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Mechanistic Aspects of the Titanocene Dichloride–Isopropyl Grignard Reduction of Alkyl Bromides

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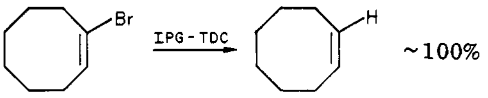
The stereochemistry of the reductions of *cis*- and *trans*-4-methylcyclohexyl-*1-d* bromide with the system isopropylmagnesium bromide–5% dicyclopentadienyltitanium dichloride (argon) and of the unlabeled bromides with (isopropyl-d_8)magnesium bromide–dicyclopentadienyltitanium dichloride has been determined by ^{2}H NMR analysis of the resulting *cis*- and *trans*-4-methylcyclohexane-*1-d*. Complete stereoequilibration occurs in some step and predominantly *equatorial* hydrogen (or deuterium) abstraction by the presumed 4-methylcyclohexyl radical is indicated. Radical involvement is confirmed by the identification of substantial amounts of cyclized hydrocarbons in the reduction of 6-bromo-hex-1-ene and 6-bromo-hept-1-ene, whereas complete cyclization and hydrogen abstraction to provide 3-methyltetrahydrofuran characterises the reduction of 2-(allyloxy)ethyl bromide. Preliminary experiments suggest that titanocene dichloride only feebly catalyzes the reduction of secondary bromides by sodium borohydride under aerobic conditions in *N*,*N*-dimethylformamide, such reductions nevertheless proceeding with predominant inversion of configuration. Cyclized hydrocarbons from suitable bromo precursors (above) were not observed, indicating a minor role for free radicals in this system. A report that dicyclopentadienyltitanium dichloride experiences a dimethyl sulfoxide induced $\pi \rightarrow \sigma$ rearrangement of both cyclopentadientyl groups is shown to be incorrect.

Introduction

Reduction of alkyl or aryl bromides to the corresponding hydrocarbons is a frequently desired transformation, and a number of recently reported procedures involve "activation" by transition-metal complexes of various types.[2–7] A simple and highly efficient procedure[8] for reducing vinyl, aryl and alkyl bromides in ether at room temperature employs isopropylmagnesium bromide in the presence of catalytic amounts (~5%) of titanocene dichloride ((η^5-$C_5H_5)_2TiCl_2$), as shown in eq 1 and 2. (This reducing system will be represented as IPG–TDC for convenience.)



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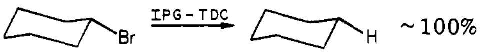
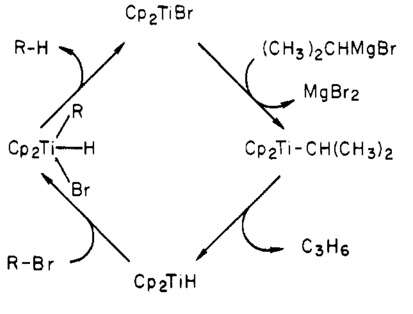


(2)

The key species in the catalytic cycle was considered to be [Cp_2TiH][9] (Cp = η^5-C_5H_5) which experienced oxidative addition of R–Br, followed by loss of R–H as shown in eq 3.



(3)

Although the relative ease of this procedure and the reported[8] high yields of hydrocarbon are attractive, insufficient is known about the proposed key steps to permit a judgement whether this reduction follows a useful stereochemical course which might allow the introduction of deuterium stereoselectively into alkyl systems. This matter forms the basis of this report. Some observations of mechanistic significance on the system sodium borohydride–Cp_2TiCl_2–DMF–air[7] are also reported.

Results and Discussion

To provide insight into the overall stereochemistry of the change R–Br → R–H for a cycloalkyl system, we examined initially[8] the reduction of *cis*- and *trans*-4-methylcyclohexyl bromides which were deuterium labeled at C-1. As demonstrated elsewhere,[10] ^{2}H NMR spectroscopy is the method of choice for determining the stereochemical situation in ^{2}H-substituted alkylcyclohexanes. Reaction of either cis or trans bromide with the IPG–TDC reagent provided essentially the same mixture of *cis*- and *trans*-4-methylcyclohexane-*1-d* in moderate yields (60–70%) (Table I).

Trace quantities of 4-methylcyclohex-1-ene-*1-d* formed in the reduction of the cis bromide, but larger amounts (7–14%) accompanied reduction of the trans bromide.

Reductions of *cis*- and *trans*-4-methylcyclohexyl bromides with $(CD_3)_2CHMgBr$–Cp_2TiCl_2 (IPG-d_6–TDC) were also conducted, and the major product was *trans*-4-methylcyclohexane-*1-d* (~65%) as determined by direct ^{2}H NMR analysis (Table 1).

This analysis is rendered imprecise by the ^{2}H signals at 0.80 and 1.00 ppm (minor) associated with the product from coupling of the Grignard reagent, which is

$$(CD_3)_2CHMgBr \rightarrow (CD_3)_2CH\text{-}CH\text{-}(CD_3)_2$$

employed in a 5–10-fold excess over the alkyl bromide. Hence, a minor degree of coupling, which accompanies most Grignard preparations, will give rise to ^{2}H signals comparable in intensity with those of the ^{2}H-substituted methylcyclohexane. Deliberate coupling of the ^{2}H-labeled Grignard reagent with Cu^I provided 2,3-dimethylbutane with a major ^{2}H signal at δ 0.75 and a minor one at δ 1.03,

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[1] To whom correspondence should be addressed.

[2] Masamune, S.; Bates, G. S.; Georghiou *J. Am. Chem. Soc.* **1974**, *96*, 3866.

[3] Tyrlik, S.; Wolvehowiez, I. *J. Chem. Soc., Chem. Commun.* **1975**, 781.

[4] Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1978**, *43*, 1263.

[5] Lin, S. T.; Roth, J. A. *J. Org. Chem.* **1979**, *44*, 309.

[6] See also: Felkin, H.; Swierczewski, G. *Tetrahedron* **1975**, *31*, 2735.

[7] Meunier, B. *J. Organomet. Chem.* **1981**, *204*, 345.

[8] Colomer, E.; Corriu, R. *J. Organomet. Chem.* **1974**, *82*, 367.

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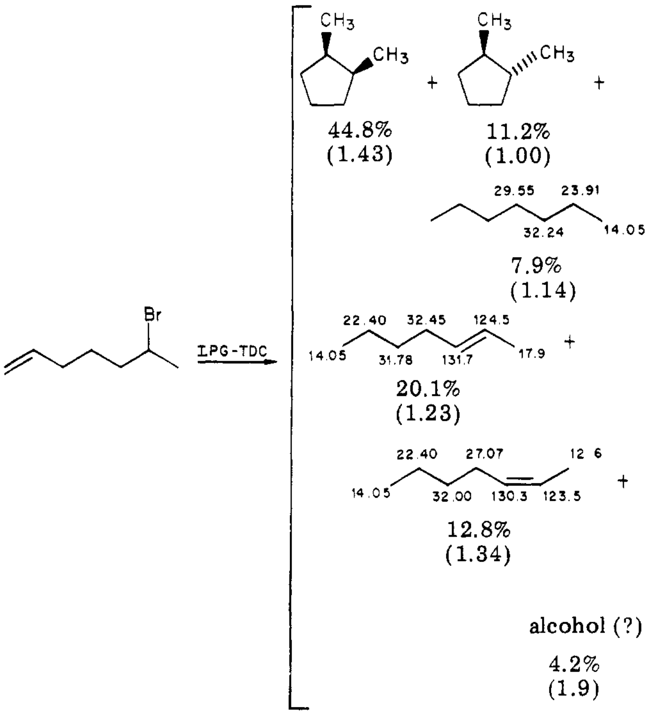
Table I. Product Distributions in Reductions of 4-Methylcyclohexyl Bromides

		products[a]			
bromide	reducing system				yield,[b,f] %
	IPG-TDC[c]	70	30	trace	~45
	IPG-TDC[c]	67	33	trace	56
	IPG-TDC	71	22	7	59
	IPG-TDC	64	21	14	53
	IPG-d_6-TDC[d]	~33	~66	e	59
	IPG-d_6-TDC[d]	~33	~66	e	53
	IPG-d_6-TDC	~35	~65	e	61
	IPG-d_6-TDG	~35	~65	e	50

[a] Based on integrated ^{2}H NMR spectra of signals (relative to internal C^2HCl_3 at δ 7.24) at ca. δ 1.09 (axial ^{2}H), δ 1.60 (equatorial ^{2}H), and δ 5.8 (vinylic ^{2}H). [b] Based on VPC comparisons against an internal standard of isooctane after work-up, extraction etc. [c] IPG-TDC represents isopropyl-Grignard-titanocene dichloride in the ratio RBr:IPG:TDC = 20:100:1. [d] IPG-d_6-TDC represents isopropyl Grignard-titanocene dichloride with CD_3 labels in the isopropyl groups. [e] Alkene would have vinylic-^{1}H and therefore not detectable by ^{2}H NMR analysis. [f] Yields not optimised and some loss of volatile hydrocarbons during quenching, work-up etc. almost certainly occurred. Yield figures do not include alcohol component.

Scheme I

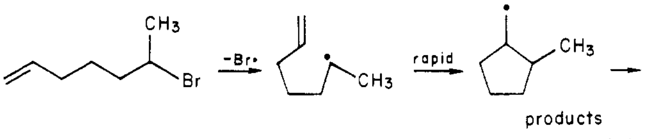


indicating slight scrambling to the methine position.

The experiments confirm the β-position of the 2-propyl group to be the source of hydrogen, as proposed, and the incorporation is preferentially from the *equatorial* direction. These results are summarised in Table I.

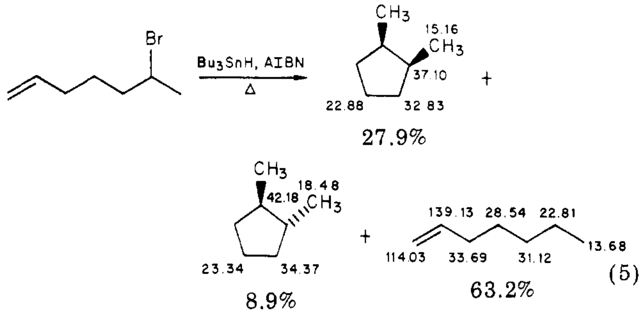
The apparently complete stereoequilibration accompanying the reductions of the 4-methylcyclohexylbromides is strongly suggestive of free radical involvement in at least one step of the overall transformation.[10-13] Furthermore, the results demonstrate a favoured *equatorial* abstraction of H· (or D·) by the suggested 4-methylcyclohexyl radical, a result with some precedent.[13,14]

To test further the proposal of free radical involvement, the reduction of the secondary 6-bromo-1-heptene was examined, as the radical (loss of Br·) is known to cyclize rapidly and irreversibly to yield (2-methylcyclopentyl)-methyl products, as shown in eq 4.[12,15,16]



cis/trans = 2.7-3.0 (4)

For calibration purposes, reduction was conducted initially by using tributylstannane–AIBN (an established free radical system)[15,16] and ^{13}C NMR analysis and capillary VPC provided the following, with $k_{cis}/k_{trans} \simeq 3.0$ (^{13}C assignments (given in ppm) indicated; see eq 5).



(5)

Reduction with IPG–TDC under the usual conditions, provided a mixture of hydrocarbons with *cis*-1,2-dimethylcyclopentane predominating. The product profile shown in Scheme I is based on ^{13}C NMR (given in ppm) and capillary VPC analyses. (Values in parentheses are retention times relative to *trans*-1,2-dimethylcyclopentane.) The suspected hept-2-enes produced above were confirmed as such by comparison (VPC behavior, enhancement of coinjenction and ^{13}C shifts) with samples

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(11) Kitching, W.; Olszowy, H.; Waugh, J.; Doddrell, D. *J. Org. Chem.* **1978**, *43*, 898.

(12) Kitching, W.; Olszowy, H.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893.

(13) Kitching, W.; Olszowy, H.; Harvey, K. *J. Org. Chem.* **1981**, *46*, 2423.

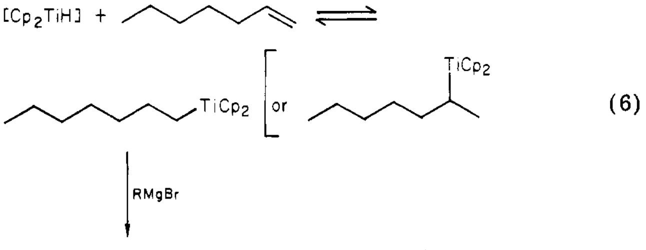
(14) See: Jensen, F. R.; Gale, L. H.; Rodgers, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 5793.

(15) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.

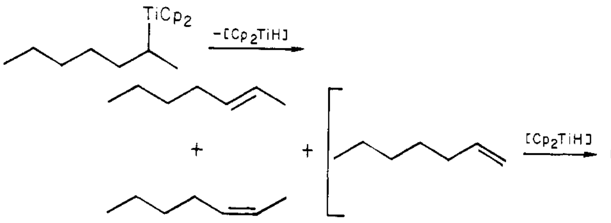
(16) Beckwith, A. L. J.; Blair, I.; Phillipou, G. *J. Am. Chem. Soc.* **1974**, *96*, 1613. Beckwith, A. L. J.; Lawrence, T. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1535.

obtained by either (basic) dehydrohalogenation of 2-bromoheptane or isomerization of 1-heptene by potassium *tert*-butoxide in dimethyl sulfoxide,[17] the latter procedure known to produce initially a predominance of the *cis*-hept-2-ene.

The production of *cis*- and *trans*-1,2-dimethylcyclopentanes, in the appropriate ratio, confirms involvement at some stage of the hept-6-en-2-yl radical, consistent with the findings for the cyclohexyl bromides. The formation of heptane and *cis*- and *trans*-hept-2-ene, and the lack of hept-1-ene suggests the latter if formed initially, is being "hydrogenated" and/or isomerized to the less reactive hept-2-enes. Cooper and Finkbeiner[18] have demonstrated that 1-alkenes undergo exchange with Grignard reagents in the presence of $TiCl_4$, and the sequence shown in eq 6, involving exchange followed by hydrolytic workup, would account for heptane production. The reversible nature of the addition $[Cp_2TiH]$ to 1-alkenes and formation of some secondary titanium addition product would account for the production and accumulation of 2-heptenes, which do not undergo the titanium-catalyzed Grignard exchange reaction (eq 7).[18] A minor product in the reduction (relative retention time 1.9; 4.2%) was considered to be an alcohol (^{13}C shift of δ 64.33) but its identity was not established.

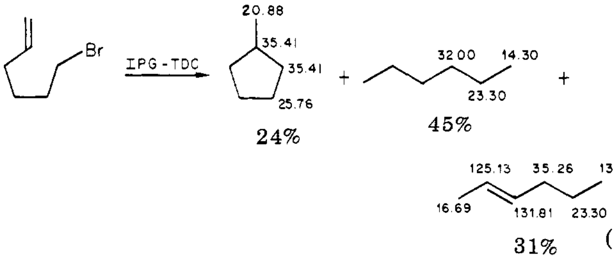


(6)



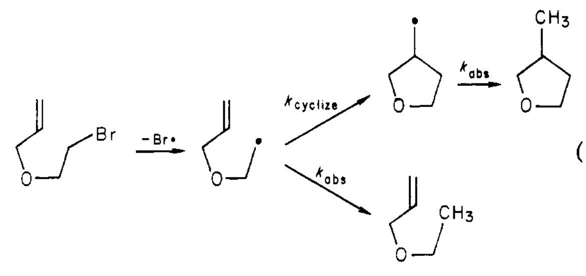
(7)

The evidence above demonstrates the involvement of free radicals in IPG–TDC reduction of secondary bromides, but because of the lowered reactivity of secondary bromides in direct (nucleophilic) displacement, it could not be assumed that radical intermediates were just as important in reduction of primary bromides. Utilizing the information that hex-5-en-1-yl radical also cyclizes rapidly and irreversibly to provide cyclopentylmethyl product,[15,16] we examined the reduction of the primary 6-bromo-1-hexene, the outcome of which is shown in eq 8 (^{13}C shifts (given in ppm) are shown). The hydrogenation and isomerization of hex-1-ene would proceed as outlined for hept-1-ene. Several unidentified minor products were also formed, and some are known to contain trans double bonds by the vinylic ^{13}C pattern, and the lack of C-1 absorption at high field (ca. 11 ppm) for a *cis*-hex-2-enyl moiety.

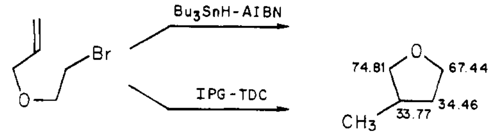


(8)

The result above is persuasive that free radicals are involved in the reduction of primary bromides, and confirmation was sought by examining 2-(allyloxy)ethyl bromide, the radical from which is considered[16,19] to cyclize about 1 order of magnitude faster than hex-5-en-1-yl radical, to yield 3-methyltetrahydrofuran after H· abstraction (eq 9).[20] Treatment of 2-(allyloxy)ethyl bromide with Bu_3SnH–AIBN in benzene provided by 3-methyltetrahydrofuran, as judged by the ^{13}C spectrum (given in ppm eq 10). A similar reduction with IPG–TDC produced 3-methyltetrahydrofuran predominantly, together with some minor product(s) which were not alcohols, allyl ethyl ether or ethyl propyl ether. (Authentic allyl ethyl ether (H· abstraction prior to cyclization) and its hydrogenated relative, ethyl propyl ether, were available for comparison).



(9)



(10)

We conclude that free radicals are the intermediates in at least one step of the IPG–TDC reductions of primary and secondary bromides and reduce the synthetic utility in systems where stereocontrol is required or radical rearrangement is likely. Another disadvantage is that excess Grignard reagent is employed, which limits the application when Grignard-sensitive functionality is present. From a mechanistic viewpoint, it is difficult to decide the step most likely to involve the radical, as the precise nature of the active species is not clear and movement between the various oxidation states of titanium is relatively facile.[9] $[Cp_2TiH]$ is paramagnetic, and either free radical oxidative addition to form $Cp_2(H\text{-})Ti(\text{-}R)\text{-}Br$ or atom transfer from R–Br could be involved. Considering the likely weakness of the Ti–H bond,[21] this would serve as a ready hydrogen (or ^2H) atom donor.

In an effort to prepare a technically more appealing reducing system based on TDC, we have employed sodium borohydride as a hydrogen source and examined some reactions of this system (NBH–TDC) which has recently been reported[7] to be effective for selective reduction of aromatic bromides or iodides. A feature of reducing systems based on sodium borohydride–transition metal complexes is the requirement that *N,N*-dimethylformamide

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(17) Price, C. C.; Snyder, W. H. *J. Am. Chem. Soc.* **1961**, *83*, 1773.

(18) Cooper, G. D.; Finkbeiner, H. L. *J. Org. Chem.* **1962**, *27*, 1493.

(19) Beckwith, A. L. J.; Gara, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 796. Carlsson, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1968**, *90*, 7047.

(20) See: Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902 for use of 2-(allyloxy)ethyl bromide in reductions by (η^5-cyclopentadienyl)tricarbonylhydridovanadate.

(21) A Ti–H bond energy of ca. 58 kcal has been estimated. See: Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(DMF) be used as solvent,[5,7] and in some cases an aerobic atmosphere is specified.[7] The possible function of DMF was intriguing considering its capability for strong O-coordination, particularly favored for titanium. It occurred to us that the report of Tsutsui and Hudman[22] that "the reaction between TDC and dimethyl sulfoxide (Me_2SO) at 70 °C resulted in π–σ rearrangement of both cyclopentadienyl groups" might be of relevance, as a η^1-C_5H_5Ti species might be especially labile and play a crucial role in TDC-catalyzed reactions in coordinating solvents. However, some aspects of the report,[22] reiterated in a later review,[23] were unconvincing, and we have reexamined the system to find that no π–σ rearrangement is involved but merely hydrolytic breakdown to cyclopentadiene and (later) dicyclopentadiene.

The evidence presented[22,23] for the irreversible formation of the nonfluxional σ-bonded species was as follows. (i) The singlet at δ 6.7 (τ 3.3) associated with titanocene dichloride diminished in intensity as a new signal, centered at δ 6.55 (τ 3.45), emerged. The new pattern was considered to be the AA′BB′ part of an AA′BB′X system, although the X part, presumably the methine proton of the assumed η^1-C_5H_5 group, was not located. Cooling the solution from 70 to 0 °C induced no change in the spectrum (ii) Addition of maleic anhydride to the reaction mixture led to the isolation of an adduct of cyclopentadiene.[24] A pale violet solid was reported to form on addition of diethyl ether to the Me_2SO reaction mixture, and on drying, this precipitate became brown. An elemental analysis corresponded reasonably with $C_{10}H_{10}TiCl_2{\cdot}4Me_2SO$, but a duplicate analysis did not. The ^1H NMR spectrum (Me_2SO) was reported to exhibit signals at δ 6.95 (τ 3.05) (1 H, t) and δ 6.50 (τ 3.50) (2 H, d) and a singlet at δ 3.0 (τ 7.0) (18–24 H) assigned to coordinated Me_2SO. The signals at δ 6.95 and 6.50 were not assigned.

A sample of titanocene dichloride, dissolved in purified Me_2SO (or Me_2SO-d_6) (orange-red solution), was sealed in a 5-mm NMR tube and heated at ca. 70 °C. After 3 h, the (initial) signal at δ 6.7 had diminished in intensity and new patterns at δ 6.5 and 2.9 in the ratio of 4:2 had emerged. After 5 h, the signal at δ 6.7 was absent and the solution was dark brown, with precipitation on some occasions. The new absorptions corresponded precisely in shape and position with those of cyclopentadiene (in Me_2SO) and the very minor ones with those of dicyclopentadiene. The ^{13}C spectrum showed major signals (relative to Me_4Si) at 133.3, 132.3, and 41.6 ppm, again in agreement with those of authentic cyclopentadiene. It is likely that the ^1H signal at δ 3.0, attributed by Tsutsui[22] to coordinated Me_2SO, corresponds to the methylene protons of cyclopentadiene. Other experiments indicated that added water and the nature of the atmosphere could influence the transformation, but there was pronounced irreproducibility in these experiments in regard to the rate of disappearance of titanocene dichloride. We did not investigate thoroughly the constitution of the precipitates reported,[22] which on the bases of analyses and ^1H NMR data appeared to be inhomogeneous.

Thus there is no evidence for the irreversible formation of a η^1-C_5H_5 titanium species[25] when titanocene dichloride is heated in Me_2SO. It is conceivable that the cyclopentadiene results from the protic capture of such a species (necessarily present in quite low concn.), but the details of cyclopentadiene formation are unclear. Given the ready $Ti^{IV} \rightleftharpoons Ti^{III}$ interconversion,[9] free radical pathways are also reasonable and could be consistent with the apparent influence of the atmosphere and other observations. Titanocene dichloride under the same conditions in *N,N*-dimethylformamide is stable.

The addition of a catalytic amount of TDC to sodium borohydride in DMF caused a vigorous reaction with gas evolution and development of a deep purple color.[26] Cyclohexyl bromide was added to the mixture, and the purple color faded, with reduction complete (VPC) after ca. 12 h. This represents a slight diminution in the time required without TDC (18 h), but the reaction is still inconveniently slow. The stereochemistry of this reduction was investigated briefly, and predominant inversion of configuration was observed in the formation of the 4-methylcyclohexane-*1-d*. Considering that catalytic quantities of TDC were used and that the reaction is slow, direct (S_N2) displacement by $NaBH_4$ (or $NaBD_4$) may be occurring as a predominant pathway,[27] with only a slight involvement of the assumed Cp_2TiBH_4 in the reduction process. 4-Methylcyclohexanols are formed in significant amounts (5–20%) with a 1:1 cis/trans ratio, suggestive of oxygenation of the 4-methylcyclohexyl radical. Reduction of 6-bromo-1-heptene and 6-bromo-1-hexene were also conducted, and no cyclized products (indicating free radical involvement) were detected by capillary VPC and ^{13}C NMR. Use of stoichiometric amounts of TDC with formations of Cp_2TiBH_4 may cause faster reduction, but this lacks the attraction of a "cataytic" system and necessarily be highly comsumptive of TDC.

Experimental Section

(a) Procedure for Reduction by Titanocene Dichloride–Isopropyl Grignard Reagent. The Grignard reagent from 2-bromopropane was prepared in ether (argon atmosphere) in the normal way, and this solution (40 mL of 1 M solution) was filtered (under argon) into the reaction vessel, which was cooled to 0 °C. Cp_2TiCl_2 (TDC) (70 mg, 0.288 mmol) was added, and the reaction mixture became dark brown, and gas evolution was noted. 4-Methylcyclohexyl bromide (996 mg, 5.62 mmol) was added immediately, and the reaction mixture was allowed to stir for 3 h or until reaction was complete (VPC). The saturated ammonium chloride solution (~20 mL) was then added dropwise to the cooled (~0 °C) reaction mixture. The organic layer was separated and added to the ether extracts (2 × 15 mL) of the aqueous layer. The combined ethereal solutions were dried ($MgSO_4$) and examined by VPC and NMR.

The molar ratio of reagents was TDC:RBr:$(CH_3)_2CHMgBr$ = 1:20:100.

(b) Procedure for Reduction by Titanocene Dichloride–Sodium Borohydride in DMF. To a round-bottomed flask fitted with a condenser and drying tube were added sodium borohydride (378 mg, 20 mmol) and TDC (62 mg, 0.25 mmol). The addition of *N,N*-dimethylformamide (DMF) (10 mL) resulted in an exothermic reaction, accompanied by gas evolution and development of a deep purple color. The organic halide (2.5 mmol) was added to the stirred reaction mixture, which was then heated (70 °C) and monitored (VPC). As reduction proceeded, the purple color faded with the formation of gray-yellow or brown products. On completion of reaction (VPC), water (10 mL) was added dropwise and the mixture extracted thoroughly with ether (3 × 10 mL); such extracts were then dried ($MgSO_4$) and examined as described above.

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[22] Tsutsui, M.; Hudman, C. E. *Chem. Lett.* **1972**, 777.

[23] Tsutsui, M.; Courtney, A. *Adv. Organomet. Chem.* **1977**, *16*, 247.

[24] Wilkinson and Piper (Wilkinson, G.; Piper, T. S. *J. Inorg. Nucl. Chem.* **1956**, *2*, 32) adduced evidence for the 1,3-dienyl nature of $(\eta^1$-$C_5H_5)_2Hg$ by isolation of a maleic anhydride adduct containing the Hg atom.

[25] See also: Calderon, J. L.; Cotton, F. A.; Takats, J. *J. Am. Chem. Soc.* **1971**, *93*, 3592. Calderon, J. L.; Cotton, F. A.; De Beer, B. G.; Takats, J. *Ibid.* **1971**, *93*, 3587. Siegent, F.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *20*, 141.

[26] Nöth, H.; Hartwimmer, R. *Chem. Ber.* **1959**, *93*, 2233.

[27] Hutchins, R. O.; Kandasamy, K.; Dux, F., III; Maryanoff, C. A.; Rotstein, D.; Goldsmith, B.; Burgoyne, W.; Cistone, F.; Dalessandro, J.; Puglis, J. *J. Org. Chem.* **1978**, *43*, 2259.

Compounds. *cis*- and *trans*-4-methylcyclohexyl-*1*-*d* bromide were obtained by applying reported procedures to 4-methylcyclohexan-ol-*1*-*d*.[10,12,28] Reduction of acetone-d_6 with $LiAlH_4$ followed by bromination in the reported fashion[24] provided 2-bromopropane-d_6.

5-Bromo-1-hexene was commercially available and 6-bromo-1-heptene was prepared in the reported way, as was tributylstannane-*d*.[12,13]

2-(Allyloxy)ethyl Bromide. Phosphorus tribromide (16.26 g, 0.06 mol) was placed in a vacuum distillation flask through which nitrogen was passed. A mixture of 2-(allyloxy)ethanol (from ethylene glycol, sodium, and allyl bromide) (17 g, 0.17 mol) and dry pyridine (4.39 g, 0.06 mol) was then added dropwise to the well-stirred, cooled (−5 °C) neat PBr_3 mixture during a period of approximately 90 min. After addition was complete, stirring was maintained at −5 °C for 30 min followed by 2 h at room temperature. The 2-(allyloxy)ethyl bromide was distilled from the flask: bp 28–30 °C (4 mm) (lit.[20] 20–40 °C (4 mm));[20] IR (neat) 1640 (w) ($\nu_{C=C}$), 1100 (s) (ν_{C-O}); ^1H NMR δ 5.8 (m, 1 H), 5.2 (m, 2 H), 3.9 (d, 2 H), 3.6 (t, 2 H), 3.3 (t, 2 H). Anal. Calcd for C_5H_9OBr: C, 36.39; H, 5.50; Br, 48.42. Found: C, 36.69; H, 5.59, Br, 48.4.

Spectra. ^1H NMR spectra were recorded on a JEOL MH-100 or a Varian EM-360 spectrometer for $CDCl_3$ solutions and referenced to residual $CHCl_3$ (7.24 ppm) or $(CH_3)_4Si$. ^{13}C and ^2H spectra were obtained on a JEOL FX-100 spectrometer operating in the FT mode for $CDCl_3$ or $CHCl_3$ solutions and referenced to the central peak of the $CDCl_3$ triplet at 77.00 ppm or internal Me_4Si. ^2H spectra were referenced to internal $CDCl_3$ (7.24 ppm).

Capillary gas chromatography was performed on a Varian Model 3700 gas chromatograph using a 50-ft OV101 capillary column. The column temperature was set at 40 °C, injector at 100 °C, and detector at 100 °C. Hewlett-Packard 5720A and 1874A gas chromatographs were also employed with injector temperature at 100 °C and detector at 150 °C and with column temperature varying from 50 to 100 °C, using a Chromosorb G packed column.

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Registry No. Cp_2TiCl_2, 1271-19-8; 2-bromopropane, 75-26-3; 5-bromo-1-hexene, 4558-27-4; 6-bromo-1-heptene, 38334-98-4; 2-(allyloxy)ethyl bromide, 15424-04-1; 2-(allyloxy)ethanol, 111-45-5; *cis*-4-methylcyclohexyl-*1*-*d* bromide, 82093-84-3; *trans*-4-methylcyclohexyl-*1*-*d* bromide, 82093-85-4; *cis*-4-methylcyclohexyl bromide, 28046-90-4; *trans*-4-methylcyclohexyl bromide, 28046-91-5.

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Communications

Induction of Olefin Metathesis by Phenylacetylene plus Tungsten Hexachloride

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Summary: Phenylacetylene induces tungsten hexachloride to initiate metatheses of *cis*-2-pentene, cyclopentene, cycloheptene, and cyclooctene. In too large amounts, however, it is ineffective. The reactions are run in the atmosphere. The stereoselectivities for cis olefins are moderate.

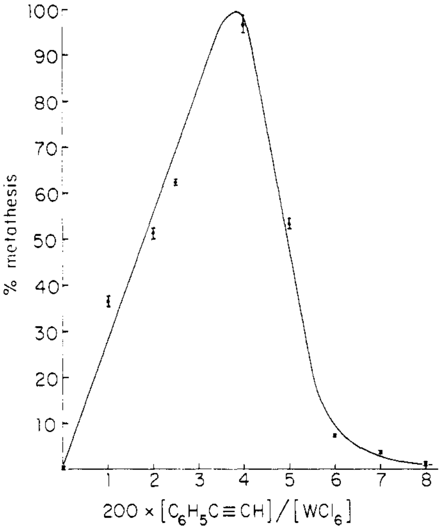

Figure 1. The extent of reaction according to eq 1 as a function of *x*. Percent metathesis is recorded as $200r/(1 + 2r)$, where *r* is the ratio in moles of either 2-butene to 2-pentene or 3-hexene to 2-pentene. The bars span the two values associated with *r* measured in the two ways.

The discovery by Masuda et al. that tungsten hexachloride initiates polymerization of phenylacetylene[1] suggests the following proposition: that phenylacetylene may effectively replace the highly reactive organoaluminum component in the mixture with tungsten hexachloride that is the archetypical[2] and still standard initiator for olefin metathesis.[3] For if the metal-catalyzed polymerization of acetylenes is an olefin metathesis,[4-6] a metallic compound that induces an acetylene to polymerize should itself be induced by the acetylene to metathesize olefins. The idea was demonstrated recently with phenylacetylene plus (phenylmethoxycarbene)penta-

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