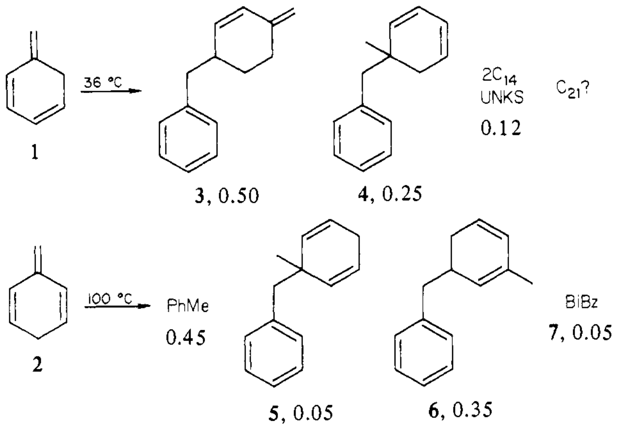
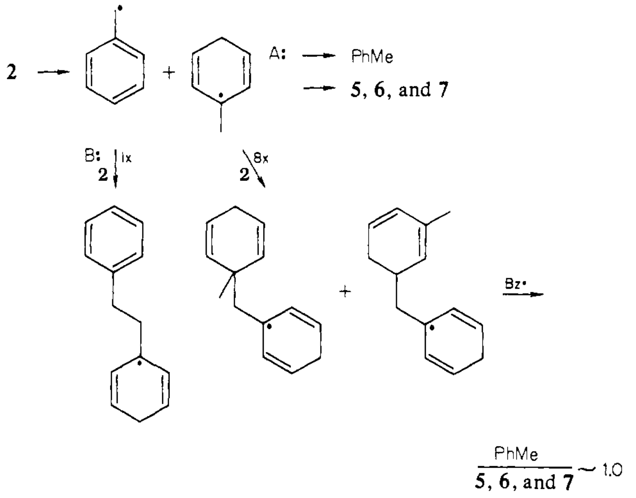
previous reports. On the other hand, *p*-isotoluene gives ca. 50% toluene as well as a 1:7:1 ratio of two dimeric products, **5** and **6**, and bibenzyl, **7**, respectively, along with small amounts of apparently trimeric material.[9] This product distribution is relatively independent of concentration of starting material.



The difference between the two isomers would appear to be their relative ability to undergo an ene reaction. Only **1** can give an aromatic nucleus directly in this concerted reaction. Thus the reaction exothermicity appears to control the relative ene reactivity of **1** and **2**. *p*-Isotoluene apparently slowly transfers its reactive hydrogen to a second molecule to give a benzyl radical and a 3-methylcyclohexadienyl radical which can either (A) disproportionate to toluene and combine to give C_{14} products in a 1:1 ratio or (B) add to more triene which disproportionates with benzyl radical. In path B the product distribution suggests that methylcyclohexadienyl radical adds to **2** roughly eight times faster than the benzyl radical, and so mostly benzyl radical is left to undergo disproportionation. Interestingly, path B *requires* a near 1:1 ratio of toluene to **5**, **6**, and **7** which is in accord with the experimental facts.



There are a number of significant observations regarding the reaction of **2**. Benzyl radicals are being generated by a retro radical–radical disproportionation (molecule assisted homolysis[4c]); yet they do not induce a long-chain isomerization of **2** to toluene. The formation of such a high proportion of potential termination products, **5**–**7**, excludes a long radical chain isomerization. Significantly, the presence of dimethylhydroxylamine, a good hydrogen donor,[10] had no effect on the reaction nor did changing the solvent to cyclohexane-d_{12}. Further, equimolar amounts of AIBN gave little if any toluene in the presence of **2** in benzene at 80 °C for 1 h; most of the *p*-isotoluene was unaffected and roughly 50% of the AIBN was converted to tetramethylsuccinonitrile.[11] It appears that the E_a for the hydrogen atom transfer path from **2** is too high to be traversed relative to recombination and disproportionation if path A is followed or relative to addition to **2** is path B is utilized.

Using thermochemical group additivity and relative heats of formation of **2** and toluene,[2] the first step of either path A or B can be calculated to be uphill 18 kcal/mol enthalpically which is only 4 kcal/mol less than the observed E_a. Interestingly, this same retrodisproportionation for *o*-isotoluene also has a calculated endothermicity of 18 kcal/mol. Significantly, it is precisely this hydrogen transfer that occurs in **1**, but it is coupled with C–C bond making and generation of an aromatic system.[12]

Acknowledgment. We thank the Department of Energy for financial support of this work and Drs. J. E. Bartmess, K. E. Gilbert, and L. K. Montgomery for enlightening discussions and Dr. W. A. Pryor for encouragement.

Registry No. 1, 20679-59-8; **2**, 3217-87-6; **3**, 80106-13-4; **4**, 80106-14-5; **5**, 80106-15-6; **6**, 80106-16-7; **7**, 101-81-5; PhMe, 108-88-3; 1-methyl-5-benzyl-1,3-cyclohexadiene, 80106-17-8.

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[9] The major dimer product **6** rearranged on the GC column, so it was identified by NMR spectrum of the nonvolatile product after the resonances of **5**, which could be purified, and bibenzyl were subtracted. 220-MHz NMR of **5**: δ 7.2 (m, 5 H), 5.57 (d, J = 10 Hz, 2 H), 5.43 (d, J = 10 Hz, 2 H), 2.55 (s, 2 H), 2.40 (m, partly obscured by the δ 2.55 resonance, 2 H), 1.03 (s, 3 H). 220-MHz NMR of **6**: δ 7.2 (m, 5 H), 5.70 (brs, 3 H), 5.30 (brs, 1 H), 2.7–2.2 (m, 3 H), 1.98 (ABq, J = 17 Hz, 2 H) (the downfield lines are doublets of doublets, J = 8, 4 Hz and the upfield lines are doubled, J = 3 Hz); 1.68 (s, 3 H).

[10] Câceres, T.; Lissi, E. A.; Sanhueza, E. *Int. J. Chem. Kinet.* **1978**, *10*, 1167.

[11] The half-life of AIBN in benzene at 80 °C is ca. 1 h, and the major product is tetramethylsuccinonitrile: Wu, C.-H.S.; Hammond, G. S.; Wright, J. M. *J. Am. Chem. Soc.* **1960**, *82*, 5386. The half-life for loss of **2** in this experiment is ca. 20 h.

[12] For early work on 1,2,4,5,6,6-hexamethyl-3-methylene-1,4-cyclohexadiene, see: Hart, H.; DeVrieze, J. D. *Tetrahedron Lett.* **1968**, 4257. *Chem. Commun.* **1968**, 1651. For related work on 6-allyl and 6-benzyl substituted materials, see: Miller, B.; Lai, K.-H. *Tetrahedron Lett.* **1971**, 1617.

Gas-Phase Ion Chemistry of 5-Methylene-1,3-cyclohexadiene (*o*-Isotoluene) and 3-Methylene-1,4-cyclohexadiene (*p*-Isotoluene)

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Received August 24, 1981

The structures of the $C_7H_8^+$ and $C_7H_7^+$ ions produced by ionization of various C_7H_8 and C_7H_7X compounds in mass spectrometers have been the subject of numerous investigations.[1-5] Studies involving photodissociation and ion–molecule reactions indicate that the long-lived radical cations formed by ionization of the various C_7H_8 isomers, such as toluene, cyclohepatriene, and norbornadiene, do not interconvert.[2,3] The $C_7H_7^+$ ions arising from

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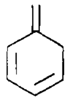
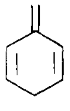
electron impact on the various precursors appear to be a mixture of benzyl and tropyl cations, at least on a millisecond time scale. The ratio of the two forms depends on the nature of the neutral precursor and the electron energy.[4,5] The recent availability[6] of two tautomers of toluene, **1** and **2**, has prompted an investigation of the energetics and reactivity of these new entries onto the $C_7H_8^{+}\cdot/C_7H_7^{+}$ surface.



1



2

The heats of formation of **1** and **2** have been determined by using ion cyclotron resonance spectrometry. We observe the onset for their deprotonation by anions of increasing base strength to give the 91^- ion. Tautomers which give a common anion on deprotonation should differ in acidity by the difference in their heats of formation, the higher energy forms being more acidic.[7] Neither **1** nor **2** give any 91^- ion on treatment with HS^- or t-BuS^-. The bases were formed by electron impact on H_2S and t-BuSS-t-Bu, respectively. Both tautomers yield small amounts of 91^- ion when reacted with i-PrS^- and appreciable amounts from CH_3S^- and stronger bases. Since the isotoluenes are both 23 ± 3 kcal/mol more acidic than toluene,[7,8] the $\Delta H_f{}^\circ{}_{298}$ for **1** and **2** must likewise be 23 ± 3 kcal/mol above that of toluene, or 35 ± 3 kcal/mol. MNDO calculations agree with these experimental results, giving $\Delta H_f{}^\circ{}_{298}$ for **1** and **2** as 23 kcal/mol greater than that of toluene.[9] These calculations also find the most stable structures for both tautomers to be within 1 degree of planarity for the carbon skeletons. This contrasts with an electron diffraction study of the 5,5-dimethyl derivative of **2**, which was found to exist in a boat conformation with approximately 7° puckering at each end.[10] The MNDO method, however, often gives ring structures more planar than are experimentally observed.[9] The 91^- ion formed from **2** by the stronger bases exchanges only two protons with D_2O and CH_3OD, indicative of the benzyl structure.

For **2**, the apparent ionization potential in the ion cyclotron resonance spectrometer by both the vanishing current method and the parallel slopes method relative to toluene under identical conditions is 8.6 ± 0.1 eV or 0.2 eV less than that of toluene. This agrees with the absolute value from MNDO calculations of 8.67 eV, although we note that such calculations do not give a good value for the toluene IP. These results put the $M^{+}\cdot$ of **2** at about 18 kcal/mol higher in energy than $M^{+}\cdot$ for toluene. The MNDO calculations also predict that the ionization potentials of **1** and **2** are identical. The 70-eV electron impact mass spectrum of **2**, obtained on a Hewlett-Packard 5992 GC/MS, resembles that of toluene, save that the proportion of fragment ions relative to the 91^+ base peak was about twice as large for **2** as for toluene while the parent $M^{+}\cdot$ was smaller.

It has been postulated that the relative amounts of benzyl and tropyl cations in the $C_7H_7^+$ population can be determined on the basis of their reactivity. Deuterium labeling studies have shown that those $C_7H_7^+$ ions that are reactive with a wide variety of neutral compounds are probably of the benzyl structure,[4,5] while tropylium ion is known to be unreactive with most compounds.[4] We find that at 30-eV electron energy more than 90% of the 91^+ ions from **2** react with the neutral to give 105^+ ions but that the corresponding reaction in **1** proceeds for only ca. 40% of the originally formed $C_7H_7^+$. These data are compared in Figure 1 with data for other precursors. It has been stated that the ratio of the two $C_7H_7^+$ forms is not set by direct interconversion but by preequilibration of the parent $M^{+}\cdot$ ions and subsequent hydrogen loss.[5] We believe it significant that the tropylium population is appreciable only for those precursors that can give **3**, a logical intermediate to tropylium as shown, by a simple bond cleavage, as with norbornadiene, or by a 1,2-hydrogen shift, as with **1** or toluene.[11]

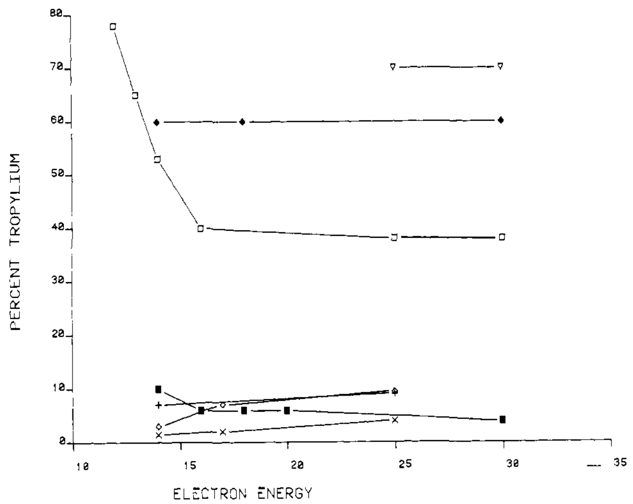
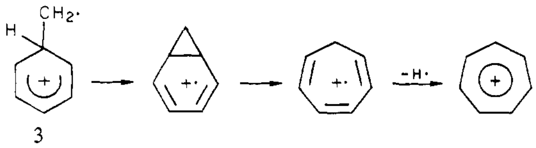


Figure 1. Percent of tropylium in the $C_7H_7^+$ population as a function of electron-impact energy on various precursors. (♦) **1**; (■) **2**; this work. (□) toluene; (▽) norbornadiene; (◇) benzyl chloride; (×) o-chlorotoluene; (+) m-chlorotoluene, ref 5.

Table I. Rate Constants and Efficiencies for Cationic Reactions of the Toluene Tautomers

	$92^+ \to 93^+$		$91^+ \to 105^+$	
tautomer	k^a	E^b	k^a	E^b
1	2.2	0.18	0.6	0.05
2	1.7	0.14	2.7	0.22
toluene	0.0	0.0^c	1.6	0.13

[a] Units of 10^{10} cm^3 $molecule^{-1}$ s^{-1}, ±20%. [b] Efficiency, k_{obsd}/k_{ADO}. [c] No 93^+ ion observed.



3

The other ion–molecule chemistry of **1** and **2** also differs significantly from that of toluene. The parent $M^{+}\cdot$ ions of **1** and **2**, unlike toluene, both react with their neutrals to give M + 1 ions. We assume protonation occurs on the exo-methylene group in **1** and **2** to give a ring-protonated toluene plus benzyl radical. That ion is the most stable of the possible products and should be identical for **1** and **2**, due to scrambling. Using literature values for $\Delta H_f{}^\circ$ for these species, plus the thermochemistry obtained in this work for the reactants, the $92^{+}\cdot$ to 93^+ reaction should be 37 ± 6 kcal/mol exothermic for **1** and **2** but 4 ± 3 kcal/mol endothermic for toluene. The rate constants in Table I for this proton-transfer reaction are comparable for **1** and **2**. In contrast, the alkylation rate for the benzyl ion reacting with the neutral to give 105^+ ion is appreciably faster for **2** than for **1**, as with the corresponding neutral chemistry.[6] The rates cannot be strictly compared with the reaction in toluene, since there is the possibility of different 105^+ structures in the reactions, such as 1-phenethyl vs. xylyl ions. Both **1** and **2** give many ionic products in the

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106–250 amu range, while toluene yields only a small amount of 128^+ and 129^+ above mass 105.

Acknowledgment. We thank J. J. Gajewski for the samples of **1** and **2** and for helpful discussions and the National Science Foundation for financial support.

Registry No. 1, 20679-59-8; **2**, 3217-87-6; toluene, 108-88-3.

Ziegler–Natta Polymerization: The Lanthanide Model[1]

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Contribution No. 4172 from the Central Research and Development Department, Experimental Station E. I. du Pont de Nemours and Company Wilmington, Delaware 19898

Received September 3, 1981

The formal insertion of an olefin into a metal–carbon (M–C) or metal–hydrogen (M–H) bond is of fundamental significance in a large number of catalytic reactions. While complexes arising from insertion of olefins into the M–H bond have been observed directly[2-4] primary insertion products from the analogous reaction with M–C bonds (reaction 1) have proved experimentally elusive.[5-8] The existence of the latter type of insertion product has often been inferred from the isolation of secondary products which derive from the initial insertion product via such processes as β-hydrogen elimination[9,10] (reaction 2) or further olefin insertion[11] (reaction 3).

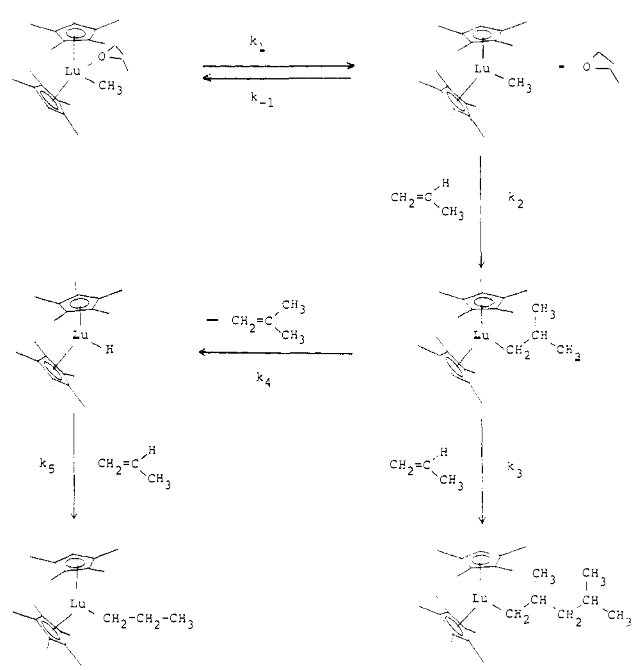
$$L_nM{-}CR_3 + CH_2{=}CH_2 \rightarrow L_nM{-}CH_2{-}CH_2{-}CR_3 \qquad (1)$$

$$L_nM{-}CH_2{-}CH_2{-}CR_3 \rightarrow L_nM{-}H + CH_2{=}CH{-}CR_3 \qquad (2)$$

$$L_nM{-}CH_2{-}CH_2{-}CR_3 + CH_2{=}CH_2 \rightarrow L_n{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CR_3 \qquad (3)$$

The direct insertion shown in reaction 3 has been postulated[12] to be a major reaction pathway for olefin polymerization using Ziegler–Natta catalysts[13,14] (group 6 transition metal with aluminum alkyl). One important difference between this insertion mechanism[15] and the alternative McKinney[16] or Green[17] mechanisms for olefin polymerization is that the latter two schemes require oxidative additions in order to generate the active metallacyclic or carbenoid intermediates. While these routes may be reasonable for transition metals having at least two d electrons, they are not so reasonable for the lanthanide elements where reversible two-electron couples are generally precluded by the lack of accessible oxidation states.

Scheme I



During our investigations of the reactivity of lanthanide–carbon bonds, we observe insertion of a variety of olefins and acetylenes into the ytterbium- and lutetium-methyl bonds of $M(\eta^5\text{-}C_5Me_5)_2CH_3\cdot$ether (M = Yb, Lu). In these reactions the primary insertion products are observable by spectroscopic and chemical techniques. This preliminary communication describes the synthesis of $M(\eta^5\text{-}C_5Me_5)_2CH_3\cdot$ether (**1**, M = Lu) and the reaction of **1** with propene to give the isobutyl complex $M(\eta^5\text{-}C_5Me_5)_2{-}CH_2{-}CH(CH_3)_2$ (**2**, M = Lu). The chemistry of $Lu(\eta^5\text{-}C_5Me_5)_2CH_3\cdot$ether and $Yb(\eta^5\text{-}C_5Me_5)_2CH_3\cdot$ether is qualitatively similar with respect to the olefin insertion reaction.

The dimethyl complexes $[M(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li(THF)_3$ (M = Yb, Lu) are prepared as described[18] earlier for M = Yb. Conversion of these complexes to the neutral monomethyl species is achieved in several steps. The THF-free materials, $[M(\eta^5\text{-}C_5Me_5)_2(CH_3)_2]Li$ (obtained from the solvated precursors by heating under vacuum at 75 °C), react with $Al(CH_3)_3$ in pentane to give the soluble adducts $M(\eta^5\text{-}C_5Me_5)_2Al(CH_3)_4$.[19] Cleavage of these adducts by dissolution in diethyl ether yields $M(\eta^5\text{-}C_5Me_5)_2CH_3\cdot$ether (M = Yb, Lu)[20,21] which can be crystallized

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[19] These complexes have been completely characterized. Anal. Calcd for $C_{24}H_{42}AlYb$: C, 54.32; H, 7.98; Al, 5.09; Yb, 32.61. Found: C, 54.05; H, 8.04; Al, 4.98; Yb, 32.81. Calcd for $C_{24}H_{42}AlLu$: C, 54.13; H, 7.95; Al, 5.07; Lu, 32.86. Found: C, 53.98; H, 7.94; Al, 5.13; Lu, 32.74. The analogous parent cyclopentadienyl complexes have been structurally characterized: Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45–53, 54–61.

[20] These complexes have been completely characterized. Anal. Calcd for $C_{25}H_{43}OYb$: C, 55.37; H, 8.14; O, 3.00; Yb, 32.49. Found: C, 56.05; H, 8.13; O, 2.90; Yb, 32.40. Calcd for $C_{25}H_{43}OLu$: C, 56.16; H, 8.11; O, 2.99; Lu, 32.73. Found: C, 55.97; H, 8.00; O, 2.90; Lu, 32.90. Also, quantitative measurements of the amounts of CH_4 and C_5Me_5H released upon hydrolysis of $M(C_5Me_5)_2CH_3\cdot$ether (M = Yb, Lu) are satisfactory.

0002-7863/82/1504-0337$01.25/0