spectrum (EI), m/z (relative intensity): 449 (M^+ - CO, 12), 421 (M^+ - 2CO, 20), 393 (M^+ - 3CO, 24), 365 (M^+ - 4CO, 15), 337 (M^+ - 5CO, 41), 309 (M^+ - 6CO, 66), 281 (M^+ - 7CO, 41), 253 (Fe_2S-t-Bu(CH=CHCH=CH)$^+$, 46), 225 (Fe_2S-t-Bu(C=C)$^+$, 100), 210 (Fe_2SH(C=CHCH=CHN)$^+$, 12), 199 (Fe_2SH(NHC=CHCH)$^+$ + 1H, 25), 160 ($Fe_2SH(NH)^+$, 19), 149 (Fe_2(C=CHCH)$^+$, 14), 144 (Fe_2S^+, 36), 125 (Fe_2CH^+, 12), 111 (FeNMeCH=CH$^+$, 18), 97 (FeNMeC$^+$, 24), 85 (FeNMe$^+$, 28), 81 (FeCCH$^+$, 33), 71 (FeNH$^+$, 35), 57 (FeH$^+$, 84), 41 (CNMe$^+$, 47).

Reaction of [Et$_3$NH][(μ-CO)(μ-t-BuS)Fe$_2$(CO)$_6$] with Bis(1-methyl-2-pyrrolyl)mercury. The standard [Et$_3$NH][(μ-CO)(μ-t-BuS)Fe$_2$(CO)$_6$] reagent solution (2.98 mmol) was generated at room temperature. Against a strong flow of nitrogen, 1.09 g (3.01 mmol) of bis(1-methyl-2-pyrrolyl)mercury was added as a solid. The reaction mixture was stirred for 2 h at room temperature during which time a color change to red-brown and the formation of a gray precipitate were observed. TLC indicated the formation of two orange products. The solvent was removed in vacuo to yield a red solid which was dissolved in pentane and filtered through a thin pad of silicic acid. Pentane eluted an orange band which gave 0.33 g (0.71 mmol, 48% based on S, a/e:e/e = 1.5) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[15] Pentane/CH_2Cl_2 (4:1 v/v) eluted a yellow band. Further purification of this product was achieved by thin-layer chromatography on preparative TLC plates of silica. Pentane eluted an orange band which yielded 0.50 g (1.04 mmol, 35%) of (μ-C(O)C=CHCH=CHNMe)(μ-t-BuS)Fe$_2$(CO)$_6$ (18) (an inseparable mixture of isomers), identified by comparison of its ^{1}H NMR with that of an authentic sample (experiment above).

Attempted Decarbonylation of (μ-C(O)C=CHCH=CHNMe)(μ-t-BuS)Fe(CO)$_6$. A 100-mL Schlenk flask equipped with a rubber septum and a stir-bar was charged with 0.22 g (0.46 mmol) of (μ-C(O)C=CHCH=CHNMe)(μ-t-BuS)Fe$_2$(CO)$_6$ (18) and degassed by three evacuation/nitrogen-back-fill cycles. The flask then was charged with 20 mL of THF and heated at reflux. After 5.5 h the color of the reaction mixture had changed from bright to dark red. TLC indicated the formation of a new product in addition to the presence of unreacted starting material and insoluble decomposition materials. The solvent was removed in vacuo to leave a brown-red oil which was purified by chromatography on preparative TLC plates of silica. Pentane eluted an orange band which gave 0.05 g (0.11 mmol, 49% based on S) of (μ-t-BuS)$_2$Fe$_2$(CO)$_6$, identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample.[23] The second band to elute was yellow and gave 0.06 g (0.14 mmol, 30%) of unreacted (μ-C(O)C=CHCH=CHNMe)(μ-t-BuS)Fe$_2$(CO)$_6$ (18) identified by comparison of its ^{1}H NMR spectrum with that of an authentic sample. A brown band of decomposed iron-containing material remained at the origin.

Acknowledgment. We at MIT are grateful to the National Science Foundation for support of the preparative work carried out at MIT. We at the University of Alberta thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support. F.V. thanks the Fulbright Commission and the Ministerio de Educación y Ciencia of Spain for a postdoctoral fellowship (1990-1991).

Supplementary Material Available: A listing of IR data for new compounds and tables of thermal parameters and hydrogen atom parameters for compound 10c (3 pages). Ordering information is given on any current masthead page.

OM9202884

Pentamethylcyclopentadienyl Ligand Activation in a Cationic Zirconocene Complex: Formation of an Unusual Pendant Allyl Ligand with 1,3-Butadiene

Andrew D. Horton

Koninklijke/Shell-Laboratorium, Amsterdam (Shell Research BV), Postbus 3003, 1003 AA Amsterdam, The Netherlands

Received April 1, 1992

Activation of a C_5Me_5 ligand on reaction of $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}$ (1) with excess 1,3-butadiene affords an unusual linked cyclopentadienyl-allyl ligand in $[(C_5Me_5)Zr\{\eta^5:\eta^3\text{-}C_5Me_4(CH_2CH_2CHCHCH_2)\}]^+$ (2). Formation of 2 proceeds via elimination of 2-pentene from an observable η^3-allyl intermediate, followed by trapping of the putative tetramethylfulvene product by diene insertion. Stable Lewis-base-free η^3-allyl complexes, $[Cp'_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}]^+$ (Cp' = C_5Me_5 (3b), $(Me_3C)C_5H_4$ (3c)), are obtained with 1,2-propadiene.

Introduction

The highly regio- and stereospecific oligo- and polymerization of 1,3-dienes using soluble Ziegler-Natta catalysts, particularly those based on lanthanide metals, is of great practical importance.[1] Although group 4 metallocene/methylaluminoxane systems catalyze the oligo- and polymerization of 1-alkenes[2] and the cyclopolymerization of nonconjugated dienes,[3] reactivity toward conjugated dienes has been observed only in copolymerization reactions with 1-alkenes.[4] Lewis-base-free d^0 metallocene cations

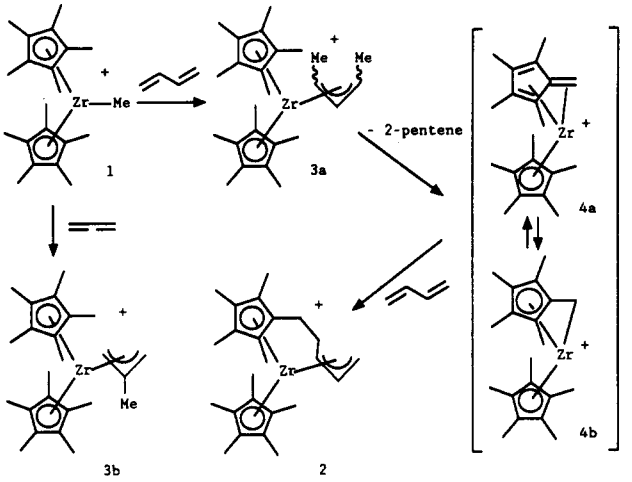
(1) (a) Keim, W.; Behr, A; Röper, M. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 8, p 371. (b) Porri, L.; Giarrusso, A.; Ricci, G. *Prog. Polym. Sci.* **1991**, *16*, 405. (c) Ricci, G.; Italia, S.; Comitani, C.; Porri, L. *Polym. Commun.* **1991**, *32*, 514.

(2) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (c) Kaminsky, W.; Kulper, K.; Brintzinger, H.-H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (d) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (e) Chien, J. C. W.; Sugimoto, R. *J. Polym. Sci., Part A* **1991**, *29*, 459. (f) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853.

(3) (a) Coates, G. W.; Waymouth, R. M. *J. Am. Chem. Soc.* **1991**, *113*, 6270. (b) Resconi, L.; Waymouth, R. M. *J. Am. Chem. Soc.* **1990**, *112*, 4953.

0276-7333/92/2311-3271$03.00/0

Scheme I. Formation of Cationic Complexes[a]



[a] The anion, $B(4\text{-}C_6H_4F)_4^-$, has been omitted.

$[Cp'_2MR]^+$ similarly show high 1-alkene oligo- and polymerization activity,[5] but reactivity studies with conjugated dienes have not been reported.[6] Investigations of diene reactivity with isoelectronic *neutral* scandium complexes[7] have provided evidence for unusual β-alkyl elimination reactions and for α-agostic bonding in the (diene cyclopolymerization) transition state.

In order to confirm whether the lack of reactivity of the aluminoxane-containing systems with conjugated dienes is due to the formation of unreactive allyl complexes or other deactivation products, we examined the reaction of electrophilic methylzirconocene cations with 1,3- and 1,2-dienes. The labile nature of the coordinated anion in the Lewis-base-free complex $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}$ (1)[8] results in a highly electrophilic and reactive metal center, such that the complex is a precursor to high-activity terminal alkyne oligomerization catalysts.[9] The high reactivity of 1 with dienes is here reflected in the activation of a C_5Me_5 ligand, on reaction of an initially formed η^3-allyl product with a second equivalent of 1,3-butadiene, to give an unusual Cp′–allyl ligand.

Results and Discussion

Reactivity with 1,3-Butadiene: C_5Me_5 Activation. Reaction of a solution of complex 1, generated in situ in bromobenzene, with excess 1,3-butadiene (−30 to +25 °C; 45 min of stirring at +25 °C) affords a single major organometallic product, as well as ca. 1.0 equiv of 2-pentene (^{1}H NMR monitoring). Product precipitation using hexane, followed by crystallization from CH_2Cl_2/hexane solution, affords pure orange crystalline 2. The complex has been characterized by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy and elemental analysis as an unusual C–H activation product containing a novel tetramethylcyclopentadienyl–$(CH_2)_2$–allyl ligand (see Scheme I). The complex is formally derived from 1,4-insertion of 1,3-butadiene into the Zr–CH_2 bond of a hypothetical tetramethylfulvene complex, $[(C_5Me_5)Zr\{C_5Me_4(CH_2)\}]^+$ (vide infra).

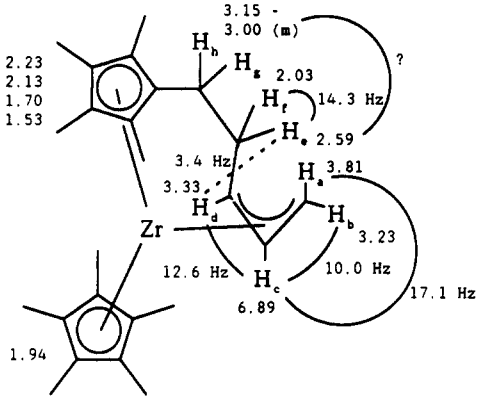


Figure 1. Assignment of ^{1}H NMR resonances for complex 2 (CD_2Cl_2, −20 °C; chemical shifts, δ, in ppm).

Pentamethylcyclopentadienyl ligand activation in 2 is confirmed by the observation of five ring methyl resonances (ratio 1:1:5:1:1) in the ^{1}H NMR spectrum (see Figure 1). The absence of a plane of symmetry containing the zirconium atom and the Cp′ ring centroids is consistent with η^3 coordination of the allyl fragment,[10-13] which has also been confirmed by assignment of all the ^{1}H NMR resonances of 2 using a 2-D COSY NMR experiment at −20 °C. The alternative η^1-allyl coordination mode in low symmetry "$[(C_5Me_5)Zr\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CH_2CH\text{-}CH{=}CH_2)\}]^+$" is inconsistent with the upfield location of terminal allyl hydrogens, H_a and H_b (see Figure 1). The observation of two moderate (10.0, 12.6 Hz) and one large (17.6 Hz) $^3J_{HH}$ coupling constant (vide infra)[6a,10-13] in-

(4) See the following and references therein: (a) Galimberti, M.; Albizzati, E.; Abis, L.; Bacchilega, G. *Makromol. Chem.* **1991**, *192*, 2591. (b) Kaminsky, W.; Drögemüller, H. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 89.

(5) (a) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1991**, *113*, 3623. (b) Chien, J. C. W.; Tsai, W.-M.; Rausch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570. (c) Hlatky, G. G.; Turner, H. W.; Eckman, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 2728. (d) Bochmann, M.; Jagger, A. J.; Nicholls, N. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 780. (e) Horton, A. D.; Frijns, J. H. G. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1152.

(6) (a) Jordan, R. F.; LaPointe, R. E.; Prudence, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892. (b) Christ, C. S., Jr.; Eyler, J. R.; Richarson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596. (c) Eshuis, J. J. W.; Tan, Y. Y.; Teuben, J. H. *J. Mol. Catal.* **1990**, *62*, 277.

(7) (a) Piers, W. E.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 9406. (b) Bunel, E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976.

(8) (a) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910. (b) Horton, A. D.; Orpen, A. G. *Organometallics* **1992**, *11*, 8.

(9) Horton, A. D. *J. Chem. Soc., Chem. Commun.* **1992**, 185.

(10) (a) Hoffmann, E. G.; Kallweit, R.; Schroth, G.; Seevogel, K.; Stempfle, W.; Wilke, G. *J. Organomet. Chem.* **1975**, *97*, 183. (b) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981. (c) Benn, R.; Rufińska, A. *Organometallics* **1985**, *4*, 209.

(11) For selected references to η^3-allyl complexes of the early transition and lanthanide metals see the following: (a) Highcock, W. J.; Mills, R. M.; Spencer, J. L.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1982**, 128. (b) Erker, G.; Engel, K.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914. (c) Erker, G.; Dorf, U.; Benn, R.; Reinhardt, R.-D.; Petersen, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 7649. (d) Berg, K.; Erker, G. *J. Organomet. Chem.* **1984**, *270*, C53. (e) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (f) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (g) Chen, J.; Kai, Y.; Kasai, N.; Yasuda, H.; Yamamoto, H.; Nakamura, A. *J. Organomet. Chem.* **1991**, *407*, 191. (h) Vance, P. J.; Prins, T. J.; Hauger, B. E.; Silver, M. E.; Wemple, M. E.; Pederson, L. M.; Kort, D. A.; Kannisto, M. R.; Geerligs, S. J.; Kelly, R. S.; McCandless, J. J.; Huffman, J. C.; Peters, D. G. *Organometallics* **1991**, *10*, 917.

(12) For references to "σ–π-distorted" allyl complexes of the group 4 metals, see the following: (a) Larson, E. L.; Van Dort, P. C.; Dailey, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Organometallics* **1987**, *6*, 2141. (b) Erker, G.; Berg, K.; Angermund, K.; Krüger, C. *Organometallics* **1987**, *6*, 2620. (c) Larson, E. L.; Van Dort, P. C.; Lakanen, J. R.; O'Neill, D. W.; Pederson, L. M.; McCandless, J. J.; Silver, M. E.; Russo, S. O.; Huffman, J. C. *Organometallics* **1988**, *7*, 1183. (d) Hauger, B. E.; Vance, P. J.; Prins, T. J.; Wemple, M. E.; Kort, D. A.; Silver, M. E.; Huffman, J. C. *Inorg. Chim. Acta* **1991**, *187*, 91.

(13) For references to η^1-allyl complexes of the group 4 metals, see references 12b,c and the following: (a) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383. (b) Erker, G.; Engel, K.; Atwood, J. L.; Hunter, W. E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 494. (c) Mashima, K.; Yasuda, H.; Asami, K.; Nakamura, A. *Chem. Lett.* **1983**, 219. (d) Wielstra, Y.; Duchateau, R.; Gambarotta, S.; Bensimon, C.; Gabe, E. *J. Organomet. Chem.* **1991**, *418*, 183.

volving the central allyl hydrogen, H_c, suggests that the η^3-allyl ligand contains two syn hydrogens and one anti hydrogen and hence that the $-CH_2CH_2C_5Me_4$ "substituent" is located in an anti position. The nonequivalence of the two syn couplings presumably results from chelation-induced asymmetry in the allyl bonding. η^3-Allyl coordination is further confirmed by the observation of characteristics ^{13}C NMR resonances for the allyl fragment[10-13] at δ 143.1 (central *C*H), 85.3 (*C*H), and 83.7 ppm (CH_2).

The dramatic color change of solutions of **2** from deep red at +40 °C to paler orange at −50 °C and the temperature dependence of the allyl ^1H NMR chemical shifts, with shift changes $\Delta\delta$ (+40 to −50 °C) varying between −1.14 (H_a) and +0.65 ppm (H_b), suggest that the allyl coordination mode varies with temperature. Stronger anion–cation interaction at lower temperature, as shown by the upfield shift of the ^{19}F NMR resonance from δ −125.9 at +30 °C to δ −128.2 ppm at −30 °C (free anion resonance at −30 °C in CD_2Cl_2: δ −122.2 ppm), may perhaps be accompanied by a change in the allyl bonding to more distorted η^3 (e.g. "σ–π")[12] or η^1 ("σ") bonding.[13] Considering, however, that η^3-allyl bonding occurs in the MeCN adduct of **2** (vide infra), distortion to η^1 bonding in **2** seems unlikely.

Interestingly, although all resonances for H_{a-h} of **2** (see Figure 1) broaden considerably at higher temperatures, resonances for the allyl anti and syn hydrogens, H_a and H_b, respectively, do not coalesce up to +40 °C. Furthermore, the pairs of ethene bridge resonances H_e/H_f and H_g/H_h and the four C_5Me_4R resonances all show no evidence for coalescence at +40 °C. If a fluxional process is responsible for the resonance broadening, it clearly does not proceed via a transitory species (such as $[(C_5Me_5)Zr\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2CH_2CH{=}CHCH_2)\}]^+$) with a plane of symmetry containing the Cp′ ring centroids and Zr. Exchange between **2** and another (minor and unobservable) complex, present to a greater extent at higher temperatures, may explain the broadening of resonances H_{a-h} (and also, perhaps, the changes in color and $^1H/^{19}F$ NMR chemical shifts with temperature). Unfortunately, complex decomposition occurs before a high-temperature limiting spectrum may be observed, and so further speculation appears unwarranted.

η^3-Allyl coordination is maintained in the adducts formed in situ on reaction of CD_2Cl_2 solutions of **2** with CD_3CN and with NEt_4Cl. **1**·CD_3CN exhibits two moderate (12.5, 9.7 Hz) and one large (17.6 Hz) $^3J_{HH}$ coupling constant involving H_c, which suggests that the $-CH_2CH_2C_5Me_4$ "substituent" again adopts the anti orientation. Similarly, neutral $(C_5Me_5)Zr\{\eta^5{:}\eta^3\text{-}C_5Me_4(CH_2CH_2CHCHCH_2)\}Cl$ also contains two syn and one anti allyl hydrogen. Protonolysis of **2** using MeOH affords a novel substituted cyclopentadienyl ligand in $(C_5Me_5)Zr\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CHCH_3)\}(OMe)_2$, identified by ^1H NMR spectroscopy.

Formation of complex **2** proceeds via an unstable η^3-allyl complex, which is rapidly formed at 0 °C on reaction of a C_6D_5Br solution of **1** with 1.0 equiv of 1,3-butadiene. Dark red/green **3a** is formulated as $[(C_5Me_5)_2Zr\{\eta^3\text{-}(Me)CHCHCH(Me)\}]^+$ (see Scheme I), on the basis of the ^1H NMR spectrum at 25 °C, which exhibits resonances for equivalent C_5Me_5 ligands and equivalent allyl methyl groups (δ 0.92 ppm, d, $^3J_{HH}$ = 5.8 Hz) and terminal hydrogens (δ 4.22 ppm, dq, $^3J_{HH}$ = 13.0 Hz). The similarity of $^3J_{HH}$ in **3a** to the exchange-averaged values of 12.7 Hz for $(C_5Me_5)_2Sc\{\eta^3\text{-}CH_2CHCH_2\}$[11f] and 12.1 Hz for $[(MeC_5H_4)_2Zr\{(\eta^3\text{-}CH_2CHCH_2\}(THF)]^+$[6a] suggests that rapid syn–anti exchange occurs in **3a**, probably via a transitory σ-allyl intermediate. However, given the high $^3J_{HH}$ values found for syn coupling in **2**, the presence of two anti methyl groups in **3a**, although sterically unlikely, cannot be entirely ruled out.

Formation of **3a** clearly involves a hydrogen shift. Initial 1,3-butadiene insertion into the Zr–Me bond in **1** likely affords $[(C_5Me_5)_2Zr\{\eta^3\text{-}CH_2CHCH(Et)\}]^+$, which may undergo "$\beta$-hydrogen elimination" (giving $[(C_5Me_5)_2Zr\{\eta^n\text{-}CH_2{=}CHCH{=}CH(Me)\}(H)]^+$),[11f] followed by insertion of the terminal double bond into the Zr–H bond to give **3a**.

In the absence of excess 1,3-butadiene, **3a** decomposes rapidly ($t_{1/2}$ < 10 min) to give a complex mixture of unidentified organometallic products, as well as 2-pentene (primarily the trans isomer by ^1H NMR spectroscopy). Formation of a "tetramethylfulvene"/metalated Cp′ ligand in unstable **4a**/**4b**, via elimination of 2-pentene from sterically crowded **3a** (see Scheme I), is the likely first step in the clean conversion of **3a** to **2**. Elimination of hydrocarbon RH, on C–H activation of a C_5Me_5 ligand in $(C_5Me_5)_2MR_n$ (M = Ti, Zr; n = 1, 2), and related complexes, giving an $\eta^6\text{-}C_5Me_4(CH_2)$ ligand[14] (or an $\eta^7\text{-}C_5Me_3(CH_2)_2$ ligand),[14h,j,15] has been well studied. The transfer of a ring methyl hydrogen to the allyl group in **3a** also has a precedent in the reaction of $(\eta^5\text{-}C_5Me_5)PdL(\eta^1\text{-allyl})$ with L (L = PR_3, $P(OR)_3$) to give $\{\eta^2\text{-}(CH_2{=})\text{-}C_5Me_4\}PdL_2$ and alkene.[16]

The instability of putative **4** is not surprising, considering the sterically and electronically unsaturated nature of the cation; the isoelectronic neutral scandium complex $\{(C_5Me_5)_2Sc(\eta^6\text{-}C_5Me_4(CH_2))\}_n$,[11f] although incompletely characterized, is isolable as an oligomeric solid, and related yttrium and lutetium complexes have been postulated as reaction intermediates.[15a,17] In the presence of 1,3-butadiene, 1,4-insertion into the Zr–CH_2 bond in **4** leads to **2**. Trapping of **4** has a precedent in the insertion reactions with ketones, aldehydes, and isonitriles of neutral group 4 fulvene complexes.[18]

Reactivity with 1,2-Propadiene: Lewis-Base-Free Allylzirconocene Cations. Although the 1,3-butadiene insertion product **3a** cannot be isolated, a more stable η^3-allyl complex is obtained in 90% yield, on reaction at −30 °C of a small excess of 1,2-propadiene with a bromobenzene solution of **1**. Addition of hexane affords red crystalline **3b** in 90% yield, which may be recrystallized from CH_2Cl_2/hexane solution. The novel base-free 2-methylallyl complex (see Scheme I), formed by insertion of diene into the Zr–Me bond in **1**, has been fully characterized by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and elemental analysis. Slow further reaction of **3b** with excess 1,2-propadiene over several hours at 25 °C leads to a complicated mixture of unidentified organic and organo-

(14) (a) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **1972**, *94*, 1219. (b) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (c) Schock, L. E.; Brock, C. P.; Marks, T. J. *Organometallics* **1987**, *6*, 232. (d) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (e) Miller, F. D.; Sanner, R. D. *Organometallics* **1988**, *7*, 818. (f) Parkin, G.; Bercaw, J. E. *Organometallics* **1989**, *8*, 1172. (g) Den Haan, K.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1986**, 682. (h) Cloke, F. G. N.; Green, J. C.; Green, M. L. H.; Morley, C. P. *J. Chem. Soc., Chem. Commun.* **1985**, 945. (i) Pattiasini, J. W.; Hissink, C. E.; De Boer, J. L.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 7758.

(15) (a) Booij, M.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 3246. (b) Carter, S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253.

(16) Werner, H.; Crisp, G. T.; Jolly, P. W.; Kraus, H.-J.; Kröger, C. *Organometallics* **1983**, *2*, 1369.

(17) Watson, P. L.; Roe, D. C. *J. Am. Chem. Soc.* **1982**, *104*, 6471.

(18) (a) Erker, G.; Korek, U. *Z. Naturforsch.* **1989**, *44B*, 1593. (b) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 2665. (c) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 1637. (d) Pattiasina, J. W.; van Bolhuis, F.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 330.

metallic products. Attempted reaction of **1** with a range of other dienes does not lead to clean product formation.[19]

Solutions of **3b** in CD_2Cl_2 exhibit distinct ^1H NMR resonances at −70 °C for the allyl syn and anti hydrogens (δ 4.49 and 1.99 ppm, respectively)[10-13] and for the inequivalent C_5Me_5 ligands (δ 1.99, 1.94 ppm). When the solutions are warmed, coalescence of the C_5Me_5 (T_c ca. −30 °C) and the syn and anti hydrogen resonances (T_c = −5 °C) occurs; at +35 °C the latter hydrogens give a broad resonance at δ 3.25 ppm. $\Delta G^{\ddagger}$ for the fluxional process causing syn–anti exchange has been estimated to be 12.1 ± 0.2 kcal mol^{-1}.[20]

Syn–anti exchange in **3b** is accelerated by addition of THF-d_8: a single *sharp* CH_2 resonance is observed at 25 °C. Formation of a transient η^1-allyl species with an equatorial plane of symmetry in **3b** appears to be favored by Lewis base addition. Rapid syn–anti exchange also occurs in the neutral η^3-allyl derivative $(C_5Me_5)_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}Cl$, formed on reaction of **3b** with NEt_4Cl. Addition to a solution of **3b** in $C_2D_2Cl_4$ of CD_3CN, which coordinates more strongly than THF to the crowded cation, affords a nonfluxional η^1-allyl species,[13] as confirmed by the observation of $ZrCH_2$ (δ 2.88 ppm) and $=CH_2$ (δ 4.92, 4.81 ppm) resonances. The increased combined steric bulk of the C_5Me_5 and 2-methylallyl ligands in **3b** (compared to the more "compact" chelating Cp′–$(CH_2)_2$–allyl ligand in **2**) apparently forces the allyl ligand in **3b** to adopt the less sterically demanding η^1 coordination mode, in contrast to the η^3 mode in **2**·MeCN.

In contrast to the ^1H NMR spectrum of **3b**, the less crowded $[\{(Me_3C)C_5H_4\}_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}]^+$ (**3c**), obtained as a red oil using a method analogous to that leading to **3b**, shows sharp syn and anti resonances and inequivalent Cp′ resonances at 25 °C. η^3- to η^1-allyl interconversion is clearly more facile in the C_5Me_5 complex than in the $(Me_3C)C_5H_4$ complex. Increased fluxionality in the more crowded complex probably reflects unfavorable steric interaction between a C_5Me_5 group and the allyl 2-Me group, which slightly destabilizes the η^3-allyl form relative to the η^1 form. Bending of the central allyl carbon away from Zr^{11g} in **3b** is reflected in the unusual downfield location of the *C*Me resonance at δ 180.9 ppm.[10-13] Further confirmatory evidence for η^3-allyl bonding in **3b** and **3c** is provided by the observation of a "free anion" resonance in the ^{19}F NMR spectrum; a formally 14-electron η^1-allyl complex would be expected to show anion coordination, by analogy to related 14-electron methyl and alkenyl complexes.[8]

Conclusions

The reaction of dienes with complex **1** leads initially to η^3-allyl complexes, which slowly react further with excess diene, giving, in the case of 1,3-butadiene, a novel ligand C–H activation product. In contrast to the oligo- or polymerization of conjugated dienes catalyzed by lanthanide and other complexes containing less bulky ligands, no such catalysis has been observed: the electrophilicity at Zr is insufficient to overcome inherent steric crowding in the equatorial plane of the initially formed allyl complexes, which hinders diene coordination. Indeed, such steric crowding in unstable **3a** appears to result in expulsion of 2-pentene to give an unstable tetramethylfulvene intermediate, which is then trapped as a 1,3-butadiene insertion product. Formation of **2**, via C–H activation of C_5Me_5, is unprecedented in cationic metallocene chemistry and suggests a possible new mechanism of deactivation of aluminoxane-containing polymerization catalysts[21] by cyclopentadienyl ligand degradation.

Experimental Section

General Comments. All experiments were performed under nitrogen in a Braun MB 200-G drybox or under argon using standard Schlenk techniques. Bromobenzene (Aldrich, "Gold Label") was dried by distillation from calcium. Other solvents were dried by refluxing over and distilling from standard reagents. NMR solvents were dried over 4-Å molecular sieves before use. 1,2-Propadiene and 1,3-butadiene were used as purchased. $(C_5Me_5)_2ZrMe_2$[22] and $\{(Me_3C)C_5H_4\}_2ZrMe_2$[23] were obtained from the reactions of Cp'_2ZrCl_2 with LiMe in ether, followed by recrystallization from toluene/hexane solution. $Na[B(4\text{-}C_6H_4F)_4]$ was obtained by literature methods[24] and converted to $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ by a metathesis reaction with $[PhMe_2NH]Cl$. All other reagents were purchased from commercial sources and used without further purification.

^1H NMR (300.00 MHz), ^{13}C NMR (75.43 MHz), and ^{19}F (283.32 MHz) NMR spectra were recorded on a Varian VXR-300 instrument. NMR data are listed in parts per million downfield from TMS for proton and carbon and relative to $CFCl_3$ for fluorine. Elemental analyses were performed by Analytische Laboratorien, Engelskirchen, Germany.

Preparation of $[(C_5Me_5)Zr\{\eta^5\text{:}\eta^3\text{-}C_5Me_4(CH_2CH_2CHCHCH_2)\}][B(4\text{-}C_6H_4F)_4]$ (2[B(4-$C_6H_4F)_4$]). Bromobenzene (8 mL) at −30 °C was added to a stirred mixture of $(C_5Me_5)_2ZrMe_2$ (200 mg, 0.51 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (265 mg, 0.52 mmol) in a Schlenk tube at −30 °C. The resulting intensely colored yellow solution was warmed to 0 °C and then cooled again to −30 °C. Addition by syringe of 57 mL of 1,3-butadiene (ca. 2.3 mmol), via a septum, resulted in a rapid solution color change to dark green/brown. After the mixture was warmed to 25 °C and stirred for 45 min, an intensely colored red solution was obtained. Excess 1,3-butadiene was removed in vacuo, and hexane was then added to precipitate a red oily solid, which was washed with hexane. Crystallization from cold CH_2Cl_2/hexane, followed by washing of the orange crystals with hexane and drying in vacuo, afforded 180 mg of product (44%). Recrystallization afforded analytically pure product. ^1H NMR (CD_2Cl_2; resonances assigned using a 2-D COSY NMR experiment): −20 °C, δ 7.15 (m, 8, *o*-C_6H_4F), 6.89 (ddd, $^3J_{ac}$ = 17.1 Hz, $^3J_{cd}$ = 12.6 Hz, $^3J_{bc}$ = 10.0 Hz, 1, H_c), 6.73 (dd, 8, *m*-C_6H_4F), 3.81 (d, 1, H_a), 3.33 (dd, $^3J_{de}$ = 3.4 Hz, H_d), 3.23 (d, 1, H_b), 3.15–3.00 (m, 2, H_g, H_h), 2.59 (dd, $^3J_{ef}$ = 14.3 Hz, H_e), 2.23, 2.13 (s, 3, C_5Me_4R), 2.03 (obsc, 1, H_f), 1.94 (s, 15, C_5Me_5), 1.70, 1.53 (s, 3, C_5Me_4R); 40 °C, δ 7.60 (br, 1, H_c), 4.62 (d, 1, H_a), 3.71 (d, 1, H_d), 3.39, 3.13 (br, 2, H_g, H_h), 2.75 (br, 2, H_b, H_e), 2.39, 2.36 (s, 3, C_5Me_4R), 2.01 (s, 15, C_5Me_5), 1.61 (s, 3, C_5Me_4R), 1.50 (br, 3, C_5Me_4R), obscured resonance for H_f not located; −50 °C, δ 6.57 (m, 1, H_c), 3.48 (d, 1, H_a), 3.40 (d, 1, H_b), 3.20 (d, 1, H_d), 2.98 (m, 2, H_g, H_h), 2.53 (m, 1, H_e), 2.17, 2.02 (s, 3, C_5Me_4R), 1.89 (s, 15, C_5Me_5), 1.73, 1.54 (s, 3, C_5Me_4R), obscured resonance for H_f not located. ^{13}C NMR (CD_2Cl_2, −30 °C): δ 159.5 (d, $^1J_{CF}$ = 237 Hz, *p*-C_6H_4F), 157.7 (q, $^1J_{CB}$ = 50 Hz, ipso C_6H_4F), 143.1 (d, $^1J_{CH}$ = 155 Hz, $C_5Me_4(CH_2CH_2CHCHCH_2)$), 141.7 ($C_5Me_4R$), 135.9 (*o*-$C_6H_4F$), 123.5, 123.0 ($C_5Me_4R$), 120.6 ($C_5Me_5$), 118.7 ($C_5Me_4R$), 111.5 (d, $^2J_{CF}$ = 17 Hz, *m*-C_6H_4F), 110.8 (C_5Me_4R), 85.3 (d, $^1J_{CH}$ = 152 Hz, $C_5Me_4(CH_2CH_2CHCHCH_2)$), 83.7 (t, $^1J_{CH}$ = 153 Hz, $C_5Me_4(CH_2CH_2CHCHCH_2)$), 37.0 (t, $^1J_{CH}$ = 129 Hz, $C_5Me_4(CH_2CH_2CHCHCH_2)$), 23.0, (t, $^1J_{CH}$ = 128 Hz, $C_5Me_4(CH_2CH_2CHCHCH_2)$), 11.5 (2 C, C_5Me_4R), 11.3 (1 C, C_5Me_4R), 11.1 (C_5Me_5), 9.7 (1 C, C_5Me_4R). ^{19}F NMR (CD_2Cl_2, 25 °C): δ

(19) Complex **1** shows no reaction with the sterically crowded substrates 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene. With 1,3-pentadiene (cis and trans isomers) and with 3-methyl-1,2-butadiene, a complex mixture of unidentified products is obtained.

(20) Anet, F. A.; Bourn, A. J. R. *J. Am. Chem. Soc.* **1967**, *89*, 769.

(21) Chien, J. C. W.; Razavi, A. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2369.

(22) Manriquez, J. M.; McAlister, D. R.; Rosenberg, E.; Shiller, A. M.; Williamson, K. L.; Chan, S. I.; Bercaw, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 3078.

(23) Howie, R. A.; McQuinlan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213.

(24) Moore, C. E.; Cassaretto, F. P.; Posvic, H.; McLafferty, J. *Anal. Chim. Acta* **1966**, *35*, 1.

−125.9 ($\Delta\nu_{1/2}$ = 45 Hz). ^{19}F NMR (CD_2Cl_2, −30 °C): δ −128.2 ($\Delta\nu_{1/2}$ = 28 Hz). Anal. Calcd for $C_{48}H_{51}BF_4Zr$: C, 71.53; H, 6.38; F, 9.43. Found: C, 71.23; H, 6.45; F, 9.18.

Addition of excess CD_3CN to a solution of **2** in CD_2Cl_2 gave a bright yellow adduct, **2**·CD_3CN. ^{1}H NMR (−30 °C): δ 7.14 (m, 8, *o*-C_6H_4F), 6.74 (dd, 8, *m*-C_6H_4F), 5.56 (ddd, $^3J_{ac}$ = 17.6 Hz, $^3J_{bc}$, $^3J_{cd}$ = 12.5, 9.7 Hz, 1, H_c), 3.32 (d, 1, H_b), 3.00 (dd, $^3J_{de}$ = 5.7 Hz, 1, H_d), 2.73 (d, 1, H_a), 2.7–2.4 (m, 3, H_f, H_g, H_h), 2.00, 1.90 (s, 3, C_5Me_4R), 1.79 (s, 15, C_5Me_5), 1.66, 1.58 (s, 3, C_5Me_4R). ^{19}F NMR (CD_2Cl_2, −30 °C): δ −122.1.

Reactions of Complex 2. Addition of 1.0 equiv of NEt_4Cl to a solution of **2** in CD_2Cl_2 gave a pale yellow solution of $(C_5Me_5)Zr\{\eta^5:\eta^3\text{-}C_5Me_4(CH_2CH_2CHCHCH_2)\}Cl$. ^{1}H NMR (25 °C): δ 5.63 (dt, $^3J_{ac}$ = 16.9 Hz, $^3J_{bc}$ = $^3J_{cd}$ = 10.8 Hz, 1, H_c), 3.54 (d, 1, H_a), 3.42 (d, 1, H_b), 3.0–2.2 (m, 5, H_d, H_e, H_f, H_g, H_h), 2.01, 1.92 (s, 3, C_5Me_4R), 1.87 (s, 18, C_5Me_5, C_5Me_4R), 1.68 (s, 3, C_5Me_4R).

Addition of excess MeOH to a solution of **2** in CD_2Cl_2 gave $(C_5Me_5)Zr\{\eta^5\text{-}C_5Me_4(CH_2CH_2CH{=}CHCH_3)\}(OMe)_2$. ^{1}H NMR (−30 °C): δ 5.37 (m, 2, −C*H*=C*H*CH_3), 3.44 (s, 6, OMe), 3.05 (m, 1), 2.62 (m, 2, $-CH_2-$), 2.43 (dd, 2, $-CH_2-$), 1.94 (s, 27, C_5Me_5, C_5Me_4R), 1.62 (d, $^3J_{HH}$ = 4.0 Hz, 3, −CH=CHCH_3).

Formation of $[(C_5Me_5)_2Zr\{\eta^3\text{-}(Me)CHCHCH(Me)\}][B(4\text{-}C_6H_4F)_4]$ (3a[B(4-$C_6H_4F)_4$]). Addition by syringe of ca. 1.0 equiv of 1,3-butadiene to a solution (C_6D_5Br, 0 °C) of $(C_5Me_5)_2ZrMe\{B(4\text{-}C_6H_4F)_4\}$ (**1**), generated in situ, afforded a dark green/brown solution, shown by ^{1}H NMR spectroscopy (25 °C) to be primarily the title complex: δ 6.71 (t, $^3J_{HH}$ = 13.0 Hz, 1, (Me)CHC*H*CH(Me)), 4.22 (dq, $^3J_{HH}$ = 5.8 Hz, 2, (Me)C*H*CHC*H*(Me)), 1.51 (s, 30, C_5Me_5), 0.92 (d, 6, (*Me*)CHCHCH(*Me*)). Attempted isolation of the complex on a preparative scale was not successful: addition of hexane at 0 °C afforded a dark green oil, which decomposed on washing with hexane and drying in vacuo.

Preparation of $[(C_5Me_5)_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}][B(4\text{-}C_6H_4F)_4]$ (3b[B(4-$C_6H_4F)_4$]). Bromobenzene (8 mL) at −30 °C was added to a stirred mixture of $(C_5Me_5)_2ZrMe_2$ (200 mg, 0.51 mmol) and $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (265 mg, 0.52 mmol) in a Schlenk tube at −30 °C, and the resulting solution was warmed to 0 °C and then cooled again to −30 °C. Addition by syringe of 13.7 mL of 1,2-propadiene (ca. 0.6 mmol), via a septum, resulted in a rapid color change to intense red. After the stirred solution was warmed to 10 °C, excess 1,2-propadiene was removed in vacuo, and hexane was then added to precipitate a red microcrystalline solid. Washing with hexane and drying in vacuo afforded 380 mg (92%) of product. An analytically pure crystalline sample was obtained from cold CH_2Cl_2/hexane solution. ^{1}H NMR (CD_2Cl_2): 35 °C, δ 7.25 (m, 8, *o*-C_6H_4F), 6.78 (dd, 8, *m*-C_6H_4F), 3.31 (br, 4, $CH_2C(Me)CH_2$), 2.58 (s, 3, $CH_2C(Me)CH_2$), 2.04 (s, 30, C_5Me_5); −70 °C, δ 4.49 (s, 2, *syn*-$CH_2C(Me)CH_2$), 2.51 (s, 3, $CH_2C(Me)CH_2$), 1.99 (obsc, 2, *anti*-$CH_2C(Me)CH_2$), 1.99, 1.94 (s, 15, C_5Me_5). ^{13}C NMR ($C_2D_2Cl_4$, −30 °C): δ 180.9 ($CH_2C(Me)CH_2$), 159.2 (d, $^1J_{CF}$ = 238 Hz, *p*-C_6H_4F), 158.5 (q, $^1J_{CB}$ = 50 Hz, ipso C_6H_4F), 135.9 (*o*-C_6H_4F), 125.3 (C_5Me_5), 111.6, (d, $^2J_{CF}$ = 17 Hz, *m*-C_6H_4F), 74.1 (d, $^1J_{CH}$ = 149 Hz, $CH_2C(Me)CH_2$), 29.5 ($CH_2C(Me)CH_2$), 11.1 (C_5Me_5). ^{19}F NMR (CD_2Cl_2, −30 °C): δ −122.2 ($\Delta\nu_{1/2}$ = 22 Hz). Anal. Calcd for $C_{48}H_{53}BF_4Zr$: C, 71.35; H, 6.61; F, 9.41. Found: C, 71.57; H, 6.80; F, 8.87.

^{1}H NMR monitoring of the reaction in C_6D_5Br of in situ generated **1** with ca. 12.0 equiv of 1,2-propadiene at 25 °C showed the initial formation of **3b**, which, after 45 min, had been completely converted to other organometallic products. After 150 min, all the 1,2-propadiene had reacted to give a mixture of unidentified compounds, and a white precipitate was observed. The insolubility of the precipitate in common solvents has prevented its identification.

Addition of excess THF-d_8 to a solution of complex **3b** in $C_2D_2Cl_4$ afforded a labile THF adduct (no colour change). ^{1}H NMR: δ 3.25 (s, 4, $CH_2C(Me)CH_2$), 2.54 (s, 3, $CH_2C(Me)CH_2$), 2.00 (s, 30, C_5Me_5).

Addition of excess CD_3CN to a solution of **3b** in $C_2D_2Cl_4$ afforded a pale yellow solution of $[(C_5Me_5)_2Zr\{\eta^1\text{-}CH_2C(Me){=}CH_2\}(CD_3CN)_n]^+$. ^{1}H NMR: δ 4.92, 4.81 (m, 1, $CH_2C(Me){=}CH_AH_B$), 2.88 (s, 2, $CH_2C(Me){=}CH_2$), 1.91 (s, 3, $CH_2C(Me){=}CH_2$), 1.85 (s, 30, C_5Me_5).

Reaction of Complex 3b with NEt_4Cl. Reaction of NEt_4Cl with **3b** in $C_2D_2Cl_4$ afforded an intensely colored yellow solution of $(C_5Me_5)_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}Cl$. ^{1}H NMR (25 °C): δ 2.72 (br, 4, $CH_2C(Me)CH_2$), 1.94 (s, 30, C_5Me_5), 1.51 (s, 3, $CH_2C(Me)CH_2$).

Preparation of $[\{(Me_3C)C_5H_4\}_2Zr\{\eta^3\text{-}CH_2C(Me)CH_2\}][B(4\text{-}C_6H_4F)_4]$ (3c[B(4-$C_6H_4F)_4$]). Reaction of $\{(Me_3C)C_5H_4\}_2ZrMe_2$ (150 mg, 0.41 mmol) with $[PhMe_2NH][B(4\text{-}C_6H_4F)_4]$ (210 mg, 0.41 mmol) in C_6H_5Br (7 mL), followed by addition of 1,2-propadiene, using conditions similar to those leading to **3b**, gave a red solution of **3c**. Addition of hexane afforded a red oil, which was redissolved in C_6H_5Br. Pure oily product was obtained by addition of hexane and drying in vacuo. Attempts to crystallize the complex were not successful. ^{1}H NMR (C_6D_5Br, 25 °C): δ 7.64 (m, 8, *o*-C_6H_4F), 6.94 (dd, 8, *m*-C_6H_4F), 6.40, 6.28, 5.90, 5.64 (m, 2, $(Me_3C)C_5H_4$), 4.44 (br, 2, *syn*-$CH_2C(Me)CH_2$), 2.00 (s, 3, $CH_2C(Me)CH_2$), 1.91 (br, 2, *anti*-$CH_2C(Me)CH_2$), 0.60, 0.40 (s, 9, $(Me_3C)C_5H_4$). ^{19}F NMR (C_6D_5Br, −30 °C): δ −122.5 ($\Delta\nu_{1/2}$ = 33 Hz).

Acknowledgment. The assistance of Mr. J. H. G. Frijns with variable-temperature NMR spectroscopy is gratefully acknowledged.

OM920181G