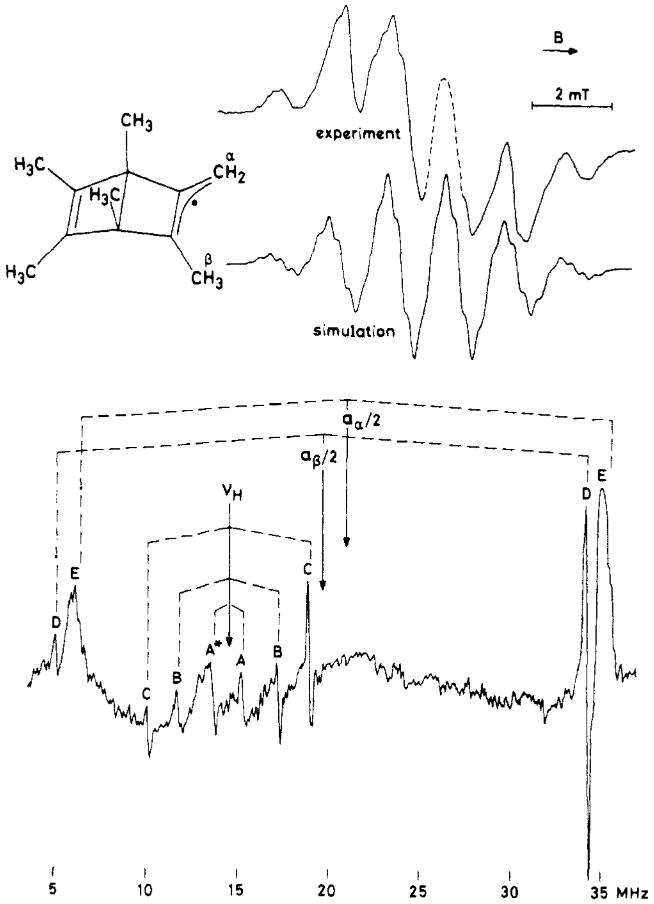
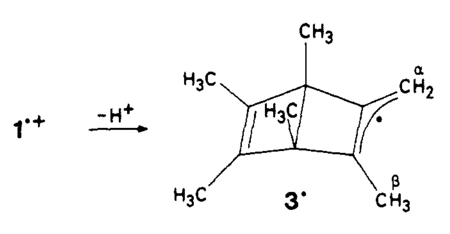


Figure 1. Top: ESR spectrum of $\mathbf{3}^{\bullet}$ in a $CF_2ClCFCl_2$ matrix at 115 K ($g = 2.0026 \pm 0.0002$). The dashed curve was obtained by deducing an absorption from the γ-irradiated quartz tube. The simulation made use of the coupling constants, in mT: 1.50 (2 H), 1.405 (3 H), 0.315 (3 H), 0.197 (3 H), and 0.056 (3 H); line shape Gaussian; line width 0.2 mT. Bottom: corresponding proton ENDOR spectrum. The low-frequency A signal, marked by an asterisk, overlaps with a ^{19}F ENDOR absorption from the matrix.

CF_3CCl_3 at the same temperature. It can reasonably be assigned to the primary radical cation $\mathbf{1}^{\bullet+}$. Conversion of $\mathbf{1}^{\bullet+}$ into $\mathbf{2}^{\bullet+}$ was also detected at elevated temperatures, this rearrangement occurring less readily in a CF_3CCl_3 than in a $CFCl_3$ matrix.

However, with $CF_2ClCFCl_2$ as the matrix, our analysis and interpretation of the ESR spectrum are at variance with those given previously.[3] The multiplet with an average spacing of 1.44 mT is clearly *a five-proton sextet and not a six-proton septet*, as revealed by the ESR spectrum in Figure 1. (The broad, weak signal at low field in Figure 1 of ref 3 does not belong to this multiplet, but stems from an unknown impurity.) As the five protons giving rise to the major hyperfine splitting of 1.4–1.5 mT must be located in one CH_3 and one CH_2 group, the obvious structure of the paramagnetic species in question is the neutral cycloallyl radical $\mathbf{3}^{\bullet}$, which has been formed from $\mathbf{1}^{\bullet+}$ by the loss of a proton.



$\mathbf{3}^{\bullet}$

The structure $\mathbf{3}^{\bullet}$ has been corroborated by the corresponding ENDOR spectrum also displayed in Figure 1. The two outer pairs of ENDOR signals (D and E), centered at $a_\beta/2 = 19.68$ and $a_\alpha/2 = 21.01$ MHz, are separated by twice the free proton frequency, $\nu_H = 14.56$ MHz.[4] In a unit of magnetic field (B), the two coupling constants amount to $a_\beta = 1.405 \pm 0.005$ and $a_\alpha = 1.50 \pm 0.10$ mT. The smaller value (1.405 mT), associated with the narrow signals D, arises from the three equivalent β-protons in the freely rotating methyl substituent of the allyl π-system, whereas the larger one (1.50 mT), represented by the broad signals E, is appropriate for the two nonequivalent α-protons of the allyl methylene group. These assignments are fully compatible with the hyperfine data for structurally related allyl radicals.[5] The broadening of the E signals is attributed to the hyperfine anisotropy of the α-protons and to the unresolved difference in the coupling constants for the endo and exo positions. The three inner pairs of ENDOR signals (A, B, and C), centered at $\nu_H = 14.56$ MHz, are separated by the coupling constants of 1.58, 5.52, and 8.84 MHz or, in a unit of the magnetic field, by 0.056 ± 0.002, 0.197 ± 0.002, and 0.315 ± 0.002 mT. They belong to the protons of three methyl substituents further removed from the allyl π-system of $\mathbf{3}^{\bullet}$; the coupling constant of the protons in one methyl group evidently fails to be observed or the associated ENDOR signals coincide with A or B or C. Assignments of the three values to methyl substituents in individual positions are difficult.[6] Nevertheless, their nonequivalence accords with the low symmetry (C_1) of $\mathbf{3}^{\bullet}$.

Additional evidence favoring the structure of a neutral allyl radical is the persistence, unusual for radical cations in freon matrices. Thus, the ESR spectrum of $\mathbf{3}^{\bullet}$ could still be observed at 150 K, well above the softening point of $CF_2ClCFCl_2$.

As stated in a paper by Williams et al.,[9] conversion of $\mathbf{1}^{\bullet+}$ to $\mathbf{3}^{\bullet}$ in the $CFCl_2CF_2Cl$ matrix occurs when the concentration of **1** exceeds ca. 1 mol %. This finding indicates that the reaction is bimolecular, i.e., the neutral **1** acts as the proton acceptor. Such ion–molecule reactions have often been observed in the relatively mobile $CF_2ClCFCl_2$ matrix.[10]

Acknowledgment. This work was supported by the Swiss National Science Foundation. We are obliged to Prof. E. Haselbach, Université de Fribourg, for the permission to use his ^{60}Co source of γ-rays and to the Bruker Analytische Messtechnik GmbH, Karlsruhe (FRG), for taking the ENDOR spectrum above 35 MHz. Our thanks are also due to Prof. F. Williams, University of Tennessee, Knoxville, TN, for a preprint of his paper.

---

(4) See, e.g.; Kurreck, H.; Kirste, B.; Lubitz, W. *Electron Nuclear Double Resonance of Radicals in Solution*; VCH Publishers: New York, 1988; Chapter 2.

(5) Landolt-Börnstein, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1977; Volume II/9b.

(6) Calculations by AM1[7] and INDO[8] (based on AM1 optimized geometry) were not very helpful in this respect.

(7) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(8) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill: New York, 1970.

(9) Williams, F.; Guo, Q.-X.; Nelsen, S. F. *J. Am. Chem. Soc.*, third of three papers in this issue.

(10) See ref 9 for the pertinent literature.

Reinvestigation of the Hexamethyl(Dewar benzene) Radical Cation in Freon Matrices

Ffrancon Williams* and Qing-Xiang Guo*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Stephen F. Nelsen*

S. M. McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received October 16, 1989

Rhodes recently reported[1,2] that the *electronic state* of the hexamethyl(Dewar benzene) (HMDB) radical cation generated

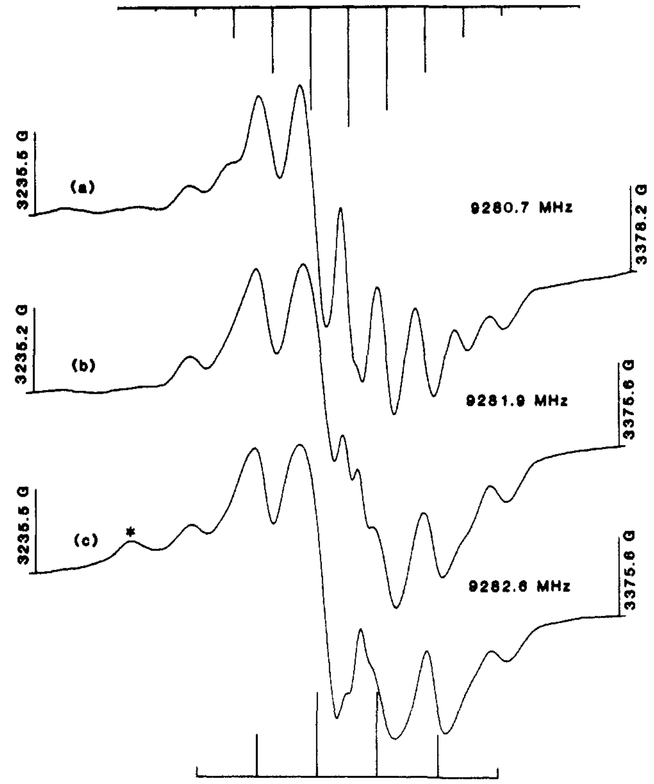


Figure 1. First-derivative ESR spectra of the radical products obtained by γ irradiation (dose, 0.25 Mrad) at 77 K of solid solutions of hexamethyl(Dewar benzene) (HMDB) in $CF_2ClCFCl_2$, showing the effects of HMDB concentration and annealing. Spectra a and b were obtained from 0.1 and 1 mol % HMDB solutions, respectively, and recorded at 85–90 K before sample annealing. Spectrum c was obtained after annealing of the 1 mol % sample to 105 K and was similarly recorded at 90 K. The feature marked by the asterisk in c is discussed in the text. The stick diagrams represent the line components of the $^2B_2$ HMDB radical cation (upper) and of the neutral allylic radical (lower) described in the text.

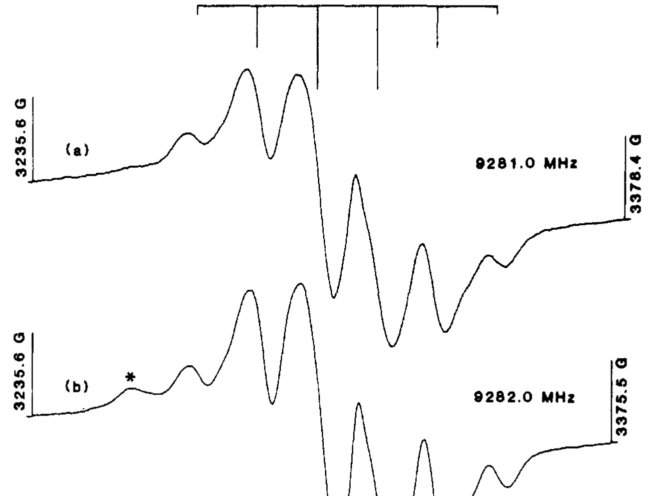
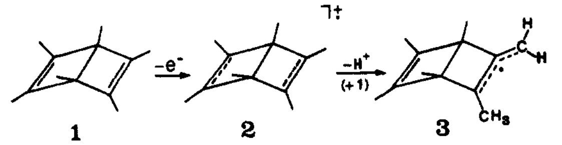


Figure 2. First-derivative ESR spectra obtained from 0.1 mol % (a) and 1.0 mol % (b) solutions of HMDB in $CF_2ClCFCl_2$ after γ irradiation (dose, 0.25 Mrad) at 77 K. The spectra were recorded at 90 K after annealing of the samples to 125 K. The stick diagram represents the line components of the neutral allylic radical described in the text. The feature marked by the asterisk in b is also discussed in the text.

by the radiolytic oxidation of the parent compound in Freon solid solutions[3] differs according to the matrix in which the cation is prepared, the $^2A_1$ and $^2B_2$ states being the dominant species formed in $CF_2ClCFCl_2$[1] and $CFCl_3$,[2] respectively. Since it is well-known that the nature of the Freon matrix can affect the course of secondary processes involving unimolecular rearrangements[4] and bimolecular reactions[5] of the radical cation, we decided to repeat Rhodes's experiments to see if such effects could have any bearing on the validity of his unusual finding.

Decisive evidence on this question comes from an ESR study of the effect of HMDB concentration on the radiolytic oxidation product in $CF_2ClCFCl_2$ (Figure 1). First, spectrum a generated from a low-concentration (≈0.1 mol %) sample clearly includes a set of hyperfine (hf) components defined by a 9.1-G spacing that corresponds closely to the hyperfine splitting (hfs) reported by Rhodes for the $^2B_2$ radical cation *in the* $CFCl_3$ *matrix*.[2] At a 10-fold higher concentration of HMDB, however, the resulting spectrum (b) shows no clearly defined signals from the $^2B_2$ radical cation. Interestingly, this spectrum changed slightly on annealing of the sample to reveal a pattern (c) that closely resembles the spectrum previously assigned to the $^2A_1$ radical cation in this matrix.[1] This assignment is erroneous since the spectrum was assumed to consist of seven lines,[1] but as Figures 1 and 2 make clear, the relative intensity of the outermost line at low field varies considerably with annealing and HMDB concentration, and therefore this feature does not belong to the remaining six-line binomial pattern. Confirmation of this revised analysis implicating a different radical (vide infra) is provided by the proper intensity balance between the undistorted $M_I = \pm^5/_2$ and $\pm^3/_2$ pairs of components in the sextet spectra[6] indicated by the stick diagrams in Figures 1 and 2. Also, the derived g factor of 2.0026 (5) is more reasonable for a hydrocarbon radical than the much higher value of 2.0063 (5), which would apply for the seven-line interpretation.[7]

Scheme I



The above results are readily interpreted by Scheme I since the bimolecular process of proton transfer would be expected to generate increasing amounts of the neutral radical **3** at the expense of the $^2B_2$ radical cation (**2**) as the concentration of the neutral

---

(1) Rhodes, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 8567.

(2) Rhodes, C. J. *J. Am. Chem. Soc.* **1988**, *110*, 4446.

(3) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

(4) (a) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974. (b) Williams, F.; Guo, Q.-X.; Bebout, D. C.; Carpenter, B. K. *J. Am. Chem. Soc.* **1989**, *111*, 4133. (c) Williams, F.; Guo, Q.-X.; Kolb, T. M.; Nelsen, S. F. *J. Chem. Soc., Chem. Commun.*, **1989**, 1835.

(5) (a) Fujisawa, J.; Sato, S.; Shimokoshi, K.; Shida, T. *J. Phys. Chem.* **1985**, *89*, 5841. (b) Toriyama, K.; Nunome, K.; Iwasaki, M. *J. Phys. Chem.* **1986**, *90*, 6836. (c) Nunome, K.; Toriyama, K.; Iwasaki, M. *Tetrahedron* **1986**, *42*, 6315. (d) Qin, X.-Z.; Williams, F. *J. Phys. Chem.* **1986**, *90*, 2292. (e) Qin, X.-Z.; Williams, F. *J. Am. Chem. Soc.* **1987**, *109*, 595. (f) Williams, F.; Qin, X.-Z. *Radiat. Phys. Chem.* **1988**, *32*, 299. (g) Dai, S.; Wang, J. T.; Williams, F. *J. Chem. Soc., Perkin Trans. 1* **1989**, 1063.

(6) Line 3 of the sextet pattern appears with enhanced intensity because of overlap with a broad unresolved signal from the $CF_2ClCFCl^{\bullet}$ radical at 85–90 K in the $g = 2.007$ region of the spectrum; cf.: Qin, X.-Z.; Guo, Q.-X.; Wang, J. T.; Williams, F. *J. Chem. Soc., Chem. Commun.* **1987**, 1553.

(7) Although g factors were not reported by Rhodes,[1,2] the internal reference provided by the spike from γ-irradiated quartz reveals that the center of the apparent seven-line pattern in Figure 1 of ref 1 is similarly displaced from the free-spin value (($g = 2.0023$) by $\Delta g \approx +0.004$, confirming that this spectrum[1] is virtually identical with that shown here in Figure 1c. We note also from our measurements that the $^2B_2$ state of the HMDB radical cation has the unexceptional g factor of 2.0030 (3) in both the $CFCl_3$ and $CF_2ClCFCl_2$ matrices.

HMDB (**1**) is raised in the sample. A propensity for ion–molecule reactions of this kind in the relatively mobile $CF_2ClCFCl_2$ matrix has been amply documented.[5] The closing argument is that the six-line spectrum can be assigned to radical **3**. This is straightforward since the average ^1H hfs of 14.4 G is typical of α- and β-hydrogen splittings for allylic radicals[5a,8] and coupling to five nearly equivalent hydrogens (H^{α}_{exo}, H^{α}_{endo}, and $3H^{\beta}_{endo}$) is predicted in this case.[8a]

We conclude that there is no credible evidence for the formation of the $^2A_1$ state of the HMDB radical cation in $CF_2ClCFCl_2$,[1] the $^2B_2$ state being produced as in $CFCl_3$.[2] The different results obtained previously in these two matrices[1,2] originate from the greater proclivity for loss of the $^2B_2$ radical cation by ion–molecule reactions in the more mobile $CF_2ClCFCl_2$ solid, especially at high HMDB concentrations. Consequently, the $^2B_2$ and not the $^2A_1$ radical cation[1] is the ground state in these Freon matrices.[9,10] Trifunac and co-workers have similarly observed only the $^2B_2$ state from measurements of time-resolved fluorescence detected magnetic resonance in liquid cyclopentane and *n*-pentane solutions,[11] and so there is no evidence for a solvent effect on the nature of the ground state as was suggested earlier.[12]

Acknowledgment. Thanks are due to Dr. Alex Trifunac for sending us a preprint of his paper on the ground state of the hexamethyl(Dewar benzene) radical cation and to Professor Fabian Gerson for an exchange of manuscripts on this subject. We are also grateful to a referee for the opportunity to elaborate on an important point covered in footnote 9. This research was supported at the University of Tennessee by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Grant DE-FG05-88ER13852), and at the University of Wisconsin by the National Science Foundation (Grant CHE-8801588).

Registry No. 1, 7641-77-2; **2**, 85293-78-3; **3**, 75650-90-7.

---

(8) Berndt, A. In *Landolt-Börnstein*; New Series, Group II, *Magnetic Properties of Free Radicals*; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin–Heidelberg, 1977; Vol. 9, Part b, pp 345–353. Berndt, A. In *Landolt-Börnstein*; New Series, Group II, *Magnetic Properties of Free Radicals*; Fischer, H., Ed.; Springer-Verlag: Berlin–Heidelberg, 1987; Vol. 17 (Supplement and Extension to Vol. 9), Subvolume c, pp 8–12 and 48–54.

(9) This conclusion rests on two counts. First, only the $^2B_2$ state of the HMDB radical cation is detected initially at 80 K; also, its signal intensity remained unchanged on thermal cycling to higher temperatures, thereby providing no evidence for a process of thermal equilibration to a lower lying state. Thus, in experiments with *dilute* HMDB solutions in both $CF_2ClCFCl_2$ and $CFCl_2CFCl_2$, the $^2B_2$ state persisted from 80 to 100 K before undergoing the ring-opening rearrangement to the hexamethylbenzene radical cation as previously observed in the $CFCl_3$ matrix.[2] Indeed, this *unimolecular* reactivity of the $^2B_2$ radical cation was found to be very similar in all three matrices, as expected for thermalized species.[9a] Secondly, the complementary relationship between the $^2B_2$ state and the allylic radical as a function of HMDB concentration in $CF_2ClCFCl_2$ clearly argues in favor of a single HMDB radical cation undergoing the bimolecular reaction in Scheme I. In sum, the evidence is overwhelming that the $^2B_2$ species is the ground state of the HMDB radical cation in these matrices. Finally, we note that the $^2A_1$ species could well be a metastable precursor to the hexamethylbenzene radical cation formed from the $^2B_2$ state on annealing although there is no direct evidence for its involvement in this reaction. A similar situation applies to the ring opening of the bicyclo[2.2.0]hexane radical cation.[4b] (a) The matrix dependence of unimolecular radical cation rearrangements mentioned in the opening paragraph refers to nonthermal activation processes that sometimes occur in the course of radical cation generation.[4] In this case, *the initial distribution* of reactant and product radical cations depends on the matrix, a good example being the very different ratios of the cyclohexane-1,4-diyl and cyclohexene radical cations produced from the radiolytic oxidation of 1,5-hexadiene in CF_3CCl_3 and $CFCl_3$.[4a]

(10) Rhodes claimed that his assignment of the apparent seven-line spectrum to the $^2A_1$ state was strongly supported by the appearance of features from the ring-opened hexamethylbenzene radical cation on annealing of the sample.[1] These features were relatively weak, however, and can now obviously be attributed to the ring opening of residual $^2B_2$ radical cations.[9]

(11) Qin, X.-Z.; Werst, D. W.; Trifunac, A. D. *J. Am. Chem. Soc.*, first of three papers in this issue.

(12) See footnote 5 of ref 1.

(13) (a) An independent ESR and ENDOR study has also assigned the six-line spectrum to radical **3**: Arnold, A.; Gerson, F. *J. Am. Chem. Soc.* **1990**, *112*, 2027.

---

rac-[Ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]dichlorotitanium and Its Homopolymerization of Propylene to Crystalline–Amorphous Block Thermoplastic Elastomers

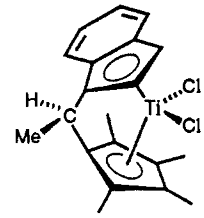
Daniel T. Mallin,[1a] Marvin D. Rausch,*[,1a] Ye-Gang Lin,[1b] Sizhong Dong,[1c] and James C. W. Chien*[,1c]

Departments of Chemistry, Chemical Engineering, and
Polymer Science and Engineering
University of Massachusetts
Amherst, Massachusetts 01003

Received October 23, 1989

ansa-Metallocene compounds have been discovered that polymerize propylene with either isospecificity[2,3] or syndiospecificity[4] to predominantly isotactic or syndiotactic polymers, respectively. In this contribution, we describe the formation of a new *ansa*-metallocene system, *rac*-[ethylidene(1-η^5-tetramethylcyclopentadienyl)(1-η^5-indenyl)]dichlorotitanium (**1**), which produces homopolypropylene having the attributes of a thermoplastic elastomeric (TPE) material.

A reaction[5] between 1,2,3,4,6-pentamethylfulvene[6] and indenyllithium in THF solution, followed by hydrolysis and distillation, afforded 1-(1-indenyl)-1-(2,3,4,5-tetramethylcyclopentadienyl)ethane (**2**) (bp 130–140 °C/0.1 Torr) in 54% yield [anal. (calcd): C, 90.63 (90.85); H, 9.25 (9.15)]. The golden orange oil **2** is an isomeric mixture according to ^1H and ^{13}C NMR. A solution of **2** (13 mmol) in 150 mL of THF was cooled to 0 °C, *n*-butyllithium (26 mmol) was added dropwise, and the mixture was stirred for several hours at 40 °C to from a deep red solution. It was cooled to −78 °C, and 13 mmol of $TiCl_4(THF)_2$[7] in THF was added dropwise. Subsequent refluxing for 18 h gave a green solution. Removal of the solvent, extraction with CH_2Cl_2, filtration, and removal of the CH_2Cl_2 gave 4.7 g of **1** in 95% crude yield. The product was purified by crystallization from CH_2Cl_2/*n*-hexane, MS *m*/*e* 381 for M^+; [anal. (calcd): C, 61.41 (63.02); H, 5.70 (5.82)]. The ^1H and ^{13}C NMR[8] spectra indicate that only one of the two possible diasteromeric pairs is isolated, with the probable structure shown based on steric considerations.



1

Polymerization of propylene[9] at 1.5 atm and 50 °C with 27 μM **1** and 54 mM methylaluminoxane (MAO)[3,9] based on Al for 1

---

(1) (a) Department of Chemistry. (b) Department of Chemical Engineering. (c) Department of Polymer Science and Engineering.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Ewen, J. A. Ligand Effects on Metallocene Catalyzed Polymerizations. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Elsevier: New York, 1986; p 271. (c) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544.

(3) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507.

(4) Ewen, J. A.; Jones, R. L.; Razavi, A. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(5) The addition reaction of organometallic compounds to fulvenes was first described by Ziegler and Schäfer: Ziegler, K.; Schäfer, W. *Justus Liebigs Ann. Chem.* **1934**, *511*, 101.

(6) (a) Bensley, D. M., Jr.; Mintz, E. A. *J. Organomet. Chem.* **1988**, *353*, 93. (b) Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organomet. Chem.*, in press.

(7) Manzer, L. E. *Inorg. Synth.* **1982**, *21*, 135.

(8) ^1H NMR: (200 MHz) 1.68 (s, 3 H), 1.95 (s, 3 H), 1.96 (s, 3 H), 1.98 (s, 3 H), 2.19 (d, 3 H, $J = 7.5$ Hz), 4.96 (q, 1 H), 5.70 (d, 1 H), 6.95–7.59 (m, 5 H). ^{13}C NMR: (200 MHz) 12.7, 12.8, 14.9, 16.1, 18.4, 30.3, 93.3, 96.8, 112.6, 121.7, 123.4, 124.4, 125.2, 126.3, 126.6, 128.1, 130.0, 133.3, 136.9, 137.9.

(9) Chien, J. C. W.; Wang, B. P. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 3089.

0002-7863/90/1512-2030$02.50/0