Calcium-Mediated Fulvene Couplings. 1. A Survey of 6,6-Dialkylfulvenes for the Formation of Bridged and Unbridged Calcocenes

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The degree to which 6,6-dimethylfulvene, 6,6-diethylfulvene, and 6-cyclopentylidenefulvene form unbridged calcocenes in reductive coupling reactions with activated calcium were compared. The identification of alkenyl substituents along with alkyl substituents among the unbridged calcocenes confirms that hydrogen atom or proton transfer between dialkylfulvenes and their radical anions or dianions is responsible for the formation of unbridged calcocenes. The tendency to form unbridged calcocenes instead of *ansa*-calcocenes is higher for 6,6-diethylfulvene and 6-cyclopentylidenefulvene than for 6,6-dimethylfulvene. 1,1′-Dicyclopentenylcalcocene, **1**, which is formed in the reaction between cyclopentylidenefulvene and calcium, was purified and crystallographically characterized. Photolysis of **1** leads to [2+2] cyclization of the cyclopentenyl substituents to form **2**, an *ansa*-calcocene with a tricyclo-[3.3.0.0]decane-1,10-diyl bridge.

Introduction

Early transition metal *ansa*-metallocene complexes have played an important role in homogeneous catalysis,[1] particularly in Ziegler−Natta type olefin polymerization.[2] Preparation of bridged dicyclopentadienyl ligands for metallocene complexes often demands multistep routes which result in low overall yields. Therefore, improved synthetic methods for preparing these ligands are desirable.

The reductive coupling of fulvenes by alkali metals,[3] alkaline earth metals,[4] low-valent transition metal species,[5] and lanthanide metals[6] provides an elegant and direct method for synthesizing *ansa*-metallocene complexes. *ansa*-Calcocenes such as $[Me_4C_2(C_5H_4)_2]Ca(THF)_2$, originally reported by Edelmann and co-workers,[4a] are of particular interest to us because they can be used as starting materials for the synthesis of *ansa*-chromocene complexes[4b,7] as well other transition metal *ansa*-metallocenes.[4c,d]

One drawback to the reaction of 6,6-dimethylfulvene with activated calcium which was not disclosed in the original report on the synthesis of $[Me_4C_2(C_5H_4)_2]Ca(THF)_2$ is the occurrence of unbridged calcocene side products besides the desired *ansa*-calcocene. The side products appear to arise from a disproportionation reaction between the neutral fulvene and either the fulvene radical anion or the fulvene dianion.

Formation of unbridged calcocenes may be circumvented by employing 6-arylfulvenes[4c,d,e] or 6-*tert*-butylfulvene,[8] which bear no reactive hydrogens β to carbon 6 of the fulvene. In these cases, a mixture of *rac* and *meso* isomers is formed. The stereoisomers are generally separable by crystallization.

Described herein are our results from the reductive coupling of 6,6-dimethylfulvene, 6,6-diethylfulvene, and 6-cyclopentylidenefulvene with $HgCl_2$-activated calcium. The latter two fulvenes were examined to determine if the amount of unbridged calcocene side products could be influenced by reducing the number of abstractable hydrogens β to carbon 6. The X-ray crystal structure of 1,1′-dicyclopentenylcalcocene, **1**, is also described along with our efforts to photocyclize the cyclopentenyl substituents intramolecularly to form **2**, an *ansa*-calcocene complex with a tricyclic bridge.

(1) (a) Hoveyda, A. H.; Morken, J. P. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1262−1284. (b) Halterman, R. L. *Chem. Rev.* **1992**, *92*, 965−994.

(2) (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) *Metalorganic Catalysts for Synthesis and Polymerization*; Kaminsky, W., Ed.; Springer: Berlin, 1999. (c) *Ziegler Catalysts: recent scientific innovations and technological improvements*; Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Berlin, 1995.

(3) (a) Sullivan, M. F.; Little, W. F. *J. Organomet. Chem.* **1967**, *8*, 277−285. (b) Rinehart, K. L.; Frerichs, A. K.; Kittle, P. A.; Westman, L. F.; Gustafson, D. H.; Pruett, R. L.; McMalson, J. E *J. Am. Chem. Soc.* **1960**, *82*, 1111−1112. (c) Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1971**, *27*, 4343−4351.

(4) (a) Rieckhoff, M.; Pieper, U.; Stalke, D.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1079−1081. (b) Foo, D. M. J.; Shapiro, P. *Organometallics* **1995**, *14*, 4957−4959. (c) Kane, K. M.; Shapiro, P. J.; Vij, A.; Cubbon, R.; Rheingold, A. L. *Organometallics* **1997**, *16*, 4567−4571. (d) Shapiro, P. J.; Kane, K. M.; Vij, A.; Stelck, D.; Matare, G. J.; Hubbard, R. L.; Caron, B. *Organometallics* **1999**, *18*, 3468−3473. (e) Matare, G. J.; Kane, K. M.; Shapiro, P. J.; Vij, A. *J. Chem. Cryst.* **1998**, *28*, 731−734.

(5) (a) Tan, T. S.; Fletcher, J. L.; McGlinchey, M. J. *J. Chem. Soc., Chem Commun.* **1975**, 771−772. (b) Eisch, J. J.; Shi, X.; Owuor, F. A. *Organometallics* **1998**, *17*, 5219−5221.

(6) (a) Recknagel, A.; Edelmann, F. T. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 693−694. (b) Edelmann, F. T.; Rieckhoff, M.; Haiduc, I.; Silaghi-Dumitrescu, I. *J. Organomet. Chem.* **1993**, *447*, 203−208. (c) Fedushkin, I. L.; Dechert, S.; Schumann, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 561−563.

(7) Matare, G. J.; Foo, D. M. J.; Kane, K. M.; Zehnder, R.; Wagener, M.; Shapiro, P. J. *Organometallics* **2000**, *19*, 1534−1539.

(8) Höhn, B.; Sinnema, P. J.; Shapiro, P. J.; Twamley, B. Manuscript in preparation.

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Table 1. Data from Reactions between Ca* and Fulvenes

entry	fulvene	activated Ca	solvent	% *ansa* product	ratio of alkyl to alkenyl substituents in unbridged metallocene product
1	Me_2C=	$Ca/HgCl_2$	THF	59	1.3:1
2	Me_2C=	$Ca/HgCl_2$	DME	54	1.1:1
3	Me_2C=	Ca powder	THF	20	1.5:1
4	Et_2C=	$Ca/HgCl_2$	THF	13	1:1
5	Et_2C=	$Ca/HgCl_2$	DME	27	1:1
6	$(CH_2)_4C$=	$Ca/HgCl_2$	THF	20	1:1

Results and Discussion

Reductive Coupling of 6,6-Dimethylfulvene by Calcium. The reaction of dimethylfulvene with $HgCl_2$-activated calcium granules affords the bridged calcocene $[Me_4C_2(C_5H_4)_2]Ca(THF)_2$ along with unbridged calcocene products containing isopropyl and isopropenyl substituents, as revealed by the ^{1}H NMR spectrum of the product. A doublet at 4.48 ppm ($^2J_{HH}$ = 3.6 Hz, 1H), a doublet at 3.84 ppm ($^2J_{HH}$ = 3.6 Hz, 1H), and a singlet at 1.88 ppm (3H) are assignable to the isopropenyl substituent, and resonances at 2.76 ppm (hept, $^3J_{HH}$ = 6.74 Hz, 1H) and 1.11 ppm (d, $^3J_{HH}$ = 6.74 Hz, 6H) are assignable to the isopropyl substituent. Cyclopentadienyl hydrogens of the unbridged calcocenes show resonances at 5.66, 5.35, 5.31, and 5.28 ppm. The distribution of propyl-substituted, propenyl-substituted, and tetramethylethanediyl-bridged calcocene products was fairly uniform over four preparations under similar reaction conditions. As determined from the ^{1}H NMR spectra of the crude reaction product, the bridged compound comprised 58−65% of the calcocenes, the unbridged compounds comprised 35−42% of the mixture, and the amount of alkyl and alkenyl substituents in the unbridged species was roughly equivalent (a slight excess of the alkyl substituent was generally observed). The ratio of THF molecules per calcium varied between 0.4 and 2 since heating the product mixture under vacuum in order to dry it liberates the coordinated THF. A similar distribution of bridged and unbridged products was found for the reaction performed in DME. As reported previously,[4c] using a more active, more finely divided form of calcium[9] in the coupling of 6,6-dimethylfulvene leads to a preponderance of the unbridged calcocene products. The bridged complex comprised only 20% of the calcocene mixture. Representative data are provided in Table 1.

Our observation of both isopropyl- and isopropenyl-substituted cyclopentadienyl calcium product supports the mechanism proposed by Schwemlein and Brintzinger,[10] in which the overreduced 6,6-dimethylfulvene dianion abstracts a proton from the neutral fulvene (Figure 1). We cannot rule out an alternate mechanism involving a hydrogen atom abstraction from the neutral fulvene by the singly reduced fulvene radical-anion.

Reductive Coupling of 6,6-Diethylfulvene and 6-Cyclopentylidenefulvene by Calcium. The occurrence of hydrogen atom transfer in the calcium-mediated reductive coupling of 6,6-dimethylfulvene prompted us to investigate other 6,6-dialkyl-substituted fulvenes bearing fewer hydrogens β to carbon 6, namely, 6,6-diethylfulvene and 6-cyclopentylidenefulvene. We expected to reduce the occurrence of unbridged calcocene side products by reducing the number of abstractable hydrogen atoms on the fulvene substrate. Instead, the ratio of unbridged to bridged calcocene products increased for these substrates relative to that of 6,6-dimethylfulvene (Table 1). The greater prevalence of unbridged calcocene products in the latter two examples can probably be attributed to the interference of the bulkier secondary alkyl substituents with bridge formation, making hydrogen atom abstraction more kinetically competitive. The reaction of 6,6-diethylfulvene with activated calcium in THF gave an intractable mixture of products, only 13% of which was $[Et_4C_2(C_5H_4)_2]Ca(THF)_2$. Performing the reaction in DME resulted in a higher, yet still very low, percentage (27%) of the bridged compound. In the reaction of 6-cyclopentylidenefulvene with activated calcium, only 20% of the bridged metallocene was observed in the ^{1}H NMR spectrum of the crude product, the balance being unbridged calcocenes with a 1:1 ratio of cyclopentyl and cyclopentenyl substitutents. The complex 1,1′-biscyclopentenylcalcocene, $[(C_5H_7)(C_5H_4)]_2Ca(THF)_2$ (**1**), could be separated from the product mixture by recrystallization from THF and was isolated in 42% yield. This material still contained some saturated, cyclopentyl-

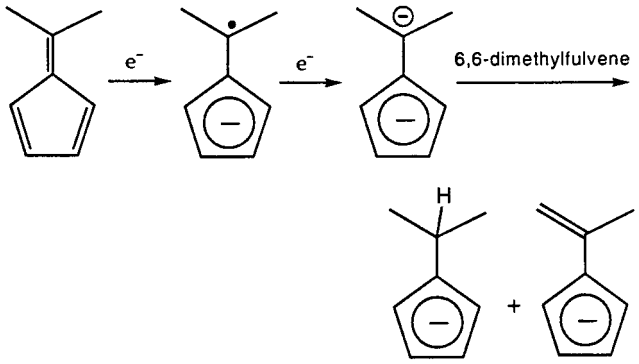


Figure 1.

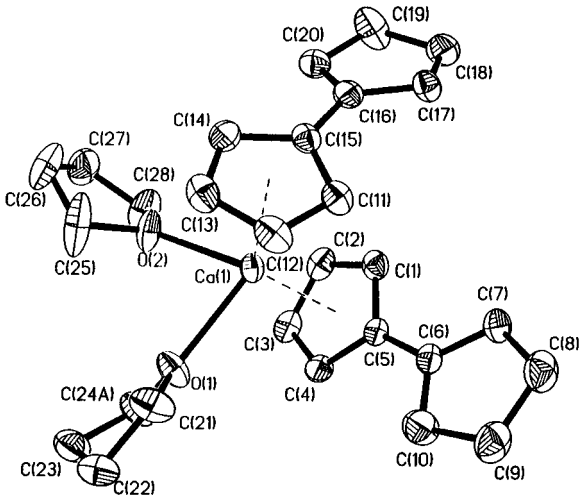


Figure 2. Molecular structure of $\{C_5H_7(\eta^5\text{-}C_5H_5)\}_2Ca(THF)_2$, **2**. Thermal ellipsoids are shown at 50% probability.

(9) (a) Wu, T.; Xiong, H.; Rieke, R. D. *J. Org. Chem.* **1990**, *55*, 5045−5051. (b) McCormick, M. J.; Moon, K. B.; Jones, S. R.; Hanusa, T. P. *J. Chem. Soc., Chem Commun.* **1990**, 776−779.

(10) Schwemlein, H.; Brintzinger, H. H. *J. Organomet. Chem.* **1983**, *254*, 69−73.

Table 2. Crystallographic Data for 2

formula	$C_{29}H_{38}CaO_2$
mol wt	446.66
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	38.3350(2)
b (Å)	8.26430(10)
c (Å)	16.1604(3)
α (deg)	90
β (deg)	98.4790(10)
γ (deg)	90
V (Å^3)	5063.85(12)
Z	8
T (K)	203(2)
λ (Å)	0.70173 (Mo Kα)
ρ_{calcd} (g/cm^3)	1.172
μ (mm^{-1})	0.269
F_{000}	1936
cryst size	0.40 × 0.40 × 0.13
θ range (deg)	1.07−25.00
hkl limits	−45/45;−9/9;−14/19
no. reflns collected	29 162
no. indep. reflns	4396 (R_{int} = 0.0456)
data/restraints/params	4396/0/292
GOF	1.067
$R(F_o)$	0.0703 ($F>2\sigma(F)$)
$R_w(F_o^2)$	0.1495
largest diff peak/hole (e Å^{-3})	0.323/−0.273

Table 3. Selected Bond Distances (Å) and Angles (deg) for 2

Ca−cent (both)	2.435	C(6)−C(10)	1.423(6)
Ca−O(1)	2.383(3)	C(16)−C(17)	1.417(5)
Ca−O(2)	2.377(2)	C(16)−C(20)	1.431(5)
Ca−C(1)	2.707(4)	C(7)−C(8)	1.500(6)
Ca−C(2)	2.711(4)	C(8)−C(9)	1.488(7)
Ca−C(3)	2.718(4)	C(9)−C910)	1.513(6)
Ca−C(4)	2.718(4)	C(17)−C(18)	1.508(6)
Ca−C(5)	2.711(3)	C(18)−C(19)	1.505(6)
Ca−C(11)	2.718(3)	C(19)−C(20)	1.510(6)
Ca−C(12)	2.720(4)		
Ca−C(13)	2.719(4)	cent−Ca−cent	131.5
Ca−C(14)	2.705(4)	O(1)−Ca−O(2)	82.44(10)
Ca−C(15)	2.710(3)	C(4)−C(5)−C(6)−C(10)	−11.7(6)
C(6)−C(7)	1.400(5)	C(11)−C(15)−C(16)−C(17)	−15.9(6)

substituted calcocene species (10−20%), but the purity could be improved by repeated crystallizations. The molecular structure of the compound was determined by single-crystal X-ray diffraction.

Molecular Structure of 1,1′-Bis(1-cyclopentenyl)-calcocene·(THF)$_2$ (1). An ORTEP drawing of **1** is shown in Figure 1. Crystallographic data and selected bond lengths and angles are listed in Table 2 and Table 3, respectively. The structure of **1** is very similar to that of related THF-solvated 1,1′-bis[(alkenyl)cyclopentadienyl]calcium complexes reported by Westerhausen and co-workers.[11a,b] The average Ca−ring centroid distance (2.435 Å) is comparable to that of other monomeric calcocene complexes with unsubstituted cyclopentadienyl and indenyl rings,[11a−d] for which Ca−centroid distances of 2.40−2.45 Å have been found. With bulkier alkyl- and silyl-substituted calcocenes the Ca−centroid distances can be substantially larger.[11e−i] The cent−Ca−cent angle of 131.5° is at the lower end of the 130.7−135.1° range observed for other unbridged calcocene species.[11a−i] It is comparable to the corresponding angle found in the B−B bridged bis(fluorenyl)calcium complex reported by Nöth and co-workers,[11j] but it is considerably wider than the 119−120° angles found for ethanediyl-bridged calcocenes.[4a,c−e] For **1** the O−Ca−O bond angle is 82.44(10)°. In other bis THF-solvated calcocene complexes this angle ranges from 82.7° to 96.9° depending on the amount of space available in the equatorial wedge of the metallocene. Anywhere from one[11c,e,f,g] to three[11k] molecules of THF can be accommodated in the equatorial wedge of the calcocene depending on the steric demands of the ligand framework. The Ca−O bond distances of 2.383(3) and 2.377(2) Å in **1** are normal for the less sterically hindered ring systems. The electron difference map for **1** revealed two hydrogens each on C(20) and C(10) and only one hydrogen each on C(7) and C(17). This should place the alkene moieties at C(16)−C(17) and C(6)−C(7), with bond distances of 1.417(5) and 1.400(5) Å, respectively. However, the bond distances for C(16)−C(20) and C(6)−C(10), at 1.417(5) and 1.423(6) Å, are of comparable length to the supposed double bonds and significantly shorter than the other C−C bonds in the cyclopentenyl rings, which range from 1.488(7) to 1.513(6) Å. Furthermore, the supposed double bonds are longer than the 1.34 Å bond lengths found in other alkenyl-substituted calcocene compounds.[11a] One explanation for this anomaly is disorder in the orientation of the C=C and C−C bonds of the cyclopentenyl substituents, the effects of which were not detected in the hydrogen atom electron densities. Another possibility is the presence of saturated, cyclopentyl-substituted calcocene impurities in the crystal lattice which make C(16)−C(17) and C(6)−C(7) artificially long (as opposed to making C(16)−C(20) and C(6)−C(10) artificially short).[12] The cyclopentenyl substituents are at the rear of the metallocene, away from the THF molecules in the wedge. A staggering of the cyclopentadienyl rings creates an angle of 107.4° between the cyclopentenyl substituents. This angle was determined by comparing two vectors projecting from each of the cyclopentadienyl ring centroids through the bonds C(15)−C(16) and C(5)−C(6). Both cyclopentenyl rings are nearly coplanar with their respective cyclopentadienyl rings, as can be seen from the small magnitudes of the torsion angles for C(4)−C(5)−C(6)−C(10) and C(11)−C(15)−C(16)−C(17) of −11.7(6)° and −15.9°, respectively.

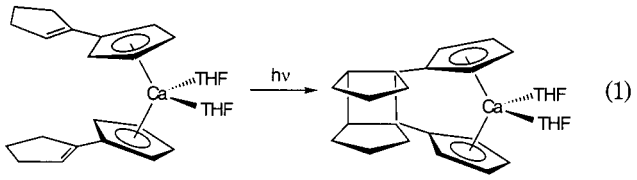
Photochemical Intramolecular Coupling of 1,1′-Bis(1-cyclopentenyl)calcocene·2THF. The generation of *ansa*-zirconocenes by the photochemical [2+2] cycloaddition of bis(alkenylcyclopentadienyl)zirconium complexes has been demonstrated by Erker and co-workers.[13] If applicable to calcocene reagents, this approach would be a useful alternative to fulvene coupling for synthesizing *ansa*-calcocene complexes since a general synthesis of alkenyl-substituted calcocenes has been demonstrated by Westerhausen et al.[11a,b] We therefore explored complex **1** as a model for

(11) (a) Westerhausen, M.; Hartmann, M.; Schwarz, W. *J. Organomet. Chem.* **1995**, *501*, 359−367. (b) Westerhausen, M.; Hartmann, M.; Heckmann, G.; Schwarz J. Organomet. Chem. **1997**, *541*, 261−268. (c) Overby, J. S.; Hanusa, T. P. *Organometallics* **1996**, *15*, 2205−2212. (d) Hammel, A.; Schwarz, W.; Weidlein, J. *J. Organomet. Chem.* **1989**, *378*, 347−361. (e) Gardiner, M.; Raston, C. L. *Organometallics* **1991**, *10*, 3680−3686. (f) Jutzi, P.; Leffers, W.; Müller, G.; Huber, B. *Chem. Ber.* **1989**, *122*, 879−884. (g) Hanusa, T. P. *Polyhedron* **1990**, *9*, 1345−1362. (h) Molander, G. A. *Organometallics* **1996**, *15*, 3817−3824. (i) Hays, M. L.; Hanusa, T. P.; Nile, T. A. *J. Organomet. Chem.* **1996**, *514*, 73−79. (j) Littger, R.; Metzler, N.; Nöth, H.; Wagner, M. *Chem. Ber.* **1994**, *127*, 1901−1908. (k) Harder, S.; Lutz, M.; Straub, A. W. G. *Organometallics* **1997**, *16*, 107−113.

(12) Parkin, G. *Acc. Chem. Res.* **1992**, *25*, 455−460.

(13) Erker, G.; Wilker, S.; Krüger, C.; Nolte, M. *Organometallics* **1992**, *12*, 2140−2151.

this photochemical coupling reaction. Photolyses were initially performed in the presence of a 12 in. Hanovia mercury arc lamp (approximately 200 W/in.) without any filters to remove infrared radiation.[14] Under these conditions a 0.18 M solution of **1** in THF-d_8 in a sealed 5 mm NMR tube required 60 h irradiation for 92% of **1** to be consumed, as determined by comparing the intensities of the signals for the starting material to the tetrahydrofuran peaks from the sample by ^{1}H NMR. A single, clean reaction product was identifiable in solution, but a brown film had also formed on the walls of the NMR tube. The chemical shifts and couplings of the ^{1}H signals for the soluble reaction product are consistent with the formation of the cyclization product shown in eq 1, which results from a *syn* coupling of the alkenes.



(1)

Stereospecific *syn* coupling of the alkene substituents was also observed in the zirconocene systems.[13] Examination of a molecular model shows that a *meso* arrangement of the alkene substituents allows more efficient overlap of the π bonds involved in the cyclization due to conformational restrictions imposed by the metallocene.[15] This arrangement leads to the formation of the C_s-symmetric *ansa*-calcocene isomer shown in eq 1.

Accomplishing the intramolecular photocyclization of **1** on a preparative scale proved to be difficult. Since irradiation of a scaled-up reaction (ca. 0.15 M) in a thick-walled glass vessel afforded only about 4% conversion of the starting material after 16 h, this approach was abandoned. The rate of conversion did not improve upon conducting the reaction in a standard preparative scale photochemistry apparatus involving a double-walled immersion well made of borosilicate glass in a water-cooled photochemical reactor with a medium-pressure mercury lamp. Using the original lamp assembly and thin-walled 10 mm NMR tubes as the reaction vessels, 90% conversion of starting material was achieved after 10 days of irradiation. The isolated yield of the photochemical coupling product, tricyclo[3.3.0.0]decane-1,10-diylcalcocene·2THF, **2**, was only 20%. There was a considerable amount of THF- and DME-insoluble polymeric material. Repeated efforts to obtain X-ray quality crystals of **2** from either THF or DME have produced only twinned crystals. Thus, efforts to obtain a publishable molecular structure of **2** have been, so far, unsuccessful; however, the data obtained to date support the expected C_s-symmetric complex.

To better characterize the photochemistry of **1** and possibly improve the efficiency of the conversion of **1** to **2**, we monitored the reaction by UV−vis spectroscopy over the course of the photolysis. A 3.33×10^{-5} M solution of **1** in THF in a quartz cuvette gives a strong absorption in the UV region starting at 330 nm, with $\epsilon_{max} = (1.6 \pm 0.2) \times 10^4$ at 290 nm. Irradiating the sample with the high-pressure mercury lamp (350 W) caused the absorption at 290 nm to decrease, with the appearance of two new absorptions at 350 nm ($\epsilon = 800 \pm 100$) and 270 nm ($\epsilon = (2.4 \pm 0.3) \times 10^4$). With only a quartz-windowed water filter for removing IR frequencies, conversion of **1** was complete in 5 min. With an additional Pyrex filter ($\lambda > 284$ nm), 10 min of photolysis was required for complete conversion of **1**. To examine if any weak absorption at a longer wavelength might be responsible for the photochemistry, the Pyrex filter was replaced with a Corning #7580 filter ($\lambda > 340$ nm). Under these conditions, no conversion of **1** was observed, even after 10 h of irradiation.

We found that the photoproduct, **2**, is not stable to further irradiation using the Pyrex filter. Prolonged irradiation (24 h) caused the absorption at 270 nm to decrease, while a broad asymmetric absorption in the range 380−240 nm appeared. This decomposition explains why the yield of **2** from our bulk photolysis was low. Replacing the Pyrex filter with a Schott WG335 filter ($\lambda > 310$ nm) slightly extended the time necessary to complete the conversion of **1** to **2** (30 min), but no decomposition of **2** was detected by UV/vis spectroscopy. In fact, **2** was found to be stable to at least 10 h of irradiation under these conditions (<1% decomposition).

In an effort to apply these wavelength-selective conditions to a preparative scale reaction, a 0.15 M THF solution of **1** in a 5 mm NMR tube was irradiated through a Schott WG335 filter. Only 25% conversion of **1** to **2** was observed after 80 h of irradiation. By contrast, similar scale photolyses performed by Erker and coworkers on bis(alkenyl)zirconocene complexes were considerably more efficient, occurring in the presence a 450 nm wavelength source and reaching completion within a few hours. The strain involved in coupling the two endocyclic double bonds in **1** to form a tricyclic bridge may be partly responsible for the low efficiency of this particular photocyclization. That the photocyclizations of the zirconocene systems are accomplished at a much longer wavelength (450 nm) indicates that identity of the metal sandwiched between the rings is also important. Application of this method to the synthesis of less strained *ansa*-metallocene species containing calcium and other metals will be investigated next as we explore the scope and limitations of this photocyclization chemistry for *ansa*-metallocene synthesis.

Conclusion

Our identification of alkenyl as well as alkyl substituents in the products of the reactions of 6,6-dialkylfulvenes with activated calcium confirms earlier proposals that the additional hydrogen atoms in the unbridged dialkylmetallocene products arise from the fulvene substrate itself as opposed to other sources such as the solvent or adventitious water. A comparison of the reactions of 6,6-dimethylfulvene, 6,6-diethylfulvene, and 6-cyclopentylidenefulvene with activated calcium was made. Reducing the number of reactive hydrogens β to carbon 6 of the fulvene led to an increase in the formation of unbridged calcocene products rather than the expected decrease based on purely statistical considerations. The increased incidence of β abstraction

(14) Calvert, J. G.; Pitts, J. N. *Photochemistry*; John Wiley & Sons: New York, 1966.
(15) Nishimura, J.; Obayashi, A.; Doi, H.; Nishimura, K. *Chem. Ber.* **1988**, *121*, 2019−2028.

products is perhaps due to an inhibition of coupling reaction by the increased steric bulk of the secondary carbon substituents. Although the synthesis of *ansa*-calcocenes via the reductive coupling of fulvenes is fairly general, these results show that not all fulvenes are suitable substrates for this reaction.

As with zirconocenes, the photochemical coupling of 1,1′-bis(alkenyl)calcocenes offers an alternative synthetic approach to *ansa*-calcocenes. The preparative scale photolysis of **1** to form **2** is less efficient and therefore less practical than analogous reactions involving bis(alkenyl)zirconcene substrates. Given the importance of the *ansa* bridge to the chemistry of a variety of metallocene systems,[16] developing a better understanding of the scope and limitations of this photocyclization chemistry is worthwhile because of its potential for improving the availability of *ansa*-metallocenes that are difficult to obtain by other means.

Experimental Section

General Considerations. Manipulations were performed under an argon or nitrogen atmosphere using Schlenk glassware, glovebox, or vacuum line techniques. HPLC grade THF and pentane were dried by passage over alumina and then stored over Na/benzophenone in vacuum line pots. DME was freshly distilled from sodium/benzophenone and stored over sodium/benzophenone in a vacuum line pot. The THF used for the UV−vis experiments had to be purified by a different method. To remove the BHT stabilizer in the commercial THF, which shows a strong absorption from 240 to 280 nm, the THF was first distilled over a 40 cm Vigreaux column. The THF was then dried over Na/K alloy instead of Na/benzophenone since small amounts of benzophenone which distills with the THF interferes with the UV−vis measurements. Argon was purified by passage over oxy tower BASF catalyst (Aldrich) and 4 Å molecular sieves. DMSO-d_6 and THF-d_8 were dried over 4 Å molecular sieves and stored in the glovebox. 6,6-Dimethylfulvene, 6,6-diethylfulvene, and cyclopentylidenefulvene were prepared according to literature procedures.[17] Granulated calcium was activated by stirring overnight in THF in the presence of 1 mol % of $HgCl_2$. Finely divided calcium was prepared as described by Hanusa and coworkers.[9b] ^{1}H and ^{13}C NMR spectra were recorded on Bruker AMX 300 (300 MHz, ^{1}H; 75 MHz, ^{13}C) and Bruker AVANCE 500 (500 MHz, ^{1}H; 125 MHz, ^{13}C) spectrometers. The chemical shifts are referenced to the residual protons in the NMR solvents (DMSO-d_6, 2.49 ppm; THF-d_8, 3.58 and 1.78 ppm). The initial photolysis experiments were performed with a medium-pressure Hanovia mercury arc lamp that was recovered from a La Jolla Scientific Co. Inc. ultra-violet photooxidation unit, model PO-24, and mounted in a homemade wooden housing along with a cooling fan from the same unit. Later photolyses were performed with a high-pressure mercury lamp, model LH-373Q, from UVP, Inc. of San Gabriel, CA, with a quartz-windowed water filter between the sample and the source to absorb infrared radiation. UV−vis spectra were recorded on a Varian CARY 2200 spectrophotometer, using 1 cm quartz cuvettes adapted with Teflon needle valves for air-sensitive samples.

Reaction of 6,6-Dimethylfulvene with Activated Calcium. To a suspension of 1.72 g (43.0 mmol) of activated calcium in 70 mL of THF was added 9.5 g (89 mmol) of 6,6-dimethylfulvene. Upon stirring overnight at room temperature, the yellow mixture became brownish in color. Filtration of the reaction mixture and removal of the THF from the filtrate by gentle heating under vacuum left a cream-colored, tarry residue. The residue was washed three times with pentane (50 mL). Drying gave an off-white foam, which solidified. Yield: 14.2 g (35.8 mmol, 80% based on fulvene). The ^{1}H NMR spectrum showed the product to be a mixture of $[Me_4C_2(C_5H_4)_2]$-$Ca(THF)_2$ (54%) and unbridged isopropyl- and isopropenyl-substituted calcocenes. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.66, 5.35, 5.28, 5.31 (4m, alkyl- and alkenyl-(C_5H_4)); 5.56, 5.39 (2m, *ansa*-(C_5H_4); 4.49, 3.85(2d, $^2J_{HH}$ = 3.6 Hz, H_2C=C(CH_3)); 2.75 (hept, $^3J_{HH}$ = 6.74 Hz, Me_2CH); 1.89 (s, H_2C=C(CH_3)); 1.77 (m, THF); 1.39 (s, $(CH_3)_4C_2$); 1.11 (d, $^3J_{HH}$ = 6.74 Hz, $(CH_3)_2$-CH).

Reaction of 6,6-Dimethylfulvene with Finely Divided Calcium. Finely divided calcium was prepared by refluxing a mixture of 2.9 g (74 mmol) of potassium with 10.86 g (37 mmol) of CaI_2 in 100 mL of THF overnight. The mixture was cooled to room temperature, and 5.6 g (52 mmol) of 6,6-dimethylfulvene was added. The mixture was stirred for 24 h at room temperature. After workup as described above, 8.34 g (80% yield, based on fulvene) of product was isolated. A ^{1}H NMR spectrum showed a mixture of **1** (20%) and the unbridged isopropyl- and isopropenyl-substituted calcocenes. Two molecules of THF per calcium center were determined.

Reaction of 6,6-Dimethylfulvene-Activated Calcium in DME. To a suspension of 1.31 g (32.7 mmol) of activated calcium in 70 mL of DME was added 5.11 g (48.1 mmol) of 6,6-dimethylfulvene. After stirring for 24 h, the yellow solution was filtered and the filtrate was dried under vacuum at 100 °C for 3 h. A pale orange foam was obtained (yield: 6.23 g, 84%, based on fulvene). The ^{1}H NMR spectrum revealed the product to be a mixture of **1** (54%) and unbridged isopropyl- and isopropenyl-substituted calcocenes. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.67, 5.36, 5.33, 5.30 (4m, 2H each, alkyl- and alkenyl-(C_5H_4)); 5.57, 5.40 (2m, *ansa*-(C_5H_4)); 4.50, 3.86 (2d, $^2J_{HH}$ = 3.6 Hz, H_2C=C(CH_3)); 3.44 (s, $-OCH_2CH_2O-$); 3.25 (s, CH_3O-); 2.76 (hept, $^3J_{HH}$ = 6.8 Hz, Me_2CH); 1.89 (s, H_2C=C(CH_3)); 1.40 (s, $(CH_3)_4C_2$); 1.12 (d, $^3J_{HH}$ = 6.8 Hz, $(CH_3)_2CH$).

Reaction of Activated Calcium with 6,6-Diethylfulvene in THF. To a mixture of 2.11 g (52.6 mmol) of activated calcium in 140 mL of THF was added 9.19 g (67.8 mmol) of 6,6-diethylfulvene. The mixture was stirred for 24 h at room temperature to yield a pale yellow-orange mixture. Filtration, followed by removal of the solvent under vacuum, gave a sticky, brown oil (yield: 9.14 g, 60%). The ^{1}H NMR spectrum revealed that 13% of the calcocene product mixture was *ansa*-calcocene. The rest of the material was unbridged calcocenes with a 1:1 ratio of 3-pentyl and 3-(2-pentenyl) substituents. The intensity of the THF signals indicated two molecules per calcium center. Washing the calcocene mixture with pentane reduces the amount of the pentyl substituents in the calcocene mixture. Further drying of the washed product under vacuum affords a more tractable orange foam with a reduced amount of THF per calcium. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.54, 5.38 (2m, *ansa*-(C_5H_4)); 5.58, 5.33, 5.29 (3m, (alkyl- and alkenyl-(C_5H_4); 5.09 (q, $^3J_{HH}$ = 6.87 Hz, 2H, MeC(H)=CCH_2CH_3); 3.62 (m, THF); 2.39 (q, $^3J_{HH}$ = 7.66 Hz, 4H, $CH_3C(H)$=CCH_2CH_3; 2.25 (quin, $^3J_{HH}$ = 7.3 Hz, $(CH_3CH_2)_2CH$); 2.19, 1.98 (2 dq, $^2J_{HH}$ = 14.1 Hz, $^3J_{HH}$ = 6.8 Hz, $(CH_3CH_2)_4C_2$); 1.78 (m, THF); 1.64 (d, $^3J_{HH}$ = 6.87 Hz, $CH_3C(H)$=CCH_2CH_3); 1.47 (dq, $^3J_{HH}$ = 7.1 Hz, 8H, $(CH_3CH_2)_2$-CH); 1.03 (t, $^3J_{HH}$ = 7.47 Hz, MeCH=CCH_2CH_3); 0.82 (t, $^3J_{HH}$ = 7.3 Hz, $(CH_3CH_2)_2CH$); the chemical shift of $(CH_3CH_2)_4C_2$ coincides with that of $(CH_3CH_2)_2CH$.

Reaction of 6,6-Diethylfulvene with Activated Calcium in DME. The reaction of 5.1 g (38.0 mmol) of 6,6-diethylfulvene with 1.00 g (24.95 mmol) of activated calcium in 70 mL of DME afforded 6.04 g (80%) of crude product. The ^{1}H NMR spectrum showed that the *ansa*-calcocene comprised 27% of the product mixture. Among the unbridged calcocenes, a 1:1 ratio of 3-pentyl to 3(2-pentenyl) substituents was found.

(16) Churchill, D.; Shin, J. H.; Hascall, T.; Hahn, J. M.; Bridgewater, B. M.; Parkin, G. *Organometallics* **1999**, *18*, 2403−2406, and references therein.

(17) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849−1853.

There was one DME molecule per calcium center. ^{1}H NMR (300 MHz, DMSO-d_6): δ 5.54, 5.38 (2m, *ansa*-(C_5H_4)); 5.56, 5.31, 5.25 (3m, (alkyl- and alkenyl-(C_5H_4); 5.07 (q, $^3J_{HH}$ = 6.9 Hz, 2H, MeC(*H*)=CCH$_2$CH$_3$); 3.44 (s, O−CH_2CH_2−O); 3.25 (s, CH_3O), 2.32−2.14 (overlapping resonances for CH$_3$C(H)=CCH_2CH$_3$, (CH$_3$CH$_2$)$_2$C*H* and (CH$_3$CH_2)$_4$C$_2$); 1.97 (dq, $^2J_{HH}$ = 14.0 Hz, $^3J_{HH}$ = 6.8 Hz, (CH$_3$CH_2)$_4$C$_2$); 1.63 (d, $^3J_{HH}$ = 6.87 Hz, CH_3C(H)=CCH$_2$CH$_3$); 1.46 (quin, $^3J_{HH}$ = 7.3 Hz, (CH$_3$CH$_2$)$_2$C*H*); 1.02 (t, $^3J_{HH}$ = 7.5 Hz, MeCH=CCH$_2$CH_3); 0.81 (t, $^3J_{HH}$ = 7.3 Hz, (CH_3CH$_2$)$_2$CH); 0.79 (t, $^3J_{HH}$ = 7.1 Hz, (CH_3CH$_2$)$_4$C$_2$).

Synthesis of [(C$_5$H$_7$)C$_5$H$_4$]$_2$Ca(THF)$_2$, 1. A large double Schlenk vessel was charged with 6.29 g (157 mmol) of activated calcium. A 150 mL sample of THF was condensed into the vessel, and 41.1 g (249 mmol) of cyclopentylidenefulvene (20% contaminated with dicyclopentadiene) was added by syringe. The mixture became hot and was stirred for 8 h. The stirring was halted and the solids were allowed to settle out overnight. After filtration the solution was dried under vacuum and washed with pentane (3 × 50 mL). After further drying under vacuum 37.6 g (82% yield based on fulvene) of crude product was obtained. The ^{1}H NMR spectrum of the product revealed unbridged calcocenes with a 1.7:1 ratio of cyclopentenyl to cyclopentyl substituents, indicating that some of the cyclopentyl-substituted material had been washed away during the pentane washing. Recrystallization of the product from THF afforded 22.5 g of material with a 4.3:1 ratio of cyclopentenyl to cyclopentyl substituents. A second crop, 4.63 g, was obtained that contained a 3:1 mixture of cyclopentenyl to cyclopentyl substituents. A third crop afforded 2.67 g of material containing a 1.5:1:0.6 mixture of cyclopentenyl-substituted, cyclopentyl-substituted, and bridged cyclopentadienylcalcium species. The total yield based on fulvene was 65%. A pure sample of **1** was obtained by double recrystallization of the first crop from THF. The purity of the other crops could be enhanced by further recrystallizations. ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.59, 5.35 (2m, 8H, C_5H_4); 4.97 (m, 2H, alkenyl-C*H* of C_5H_7); 3.62 (m, 8H, THF); 2.45, 2.34 (2m, 8H, CH_2 of C_5H_7); 1.79 and 1.78 (m, 12 H, overlapping resonances of CH_2 and THF). ^{13}C NMR (125 MHz, DMSO-d_6): δ 144.31 (s, C-ipso of C_5H_4); 116.66 (s, C-ipso of C_5H_7); 105.15 (d, $^1J_{CH}$ = 157.5 Hz, C_5H_4); 104.51 (d, $^1J_{CH}$ = 150.0 Hz, C_5H_7); 103.77 (d, $^1J_{CH}$ = 157.0 Hz, C_5H_4); 67.05 (t, $^1J_{CH}$ = 144.0 Hz, THF); 34.20 (t, $^1J_{CH}$ = 124.5 Hz, C_5H_7); 32.57 (t, $^1J_{CH}$ = 125.6 Hz, C_5H_7); 25.17 (t, $^1J_{CH}$ = 129.0 Hz, THF), 23.48 (t, $^1J_{CH}$ =127.9 Hz, C_5H_7). Anal. Calcd for $C_{29}H_{38}CaO_2$: C, 75.28; H, 8.58. Found: C, 72.68; H, 8.86. Carbon was consistently low upon reanalysis. Electrospray ionization mass spectrometric analysis verified the identity of the product, with negative ion masses at 433.2221 (theor. 433.2208 for ($C_{20}H_{22}Ca$) + $C_{10}H_{11}^-$) and 735.3532 (theor. 735.3555 for ($C_{20}H_{22}Ca)_2$ + $C_{10}H_{11}^-$) and positive ion masses at 473.2 (theor. 473.2 ($C_{20}H_{22}Ca$)+$C_{10}H_{11}^+$) and 545.2 (theor. 545.2 ($C_{20}H_{22}Ca$) + $C_{10}H_{11}^+$ + THF).

X-ray Crystallographic Studies. Crystals of **1** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream.[18] Data for **1** were collected at 203 K using a Siemens SMART 1000 instrument (Mo Kα radiation, λ = 0.71073 Å) equipped with a Siemens LT-2A low-temperature device. The SHELXTL v. 5.10 program package was used for structure solution and refinement.[19] An absorption correction was applied using SADABS.[20] The structure was solved by direct methods and refined by full-matrix least-squares procedures. All nonhydrogen atoms were refined anisotropically. One of the THF molecules coordinated to the calcium atom is disordered with the refined occupancy of C(24a) 83% and C(24b) 17%. Details of the data collection and refinement are given in Table 2. Further details are provided in the Supporting Information.

NMR Tube Scale Photolysis of 1. In the glovebox, 40 mg (0.90 mmol) of **1** was dissolved in 0.5 mL of THF-d_8, and the solution was transferred to an NMR tube equipped with a Young valve. The tube was irradiated using an ultraviolet mercury arc lamp. The reaction was checked by ^{1}H NMR after 0.5, 1.5, 3.5, 8, 14, 30, and 60 h. After 60 h, a 92% conversion of **1** to **2** was reached, and no other products were apparent in the ^{1}H NMR spectrum, although a small amount of a brown film had formed on the walls of the NMR tube.

Bulk Photolysis of 1 to Prepare 2. A solution of 1.40 g (3.13 mmol) of **1** in 20 mL of THF was divided between two 10 mm NMR tubes. The tubes were sealed and irradiated with the Hanovia mercury arc lamp. After 10 days the conversion of **1** was more than 90%, as determined by ^{1}H NMR. A cream-colored solution was obtained. A brown film had also formed in each of the NMR tubes. In the glovebox the tubes were opened and the solution was transferred to a double Schlenk vessel. The THF was removed under vacuum, and the tarry residue was extracted into DME, leaving behind some insoluble material, possibly polymeric photolysis products. After removal of the DME, the residue was washed with pentane. When the residue was extracted with THF, not all of the material redissolved. The solution was filtered from the insolubles and concentrated to 4 mL. The product was precipitated by slowly condensing pentane onto the THF layer. The product was isolated as a cream-colored powder. Yield: 0.28 g (0.63 mmol, 20%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 5.56, 5.46, 5.37, 5.34 (4m, 8H, C_5H_4); 3.60 (m, 8H, THF); 2.98 (m, 2H, C*H* of C_5H_7); 2.24 (dt, $^2J_{HH}$ = 12.7 Hz, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2 of C_5H_7); 1.78 (dt, $^2J_{HH}$ = 7.43 Hz, $^3J_{HH}$ = 5.55 Hz, 2H, CH_2 of C_5H_7); 1.76 (m, 8H, THF); 1.71 (dquin, $^2J_{HH}$ = 18.1 Hz, $^3J_{HH}$ = 5.86 Hz, 2H, CH_2 of C_5H_7 part); 1.58 (m, 4H, CH_2 of C_5H_7); 1.37 (dquin, $^2J_{HH}$ = 11.7 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, CH_2 of C_5H_7 part). ^{13}C NMR (125 MHz, DMSO-d_6): δ 132.93 (s, C_5H_4-ipso); 106.64 (d, $^1J_{CH}$ = 160 Hz, C_5H_4); 104.26 (d, $^1J_{CH}$ = 158 Hz, C_5H_4); 103.57 (d, $^1J_{CH}$ = 158 Hz, C_5H_4); 103.53 (d, $^1J_{CH}$ = 159 Hz, C_5H_4); 67.01 (t, $^1J_{CH}$ = 144 Hz, THF); 57.17 (s, 4° carbon of C_5H_7); 41.40 (d, $^1J_{CH}$ = 1.06 35 Hz, *C*H of C_5H_7); 38.06 (t, $^1J_{CH}$ = 126 Hz, *C*H$_2$ of C_5H_7); 27.89 (t, $^1J_{CH}$ = 121.5 Hz, *C*H$_2$ of C_5H_7); 26.36 (t, $^1J_{CH}$ = 123.5 Hz, CH$_2$ of C_5H_7); 25.12 (t, $^1J_{CH}$ = 131.5 Hz, THF).

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Supporting Information Available: 1-D (^{1}H, ^{13}C{^{1}H}, ^{13}C−^{1}H DEPT) and 2-D (^{13}C−^{1}H HMQC, ^{1}H−^{1}H DQF COSY) NMR spectra of **1** and **2**. Details of the structure determination determination for **1** including an ORTEP drawing, listings of atomic coordinates, thermal parameters, complete bond distances and angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Hope, H. *Prog. Inorg. Chem.* **1995**, *41*, 1.
(19) *SHELXTL* Ver. 5.10 PCNT; Bruker AXS Inc.: Madison, WI, 1999.
(20) Sheldrick, G. M. *SADABS* (Bruker/Siemens Area Detectro ABSorption correction program), an empirical absorption program; Bruker AXS Inc.: Madison, WI, 1999.