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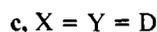
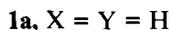
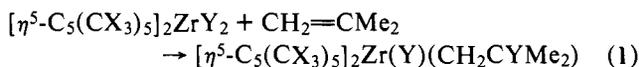
Reductive Elimination of Isobutane from an Isobutyl Hydride Derivative of Bis(pentamethylcyclopentadienyl)zirconium

Sir:

The majority of transition metal complexes bearing *cis*-hydride and alkyl ligands are evidence only by the detection of alkane, presumably generated by facile reductive elimination from the unstable hydridoalkyl compounds.¹ In several cases such intermediates have been characterized in solution,^{1,2} but there appear to be very few hydridoalkyl metal complexes which are sufficiently stable for their isolation at room temperature.^{3–7} Consequently there have been few systematic investigations of this important class of compounds with regard to the preferred modes of decomposition or their reactivity toward H₂, olefins, or donor ligands.

The paucity of stable hydridoalkyl compounds has been recognized by Norton,⁶ who noted further that, within a homologous series of *cis*-dihydrido-, -dialkyl-, and -hydridoalkyl metal complexes, the last is always least stable. This same relative order of stability is displayed within the homologous series of bis(pentamethylcyclopentadienyl)zirconium(IV) compounds. Thus, while toluene solutions of the dihydrido derivative, (η⁵-C₅Me₅)₂ZrH₂,⁸ and dimethyl derivative, (η⁵-C₅Me₅)₂Zr(CH₃)₂,⁹ are stable for weeks at 100 °C, the isobutyl hydride complex, (η⁵-C₅Me₅)₂Zr(H)(CH₂CHMe₂) (**1**),⁹ decomposes during the course of several hours at 75 °C providing isobutane quantitatively (NMR). Isobutane is formed at lower temperatures during the reaction of **1** with ethylene (25 °C) or H₂ (–15 °C). The relatively high thermal stability of **1**, the ease with which regiospecific deuterium labeling of **1** can be accomplished,^{10,11} and the clean, stoichiometric character of these reactions have permitted some studies, reported herein, which bear on the mechanism of isobutane formation in this system.

[η⁵-C₅(CH₃)₅]₂Zr(H)(CH₂CHMe₂) (**1a**), [η⁵-C₅(CH₃)₅]₂Zr(D)(CH₂CDMe₂) (**1b**), and [η⁵-C₅(CD₃)₅]₂Zr(D)(CH₂CDMe₂) (**1c**) are obtained quantitatively (NMR) via treatment of benzene solutions of [η⁵-C₅(CH₃)₅]₂ZrH₂, [η⁵-C₅(CH₃)₅]₂ZrD₂, and [η⁵-C₅(CD₃)₅]₂ZrD₂, respectively, with isobutylene at 25 °C (eq 1). Compound **1** may be isolated as a pale yellow microcrystalline material, which on the basis of analytical, IR, ¹H NMR,⁹ and molecular weight data¹² appears to have the normal monomeric, pseudotetrahedral arrangement of ligands around Zr.



When pyrolyzed in benzene or toluene solution in vacuo at 74 °C, **1** quantitatively liberates isobutane (NMR). Under these conditions the organozirconium products appear to un-

Table I. Isotopic Distribution of Isobutanes Obtained from **1a**, **1b**, and **1c**

	solvent	product
		Pyrolysis
1a	C ₇ D ₈	CH ₃ CH(CH ₃) ₂ (2a)
1b	C ₇ D ₈	CH ₃ CD(CH ₃) ₂ (2b)
1c	C ₇ H ₈	CH ₂ D ₂ CD(CH ₃) ₂ (2c)
1a + 1c	C ₇ H ₈	2a + 2c
		Reaction with H ₂
1a	C ₆ D ₆	2a
1b	C ₇ D ₈	2b
1c	C ₇ D ₈	2b
		Reaction with D ₂
1a	C ₇ H ₈	(CH ₂ D)CH(CH ₃) ₂ (2d)
1b	C ₇ D ₈	2c
		Reaction with C ₂ H ₄
1a	C ₆ D ₆	2a
1b	C ₇ D ₈	2b (+2c) ^a
		Reaction with C ₂ D ₄
1a	C ₇ D ₈	2a + 2d ^b

^a Not detected; large excess of C₂H₄ used. ^b See text.

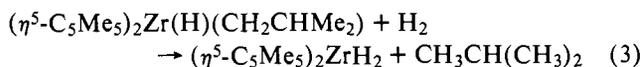
dergo further reaction(s) and the final products have not all been identified.¹³ Nonetheless, the rate of disappearance of **1** and the rate of appearance of isobutane, monitored by ¹H NMR spectrometry (benzene-*d*₆), are in very good agreement and obey a first-order relationship

$$-d[\mathbf{1a}]/dt = d[\text{CHMe}_3]/dt = k_{\mathbf{1a}}[\mathbf{1a}] \quad (2)$$

with $k_{\mathbf{1a}} = (7.2 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ at 74 °C. Activation parameters, calculated from rate data obtained at 105, 90, and 74 °C were $\Delta H^\ddagger = 21 \pm 1 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -5 \pm 0.5 \text{ eu}$. Pyrolysis of **1b** at 74 °C proceeds at a nearly identical rate ($k_{\mathbf{1b}} = (7.7 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$), whereas **1c** decomposes roughly half as fast ($k_{\mathbf{1c}} = (3.8 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$).

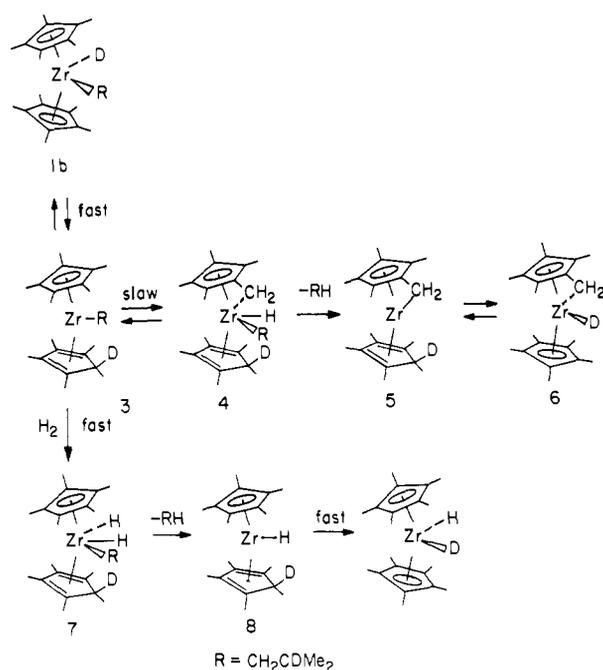
The isotopic distributions for the isobutanes obtained on pyrolysis of **1a**, **1b**, and **1c** were determined by a combination of IR and mass spectrometry^{14a} and are summarized in Table I. Surprisingly, pyrolysis of **1b** gives only 2-deuterio-2-methylpropane (**2b**). The results obtained for **1c** and for a 1:1 mixture of **1a** and **1c** confirm that isobutane is generated by *intramolecular* coupling of the isobutyl moiety with a hydrogen from a cyclopentadienyl methyl group. Simple coupling of the alkyl and hydride substituents originally *cis* in **1** is thus contradicted as are radical or other bimolecular processes.

Compound **1** reacts rapidly with a H₂ (1 atm) in toluene at –15 °C (*t*_{1/2} ≈ 5 min) to give (η⁵-C₅Me₅)₂ZrH₂ and isobutane (eq 3). Once again the mechanism which first comes to mind, namely reductive elimination of alkane followed by trapping of the permethyl zirconocene fragment with H₂, is not observed. Rather, the labeling pattern for the isobutanes (Table I) indicates exclusive coupling of the isobutyl group with hydrogen (or deuterium) from the ambient gas.



The mechanism outlined in Scheme I accounts for these data for the pyrolysis of **1** and its reaction with H₂. Thus the first-order dependence on [**1**] observed for the rate of pyrolytic decomposition, the small, negative entropy of activation ($\Delta S^\ddagger = -5 (\pm 0.5) \text{ eu}$), and the observation of a kinetic deuterium isotope effect only on deuteration of the cyclopentadienyl methyl groups^{14b} are fully in accord with a rate-determining, unimolecular rearrangement of **3** to **4** followed by reductive elimination of isobutane with the generation of **5**. The final

Scheme I



organozirconium products obtained in the pyrolysis of **1** exhibit NMR spectra very similar to those obtained for thermal decomposition of **6**,^{13,15} a tautomer of **5**.

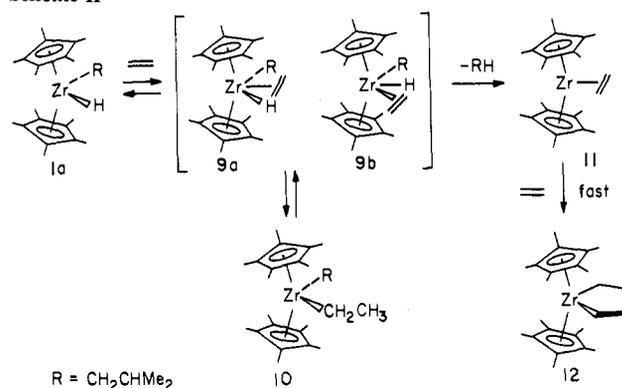
The facile reaction of **1** with H₂ can also be accommodated within the same mechanistic framework (Scheme I). Thus oxidative addition of H₂ to **3**, followed by reductive elimination of isobutane from **7**, leaves **8** a tautomer of (η⁵-C₅Me₅)₂ZrH₂. The key step in both reactions involves a facile and reversible metal-to-ring hydrogen transfer (**1** ⇌ **3**) affording (pentamethylcyclopentadienyl)(1-*exo*-methyltetramethylcyclopentadiene)hydrido-zirconium(II). Scheme I is closely analogous to that proposed for D₂ exchange with the hydride and ring methyl hydrogens of (η⁵-C₅Me₅)₂ZrH₂.^{10,11} Similar, reversible hydride or alkyl transfer to a (η⁵-C₅H₅) has been previously proposed for cyclopentadienyl derivatives of molybdenum,¹⁶ tungsten,¹⁷ and cobalt.¹⁸

Treatment of **1** with excess ethylene for several hours at 25 °C yields isobutane and the previously reported zirconacyclopentane derivative, (η⁵-C₅Me₅)₂ZrCH₂CH₂CH₂CH₂ (**12**).⁹ Treatment of **1b** with a large excess (>10:1) of C₂H₄ yielded 2-deuterio-2-methylpropane, whereas **1a** and 3.4 molar equiv C₂D₄ gave a (~65:35) mixture of **2a** and **2d** (Table I). The 1.4 molar equiv of excess deuterioethylene contained ~8% C₂D₃H. Furthermore, progressive replacement of the deuterium on zirconium by hydrogen was observed by NMR and IR spectrometry during the reaction of **1b** with excess C₂H₄ at 0 °C.

The mechanism outlined in Scheme II accounts for our results for the reaction of **1** with ethylene. An exchange between the hydride position of **1** and ethylenic hydrogen is clearly indicated. Formation of a ethylene complex such as **9a** or **9b** which undergoes a fast, reversible insertion of C₂H₄ into the Zr-H bond (**9** ⇌ **10**) competitive with reductive elimination of isobutane from **9** (and a rapid subsequent generation of **12**) would be entirely in accord with our data.¹⁹

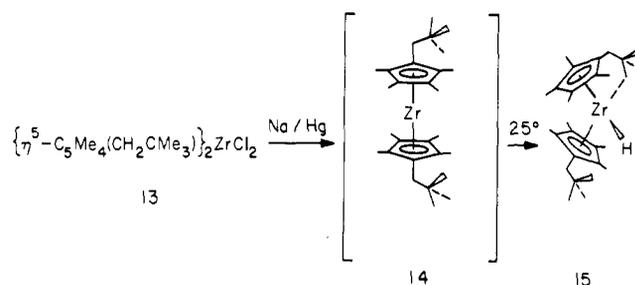
These results demonstrate that the most straightforward mechanism for the reductive elimination of isobutane from **1**, simple coupling of *cis*-isobutyl and hydride fragments, is highly unfavorable unless promoted by an incoming ligand such as ethylene which is capable of stabilizing the permethylzirconocene fragment. We have observed that CO and 2,6-dimethylphenyl isocyanide²⁰ also greatly accelerate reductive elimination of isobutane from **1**, although the reaction of **1** with

Scheme II



CO leads primarily (~95%) to another product derived from CO insertion into the Zr-alkyl bond.⁹ H₂ also promotes reductive elimination, but through a different mechanism involving oxidative addition to a tautomer of **1**.²¹ In the absence of added substrates **1** resorts to oxidative addition across one of its cyclopentadienyl methyl C-H bonds in order to generate a species (**4**) apparently better suited to reductive elimination. Whether facile reductive elimination from **4** vis-à-vis **1** is due to the closer proximity of its *cis*-alkyl and hydride ligands or a higher stability for the resulting organozirconium fragment is not clear at present.

Halpern, Abis and Sen have recently found that facile unimolecular reductive elimination of methane occurs from *c*-[Pt(H)(CH₃)(PPh₃)₂] even at -25 °C and that the rate of this process is unaffected by added phosphine or acetylene.² It could be concluded that, unlike the bis(triphenylphosphine)platinum system, simple unimolecular reductive elimination of alkane from alkyl hydride derivatives of permethylzirconocene is thermodynamically unfavorable. The facile insertion of zirconium into ligand C-H bonds (e.g., **14** → **15**) of a variety



of zirconocenes (generated in situ) bearing alkyl-substituted cyclopentadienyl ligands is supportive of this conclusion.

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- (12) Molecular weight determined cryoscopically for 82.4 mg of **1a**/g of C₆H₆.

- 460 ± 30 (calcd 420).
- (13) The major products are $(\eta^5\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ and a new organozirconium complex tentatively assigned the empirical formula $\{(\eta^5\text{-C}_5\text{Me}_5)[\text{C}_5(\text{CH}_3)_3(\text{CH}_2)_2\text{Zr}]_n$ (NMR).
- (14) (a) Unfortunately, 2-methylpropane suffers severe fragmentation upon ionization even at low energies, loss of CH_3 being the primary process. Comparison of the relative intensities of the parent ion and the next two lower mass ions gave fairly reliable results; however, supplementation of these mass spectral data with infrared spectra was necessary. The characteristic IR bands used were as follows. **2a**: $\delta(\text{CH}_3)$ 1480, 1380, 1335 cm^{-1} ; $\nu(\text{C}-\text{C})$ 1180 cm^{-1} . **2b**: $\nu(\text{C}-\text{D})$ 2145 cm^{-1} ; $\delta(\text{CH}_3)$ 1475, 1380 cm^{-1} ; $\nu(\text{C}-\text{C})$ 1235, 1225 cm^{-1} . **2c**: $\nu(\text{C}-\text{D})$ 2180, 2160 cm^{-1} ; $\delta(\text{CH}_3)$ 1470, 1385 cm^{-1} ; $\nu(\text{C}-\text{C})$ 1295, 1220 cm^{-1} . **2d**: $\nu(\text{C}-\text{D})$ 2165 cm^{-1} ; $\delta(\text{CH}_3)$ 1470, 1385 cm^{-1} ; $\nu(\text{C}-\text{C})$ 1285, 1155 cm^{-1} . (b) According to Scheme I the observed ratio of $k(\text{H})/k(\text{D})$ is a composite of a kinetic deuterium isotope effect for $3 \rightarrow 4$ and a thermodynamic deuterium isotope effect for the fast pre-equilibrium step $1 \rightleftharpoons 3$.
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- (19) Although $\beta\text{-H}$ abstraction from the isobutyl group of intermediate **10** could conceivably lead to isobutylene and an ethyl hydride derivative, no evidence of this reaction is observed. We attribute the much greater preference for $\beta\text{-H}$ abstraction from the ethyl group to steric factors which disfavor coordination of the bulky olefin isobutylene in the coordination of the sphere of the alkyl hydride (as would be required for generation of the ethyl hydride). This argument is supported by the observation that isobutylene does not promote reductive elimination of isobutane from **1**.⁹
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- (21) Gell and Schwartz have postulated that reaction of the closely related alkyl hydride complex, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{H})(\text{CH}_2\text{C}_6\text{H}_{11})$, with H_2 proceeds via a fundamentally different mechanism involving hydride abstraction from H_2 by the formal Zr(IV) center.⁷ Elimination of methylcyclohexane is postulated to occur in a subsequent step by electrophilic attack of H^+ on the resulting five-coordinate intermediate. A faster, competitive attack of H^+ on this intermediate to regenerate H_2 was postulated to account for the observed incorporation of deuterium into the hydride position of the alkyl hydride upon exposure to D_2 . We find no such exchange when **1a** is exposed to D_2 . Thus treatment of a toluene solution of **1a** with a 5 M excess of D_2 (1 atm) at -15°C for 3 min led to a 3:1 mixture of **1a** and $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Zr}(\text{H})(\text{D})_{2-n}$ ($n = 0, 1, \text{ or } 2$). Analyses of the residual gas phase by mass spectrometry and the resulting mixture of the two organozirconium compounds by ^1H NMR indicated no detectable exchange of deuterium with the hydride position of residual **1a**.
- (22) Alfred P. Sloan Fellow, 1976–1978.
- (23) Camille and Henry Dreyfus Teacher–Scholar, 1977–1982.

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On the Existence of Colorless Europium(IV)

Sir:

Recently, Firor and Seff¹ presented crystallographic evidence for the novel oxidation state europium(IV) in zeolites. Obviously, it is interesting to determine the local symmetry, the coordination number N , and the preponderant electron configuration² defining the oxidation state in noncatenated transition-group (and other) atoms. However, here is a case where visible spectra can be used to render the conclusion highly improbable. First of all, it is well known^{3,4} that the difference, 3.6 eV, between the ionization energies¹ of gaseous Eu^{3+} and Pr^{3+} for the greatest part is conserved in the standard oxidation potential, E^0 , of $\text{Eu}(\text{III})/\text{Eu}(\text{IV})$ and $\text{Pr}(\text{III})/\text{Pr}(\text{IV})$ (estimated from the refined spin-pairing theory for the aqua ions, +6.4 and +3.4 V, respectively). This constitutes a major distinction from the other transition groups² where such differences can be highly attenuated. It is always conceivable that a new type of ligand may be found, such as the bidentate phosphine⁵ stabilizing $\text{Fe}(\text{IV})$, $\text{Ni}(\text{IV})$, and $\text{Cu}(\text{III})$ by unexpectedly effective covalent bonding. However, it is excluded that $4f^5$ $\text{Eu}(\text{IV})$ could be colorless. Traces of $\text{Pr}(\text{IV})$ and

$\text{Tb}(\text{IV})$ in mixed oxides provide strong colors, such as purple ThO_2 , chamois CeO_2 and orange Y_2O_3 , and it can be easily extrapolated from the observed positions⁶ of electron-transfer bands^{7,8} that the strong transitions of $\text{Eu}(\text{IV})$ surrounded by oxygen-containing ligands would start in the far-infrared and probably would correspond to lower minimum energy of the potential surface⁶ producing spontaneous redox reactions. It has previously been pointed out⁹ that such strong colors might be a helpful indicator for ephemeric formation of quadrivalent intermediates (say, at low temperature) in solution. Though the positions of electron-transfer bands to a certain extent⁶ depend on the distances to the ligating atoms, they are not exceedingly sensitive to changes of the coordination number, N , and, for instance, $\text{M}[\text{N}[\text{Si}(\text{CH}_3)_3]_2]_3$ having $N = 3$ shows the same colors³ (orange for $\text{M} = \text{Eu}$ and yellow for $\text{M} = \text{Yb}$) as $\text{M}[\text{S}_2\text{CN}(\text{C}_4\text{H}_9)_2]_4^-$ with $N = 8$.

A closer analysis of the crystallographic data¹ shows some similarity with the classical case¹⁰ of $\text{Cr}(\text{NH}_3)_3(\text{O}_2)_2$ originally described as a chromium(II) superoxo complex (based on the intraligand oxygen–oxygen distance) but now recognized as $\text{Cr}(\text{IV})$ and peroxy ligands. A review of a large number of $\text{Eu}(\text{III})$ –oxygen internuclear distances¹¹ shows a remarkably large dispersion (e.g., 2.29 Å in EuOCl and six distances between 2.31 and 2.37 in Å $\text{Eu}(\text{dpm})_3(\text{py})_2$ with $N = 8$ compared with B-type Sm_2O_3 where the average $\text{Sm}-\text{O}$ distance, 2.46 Å, is the mean value of lengths scattered from 2.25 to above 2.7 Å). It may be argued that the oxidized zeolite¹ has the low $N = 4$ predisposing to shorter distances. Anyhow, the values 2.28 and 2.13 ± 0.04 Å cannot prove the presence of $\text{Eu}(\text{IV})$. The situation is rather different in the product obtained by reaction with chlorine where the lower of the two $\text{Eu}-\text{Cl}$ distances ($N = 5$), 2.06 and 2.31 Å, is exorbitantly shorter than 2.835 and 2.919 Å observed¹¹ in EuCl_3 ($N = 9$). Nevertheless, the lack of color strongly suggests an alternative explanation involving $\text{Eu}(\text{III})$.

Acknowledgment: I thank Professor Michel Che for many interesting discussions and benevolent hospitality at his laboratory.

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- (12) On sabbatical leave of absence from Département de Chimie minérale, analytique et appliquée, Université de Genève, Switzerland.

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Homogeneous Catalysis of the Water Gas Shift Reaction Using a Platinum Chloride–Tin Chloride System

Sir:

The water gas shift reaction

