.9830(10)
V, Å^3	3150.40(9)
ρ_{calcd}, mg/mm^3	1.333
cryst dimens, mm^3	0.12 × 0.14 × 0.16
temp, °C	−80
Measurement of Intensity Data and Refinement Parameters	
radiation (λ, Å)	Mo Kα (0.710 73)
2θ range, deg	3−46.6
total no. of data	12 511
no. of unique data	4414
R_{int}, R_{sigma} (%)[b]	4.17, 5.15
no. of obsd data ($I > 2\sigma(I)$)	3602
no. of params varied	350
μ, mm^{-1}	0.377
abs cor	empirical (SADABS)[c]
range of transmissn factors	0.928−0.802
GOF[d]	1.150
R1(F_o), wR2(F_0^2)[b] (%)[e]	5.46, 12.70
R1(F_o), wR2(F_0^2)[b] all (%)	7.38, 13.49

[a] See ref 27. [b] See ref 26. [c] See ref 28. [d] See ref 30. [e] See ref 31.

$[\eta^5\text{-}C_5H_4(CMeCH_2)]Zr(NMe_2)_3$ (4). 6,6-Dimethylfulvene (90 mg, 0.85 mmol) and $Zr(NMe_2)_4$ (228 mg, 0.854 mmol) were placed in a 100 mL round-bottom flask with a stir bar and 4 mL of benzene. The resulting mixture was heated to 80 °C for 2 h in the absence of light and cooled and the volatiles were removed in vacuo. The resulting yellow oil was extracted with pentane, and the extracts were filtered and placed under vacuum, giving a highly air sensitive, bright yellow oil (244 mg, 0.743 mmol, 87% isolated yield). ^1H NMR (C_6D_6, 400 MHz): δ 1.92 (m, 3H, $C_5H_4C(C\mathit{H}_3){=}CH_2$, $^4J_{HH} = 1$ Hz), 2.91 (s, 18H, $Zr(N(C\mathit{H}_3)_2)_3$), 4.85 (m, 1H, $C_5H_4C(Me){=}CH_{endo}\mathit{H}_{exo}$, $^2J_{HH} = 1$ Hz), 5.23 (m, 1H, $C_5H_4C(Me){=}C\mathit{H}_{endo}H_{exo}$, $^2J_{HH} = 1$ Hz), 6.02 (t, 2H, Cp, $^3J_{HH} = 3$ Hz), 6.16 (t, 2H, Cp, $^3J_{HH} = 3$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 21.6 ($C_5H_4C(\mathit{C}H_3){=}CH_2$), 44.8 ($Zr(N(\mathit{C}H_3)_2)_3$), 94.4 (${=}\mathit{C}H_2$), 107.4 (Cp), 109.9 ($C_5H_4\mathit{C}(CH_3){=}CH_2$), 110.7 (Cp), 137.9 (Cp). MS: calcd ($C_{14}H_{27}N_3Zr$), 327.1243; found, 327.1252.

$[\eta^5\text{-}C_5H_4(CMeCH_2)]_2Zr(NMe_2)_2$ (5). 6,6-Dimethylfulvene (187 mg, 1.76 mmol) and $Zr(NMe_2)_4$ (236 mg, 0.883 mmol) were placed in a 100 mL round-bottom flask with a stir bar and 4 mL of benzene. The resulting mixture was heated to 90 °C for 21 h in the absence of light, cooled, and removed of volatiles in vacuo. The resulting orange-yellow oil was extracted with pentane, and the extracts were filtered and placed under vacuum, giving the product as a highly air sensitive orange-yellow oil (282 mg, 0.724 mmol, 82% isolated yield). ^1H NMR (C_6D_6, 400 MHz): δ 1.86 (m, 6H,, $^4J_{HH} = 1$ Hz), 2.83 (s, 12H, $Zr(N(C\mathit{H}_3)_2)_2$), 4.85 (m, 2H, $C_5H_4C(Me){=}CH_{endo}\mathit{H}_{exo}$, $^2J_{HH} = 2$ Hz), 5.14 (m, 2H, $C_5H_4C(Me){=}C\mathit{H}_{endo}H_{exo}$, $^2J_{HH} = 2$ Hz), 5.91 (t, 4H, Cp, $^3J_{HH} = 3$ Hz), 6.17 (t, 4H, Cp, $^3J_{HH} = 3$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz): δ 21.5 ($C_5H_4C(\mathit{C}H_3){=}CH_2$), 49.3 ($Zr(N(\mathit{C}H_3)_2)_2$), 109.6 (${=}\mathit{C}H_2$), 109.9 ($C_5H_4\mathit{C}(CH_3){=}CH_2$), 110.9 (Cp), 123.7 (Cp), 138.4 (Cp). MS: calcd ($C_{20}H_{30}N_2Zr$), 388.1451; found, 388.1456.

$[\eta^5\text{-}C_9H_6(CMeCH_2)]Zr(NMe_2)_3$ (6). 8,8-Dimethylbenzofulvene (162 mg, 1.04 mmol) and $Zr(NMe_2)_4$ (277 mg, 1.03 mmol) were placed in a 100 mL round-bottom flask with a stir bar and 4 mL of benzene. The flask was heated to 85 °C for 22 h

---

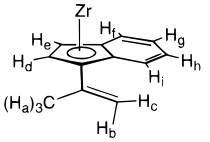
(23) Felten, J. J.; Anderson, W. P. *J. Organomet. Chem.* **1972**, *36*, 87.

(24) Yates, P.; Kronis, J. D. *Can. J. Chem.* **1984**, *62*, 1751.

(25) 8,8-Dimethylbenzofulvene was prepared in the exact manner as 6,6-diphenylfulvene.[15]

in the absence of light and cooled and the volatiles were removed in vacuo. The resulting orange-yellow oil was extracted with pentane, and the extracts were filtered and placed under vacuum, yielding a highly air sensitive, orange-yellow oil (348 mg, 0.920 mmol, 89% isolated yield). ^{1}H NMR (C_6D_6, 400 MHz): δ 2.11 (m, 3H, H_a, $^4J_{HH} = 1$ Hz), 2.76 (s, 18H, Zr-(N(CH_3)$_2$)$_3$), 5.20 (m, 1H, H_b, $^2J_{HH} = 2$ Hz), 5.47 (m, 1H, H_c, $^2J_{HH} = 2$ Hz), 6.18 (d, 1H, H_d, $^3J_{HH} = 3$ Hz), 6.50 (d, 1H, H_e, $^3J_{HH} = 3$ Hz), 6.92 (td, 1H, H_g, $^4J_{HH} = 2$ Hz, $^3J_{HH} = 8$ Hz), 6.96 (td, 1H, H_h, $^4J_{HH} = 2$ Hz, $^3J_{HH} = 8$ Hz), 7.52 (dd, 1H, H_f, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 8$ Hz), 7.94 (dd, 1H, H_i, $^4J_{HH} = 1$ Hz, $^3J_{HH} = 8$ Hz).

Assignments were made according to



^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ 23.9 (IndC(CH$_3$)=CH$_2$), 44.0 (Zr(N(CH$_3$)$_2$)$_3$), 97.1 (=CH$_2$), 111.4, 114.7, 115.7, 122.6, 123.2, 123.3, 125.0, 126.4, 127.4, 139.5. MS: calcd ($C_{18}H_{29}N_3$-Zr), 377.1418; found, 377.1409.

Structure Determination for 1. Crystal data are summarized in Table 1. A yellow crystal of approximate dimensions 0.12 × 0.14 × 0.16 mm^3 was mounted under Paratone-8277 onto a glass fiber and immediately placed in a cold nitrogen stream at −80 °C on the X-ray diffractometer. The X-ray intensity data were collected on a standard Siemens SMART CCD area detector system equipped with a normal focus molybdenum-target X-ray tube operated at 2.0 kW (50 kV, 40 mA). A total of 1321 frames of data (1.3 hemispheres) were collected using a narrow frame method with scan widths of 0.3° in ω and exposure times of 30 s/frame using a detector-to-crystal distance of 5.09 cm (maximum 2θ angle of 56.5°). The total data collection time was approximately 12 h. Frames were integrated to a maximum 2θ angle of 46.6° with the Siemens SAINT program to yield a total of 12 511 reflections, of which 4414 were independent ($R_{int} = 4.17\%$, $R_{sigma} = 5.15\%$)[26] and 3602 were above $2\sigma(I)$. Laue symmetry revealed a monoclinic crystal system, and the final unit cell parameters (at −80 °C) were determined from the least-squares refinement of three-dimensional centroids of 6181 reflections.[27] Data were corrected for absorption with the SADABS[28] program.

The space group was assigned as $P2_1/c$, and the structure was solved by using direct methods and refined employing full-matrix least squares on F^2 (Siemens, SHELXTL,[29] version 5.04). For a Z value of 4, there is one molecule, and a disordered partially occupied pentane was located in the asymmetric unit. All of the non-H atoms, except those of pentane, were refined with anisotropic thermal parameters, and hydrogen atoms were included in idealized positions giving a data to parameter ration of greater than 10:1. H atoms were not included for the pentane. The structure was refined to a goodness of fit (GOF)[30] of 0.952 and final residuals[31] of $R1 = 5.46\%$ ($I > 2\sigma(I)$) and $wR2 = 12.7\%$ ($I > 2\sigma(I)$).

Acknowledgment. G.C.B. is an Alfred Sloan Fellow and a Henry and Camille Dreyfus Teacher-Scholar. We are grateful to the donors of the Petroleum Research Fund (administered by the American Chemical Society) and the Department of Energy (Contract No. DE-FG03-98ER14910) for financial assistance and to Dr. James Pavlovich for assistance with mass spectrometry measurements.

Supporting Information Available: Tables and a figure giving complete details for the crystallographic structure analysis of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990402J

---

(26) $R_{int} = |F_o^2 - F_o^2(\text{mean})/[F_o^2]$; $R_{sigma} = [\sigma(F_o^2)]/[F_o^2]$.

(27) It has been noted that the integration program SAINT produces cell constant errors that are unreasonably small, since systematic error is not included. More reasonable errors might be estimated at 10× the listed value.

(28) The SADABS program is based on the method of Blessing; see: Blessing, R. H. *Acta Crystallogr., Sect A* **1995**, *51*, 33.

(29) SHELXTL: Structure Analysis Program, version 5.04; Siemens Industrial Automation Inc., Madison, WI, 1995.

(30) $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{1/2}$, where n and p denote the number of data and parameters.

(31) $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [(\text{Max};0, F_o^2) + 2F_c^2]/3$.