

(CH<sub>2</sub>CMe<sub>3</sub>)Cl<sub>3</sub> is treated with 2 mol of LiCH<sub>2</sub>CMe<sub>3</sub> in pentane at -78 °C:  $\delta$  (CHCMe<sub>3</sub>) 232 ( $J_{\text{CH}} = 76 \pm 2$  Hz),  $\tau$  (CHCMe<sub>3</sub>) 6.25,  $\tau$  (CH<sub>A</sub>H<sub>B</sub>CMe<sub>3</sub>) 9.08,  $\tau$  (CH<sub>A</sub>H<sub>B</sub>CMe<sub>3</sub>) 9.25 ( $J_{\text{H}_A\text{H}_B} = 14$  Hz). (b) Ta( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)(CHPh)(CH<sub>2</sub>Ph)Cl is formed when Ta(CH<sub>2</sub>Ph)<sub>3</sub>Cl<sub>2</sub> is treated with LiC<sub>5</sub>Me<sub>5</sub> in THF for 1 day:  $\delta$  (CHPh) 222 ( $J_{\text{CH}} = 85 \pm 2$  Hz),  $\tau$  (CHPh) 6.71,  $\tau$  (CH<sub>A</sub>H<sub>B</sub>Ph) 7.66,  $\tau$  (CH<sub>A</sub>H<sub>B</sub>Ph) 7.82 ( $J_{\text{H}_A\text{H}_B} = 11$  Hz). Ta( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>Et)(CHPh)(CH<sub>2</sub>Ph)Cl forms similarly and has been analyzed. Calcd for TaC<sub>25</sub>H<sub>30</sub>Cl: C, 54.91; H, 5.52; Cl, 6.46. Found: C, 54.30; H, 5.40; Cl, 6.37.

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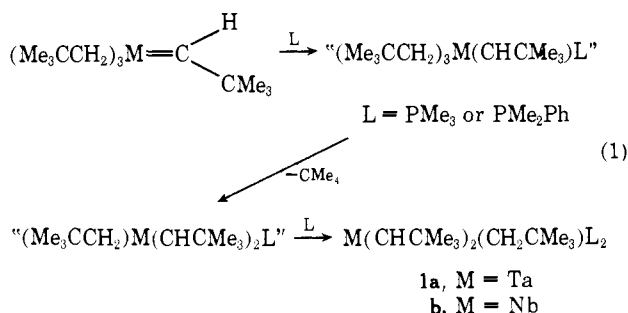
Received January 20, 1978

## Multiple Metal–Carbon Bonds. 11.<sup>1</sup> Bisneopentylidene Complexes of Niobium and Tantalum

Sir:

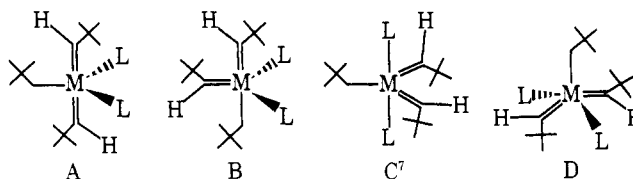
In a recent communication<sup>1</sup> we showed that alkylidyne complexes can be prepared from alkyl/alkylidene complexes by "accelerating" (with PMe<sub>3</sub>) the nondegenerate  $\alpha$ -hydrogen atom transfer from the alkylidene  $\alpha$ -carbon atom to the alkyl  $\alpha$ -carbon atom. An interesting question is what happens if  $\alpha$ -hydrogen abstraction occurs in a di- or trialkyl-alkylidene complex? Either an alkyl/alkylidyne or a bisalkylidene complex in principle could be formed. Dimeric alkyl-"alkylidyne" complexes are known.<sup>1,2</sup> We now want to show that bisneopentylidene complexes (of Nb and Ta) can also be the ultimate products of accelerated  $\alpha$ -hydrogen abstraction reactions in di- or trineopentyl-neopentylidene complexes. They can also be prepared from alkylidyne-chloride complexes by substituting the chloride with the alkyl.<sup>3a</sup>

Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(CHCMe<sub>3</sub>)<sup>3b,c</sup> is relatively stable thermally as a solid or in pentane or benzene (for weeks at 25 °C) probably because (i) intermolecular decomposition pathways are slow and (ii) the first observed change is a degenerate intramolecular scrambling of  $\alpha$ -hydrogen atoms ( $\Delta G^\ddagger \approx 28$  kcal mol<sup>-1</sup>; no neopentane evolves during the scrambling process<sup>3b</sup>). In the presence of at least 2 mol of L (L = PMe<sub>3</sub> or PMe<sub>2</sub>Ph), however, neopentane (1 mol) does evolve, comparatively rapidly when L = PMe<sub>3</sub> (2 h at 25 °C) but more slowly (2 weeks at 25 °C) when L = PMe<sub>2</sub>Ph. We therefore propose that a five-coordinate intermediate is formed (eq 1) in which  $\alpha$ -



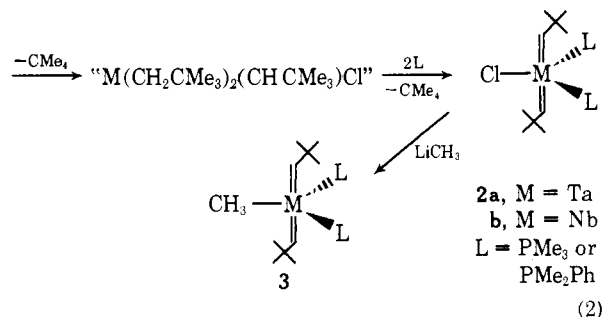
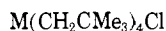
hydrogen atom abstraction is easier<sup>3b</sup> and that the final product (in essentially quantitative yield) is a bisneopentylidene complex, **1a**. It is not necessarily true that the immediate precursor is also a bisneopentylidene complex (see later), although this is what we have assumed for the present. The evolution of neopentane from Nb(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(CHCMe<sub>3</sub>)<sup>3b</sup> is also accelerated dramatically on adding L and the analogous products, **1b**, can be isolated in ~75% yield. All complexes are orange to red, crystalline, sensitive to air and moisture, and moderately soluble in pentane. A molecular weight determination for Ta(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub> in cyclohexane (cryoscopically) showed it to be a monomer (mol wt found, 540  $\pm$  40; two runs at 0.006 and 0.011 M). The presence of two neopentylidene ligands is suggested by the instantaneous reaction of **1** with acetone to give 2 mol of disobutylene.<sup>4</sup>

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1** show that (i) it has a plane of symmetry and (ii) the neopentylidene ligands are nonequivalent on the NMR time scales (60–270 MHz) at 30 °C. For example, the <sup>1</sup>H NMR spectrum of Ta(CHCMe<sub>3</sub>)<sub>2</sub>(CH<sub>2</sub>CMe<sub>3</sub>)(PMe<sub>3</sub>)<sub>2</sub> at 270 MHz shows three CMe<sub>3</sub> singlets, a PMe<sub>3</sub> triplet ( $J_{\text{HP}} = 2.4$  Hz), a neopentyl H $_{\alpha}$  triplet at  $\tau$  9.39 ( $J_{\text{HP}} = 19$  Hz), and two neopentylidene H $_{\alpha}$  resonances at  $\tau$  7.92 and 3.07 ( $J_{\text{HP}} \leq 2$ ). On broad-band-decoupling <sup>31</sup>P the neopentyl H $_{\alpha}$  triplet resonance becomes a singlet and the broadened neopentylidene H $_{\alpha}$  resonances sharpen. In the gated decoupled <sup>13</sup>C spectrum we find two neopentylidene C $_{\alpha}$  doublet resonances at  $\tau$  274 and 246 with low CH coupling constants ( $J_{\text{CH}} = 95$  and 85 Hz, respectively,  $J_{\text{CP}} \leq 5$  Hz) characteristic of neopentylidene ligands in crowded environments.<sup>5</sup> When L = PMe<sub>2</sub>Ph (and M = Ta) the gated decoupled <sup>13</sup>C NMR spectrum establishes that the phosphine's methyl groups are diastereotopic; two *P*-Me quartets are found (at  $\delta$  22.5 and 19.2;  $J_{\text{CH}} = 128$  Hz) but only one type of phenyl ring. In the four most likely structures



(A–D) the neopentylidene ligands *must not freely rotate about the M=C axis*.<sup>6</sup> We favor A, based only on the relatively large -CH<sub>2</sub>-phosphorus coupling constant (19 Hz) vs. the relatively small =CH-phosphorus coupling constant ( $\leq 5$  Hz).

Thermally unstable Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>Cl can be prepared by adding HCl to Ta(CH<sub>2</sub>CMe<sub>3</sub>)<sub>3</sub>(CHCMe<sub>3</sub>) at -78 °C in pentane.<sup>3b</sup> We added PMe<sub>3</sub> in an attempt to trap the proposed decomposition product, M(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(CHCMe<sub>3</sub>)Cl,<sup>8</sup> the high yield product is, instead, Ta(CHCMe<sub>3</sub>)<sub>2</sub>(Cl)(PMe<sub>3</sub>)<sub>2</sub> (**2a**, eq 2). Analogous procedures give thermally stable products



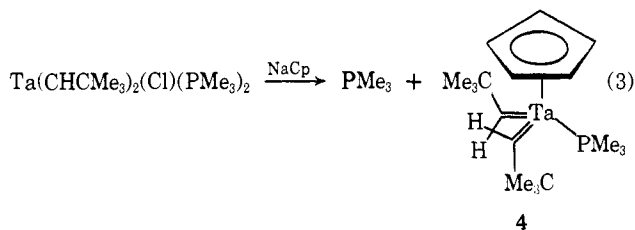
where L = PMe<sub>2</sub>Ph or M = Nb. Apparently even the larger, less basic PMe<sub>2</sub>Ph can coordinate to incipient M(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub>(CHCMe<sub>3</sub>)Cl to give (most likely) thermally

unstable  $M(\text{CH}_2\text{CMe}_3)_2(\text{CHCMe}_3)(\text{Cl})(\text{L})$  which eliminates neopentane and adds another L to give **2**. These species are much more soluble in pentane than **1** and also more volatile;  $\text{Ta}(\text{CHCMe}_3)_2(\text{Cl})(\text{PMe}_3)_2$  sublimates without decomposition at 80 °C (1  $\mu$ ). A cryoscopic molecular weight determination showed  $\text{Ta}(\text{CHCMe}_3)_2(\text{Cl})(\text{PMe}_3)_2$  to be a monomer in cyclohexane (mol wt found, 550).

The reaction of **2a** with  $\text{LiCH}_2\text{CMe}_3$  gives **1** and with  $\text{LiCH}_3$  gives **3**. On reaction with  $\text{LiCD}_2\text{CMe}_3$ ,  $\text{Ta}(\text{CHCMe}_3)_2(\text{Cl})(\text{PMe}_3)_2$  gives  $\text{Ta}(\text{CHCMe}_3)_2(\text{CD}_2\text{CMe}_3)(\text{PMe}_3)_2$  specifically; the signal for the neopentyl  $\text{H}_\alpha$  protons is absent in the  $^1\text{H}$  NMR spectrum and solely diisobutylene- $d_0$  is formed on reaction with acetone. Therefore,  $\text{H}_\alpha$  scrambling in **1a**, as in  $\text{Ta}(\text{CH}_2\text{CMe}_3)_3(\text{CDCMe}_3)$ ,<sup>3b</sup> is slow.

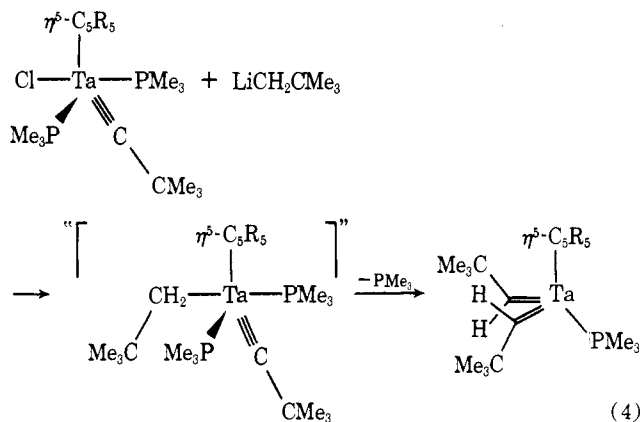
The -30 to -50 °C  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **2** and **3** are entirely analogous (including chemical shifts and coupling constants) to those of **1**. We therefore propose the structures of **2** and **3** are analogous to that of **1**. However, as the temperature is raised, the two neopentylidene groups equilibrate. For example, in  $\text{Ta}(\text{CHCMe}_3)_2(\text{Cl})(\text{PMe}_3)_2$ , the two  $\text{C}_\alpha$  signals at  $\delta$  273 ( $J_{\text{CH}} = 98 \pm 3$  Hz;  $J_{\text{CP}} \approx 5 \pm 2$  Hz) and 241 ( $J_{\text{CH}} = 86 \pm 3$  Hz;  $J_{\text{CP}} \approx 5 \pm 2$  Hz) coalesce (at  $\sim 300$  K, 22.63 MHz) to give a doublet ( $J_{\text{CH}} = 91 \pm 3$  Hz) at 257 (50 °C at 15.1 MHz); therefore,  $\Delta G^\ddagger_{300} \approx 13.2$  kcal mol $^{-1}$ . For  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_3)(\text{PMe}_3)_2$   $\Delta G^\ddagger_{353} \approx 16.3$  kcal mol $^{-1}$  and for  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$   $\Delta G^\ddagger_{373} \approx 17.2$  kcal mol $^{-1}$  by both  $^{13}\text{C}$  and  $^1\text{H}$  NMR. Added  $\text{PMe}_3$  does not exchange with coordinated  $\text{PMe}_3$  during the equilibration<sup>9</sup> and  $\Delta G^\ddagger$  is independent of complex concentration. We therefore propose that the equilibration process is intramolecular but do not yet know whether the TBP skeleton rearranges or whether the neopentylidene ligands only rotate (synchronously or separately) about the axial  $\text{M}=\text{C}$  bonds.<sup>6</sup>

The reaction of **2a** (L =  $\text{PMe}_3$ ) with  $\text{NaCp}$  yields 1 mol of  $\text{PMe}_3$  and monomeric **4** (mol wt found, 482, in cyclohexane) in which the two neopentylidene ligands (eq 3) are nonequivalent



alent on the NMR time scales at low temperatures ( $^{13}\text{C}_\alpha$  (67.89 MHz) at  $\delta$  255 and 235 at -30 °C ( $J_{\text{CH}} = 97 \pm 3$  and  $90 \pm 3$  Hz, respectively),  $^1\text{H}_\alpha$  (60 MHz) at  $\tau$  1.74 and 7.97 at -60 °C, both in toluene- $d_8$ ). On warming the sample they equilibrate ( $^{13}\text{C}_\alpha$  at  $\delta$  247 ( $J_{\text{CH}} = 94 \pm 3$  Hz at 60 °C),  $^1\text{H}$  at  $\tau$  4.65 at 80 °C,  $\Delta G^\ddagger \approx 12.5$  kcal mol $^{-1}$ ) most likely by rotation of the neopentylidene ligands about the  $\text{M}=\text{C}$  bonds. The fact that the ground state is not an olefin complex cannot be ascribed to their being mutually trans (as in the proposed ground state structures of **1** or **2**). The stability of **4** (a 16e complex) relative to the *trans*-di-*tert*-butylethylene complex (**14e**) might then be ascribed to the fact that Ta is electron deficient and would prefer a 16e count and/or that the activation energy to form the hindered *trans*-di-*tert*-butylethylene is prohibitively high.

It is noteworthy that **4** is also formed quantitatively on treating  $\text{TaCp}(\text{CCMe}_3)(\text{Cl})(\text{PMe}_3)_2$ <sup>1</sup> with  $1/2\text{Mg}(\text{CH}_2\text{CMe}_3)_2$  (dioxane) in ether; an analogue containing  $\eta^5\text{-C}_5\text{Me}_5$  can be prepared similarly employing  $\text{LiCH}_2\text{CMe}_3$  in pentane. (eq 4). This finding suggests that monomeric neopentyl-neopentylidene complexes can rearrange to bisneopentylidene complexes. Whether they always do and how general this re-



arrangement is if  $\text{R} = \text{R}' \neq \text{CMe}_3$  or if  $\text{R} \neq \text{R}'$  in a  $\text{RCH}_2\text{M}=\text{CR}'$  complex remains to be seen. Also, our findings still do not tell us whether alkyl-alkylidene or bisalkylidene complexes form first when di- or trialkyl-alkylidene complexes lose alkane.<sup>10</sup>

We are in the process of preparing and studying the formation and reactions of other bisalkylidene complexes. Among other things we hope to determine under what conditions, if any, an olefin complex does form, and whether this olefin might be in equilibrium with the free olefin.<sup>12</sup> We have found so far that *small* olefins react with **2** in a characteristic way.<sup>13</sup> For example, ethylene produces 2 mol of 4,4-dimethyl-1-pentene. Surprisingly, however, 3 mol are formed when ethylene reacts with **1**.

**Acknowledgments.** Acknowledgment is made to the National Science Foundation (CHE76-07410) for support of this research and to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support in the form of a fellowship to G. A. R. We also thank the Francis N. Bitter National Magnet Laboratory for use of their high-field NMR facilities.

## References and Notes

- S. J. McLain, C. D. Wood, L. W. Messerle, R. R. Schrock, F. J. Hollander, W. J. Youngs, and M. R. Churchill, *J. Am. Chem. Soc.*, in press.
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- (a) Satisfactory elemental analyses have been obtained for the reported complexes. (b) R. R. Schrock and J. D. Fellmann, *J. Am. Chem. Soc.*, **100**, 3359 (1978). (c) R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974).
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- Why  $J_{\text{CH}}$  varies so greatly (from 76 Hz in  $\text{Ta}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{CMe}_3)(\text{CHCMe}_3)\text{Cl}^1$  to 131 Hz in  $\text{Nb}(\eta^5\text{-C}_5\text{H}_5)(\text{CHMe}_3)\text{Cl}^6$ ) will be discussed elsewhere. We should note that the  $\text{C}_\alpha$  and  $\text{H}_\alpha$  signals in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra of Nb complexes are broadened significantly owing to coupling to  $^{93}\text{Nb}$  ( $I = 9/2$ , 100 %).
- The barrier to rotation of the methylene ligand in  $\text{TaCp}_2(\text{CH}_2)(\text{CH}_3)$  is estimated to be  $\geq 21$  kcal mol $^{-1}$ . The barriers to rotation in similar  $=\text{CHPh}$  and  $=\text{CHCMe}_3$  complexes are 19.3 and 16.8 kcal mol $^{-1}$ , respectively, most likely due to progressively greater steric crowding in the coordination sphere: R. R. Schrock, C. D. Wood, L. W. Messerle, and L. J. Guggenberger, *J. Am. Chem. Soc.*, **100**, 3793 (1978).
- The two  $=\text{CHCMe}_3$  ligands and the  $\text{CH}_2\text{CMe}_3$  ligand are coplanar and arranged in a pinwheel fashion. Note that the  $=\text{CHCMe}_3$  ligand is *perpendicular* to the trigonal pseudoplane in **B** but lies *in* the plane in **C**.
- This product can be trapped with  $\text{TiCl}_5\text{H}_5$  ( $\text{M} = \text{Ta}$ ) to give  $\text{Ta}(\eta^5\text{-C}_5\text{H}_5)(\text{CH}_2\text{CMe}_3)_2(\text{CHCMe}_3)$ .<sup>3b</sup>
- The triplet signal for bound  $\text{PMe}_3$  does eventually collapse to a singlet and bound  $\text{PMe}_3$  exchanges with any added  $\text{PMe}_3$ . This process is most facile in more crowded  $\text{Ta}(\text{CHCMe}_3)_2(\text{CH}_2\text{CMe}_3)(\text{PMe}_3)_2$ . It clearly is not related to the lower temperature intramolecular alkylidene ligand equilibration.
- We now believe that this may depend on the structure of both the starting material and the product and the types of ligands in each. In one case, which may eventually prove to be a special case, a neopentylidene  $\alpha$  hydrogen is removed by an external base.<sup>11</sup>
- L. J. Guggenberger and R. R. Schrock, *J. Am. Chem. Soc.*, **97**, 5935 (1975).
- Electron rich olefins such as  $\text{PhNCH}_2\text{CH}_2\text{NPh}=\text{CNPhCH}_2\text{CH}_2\text{NPh}$  will add to metals in low oxidation states to give bis "carbene" complexes (see M. F. Lappert and P. L. Pye, *J. Chem. Soc., Dalton Trans.*, 2172 (1977), and references therein). In one case such olefins could be metathesized slowly by a rhodium catalyst (D. J. Cardin, M. J. Doyle, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 927 (1972)). However, to what extent these findings are related to the corresponding reactions of ordinary olefins remains an open question. (See R. J. Haines and C. J. Leigh, *Chem. Soc. Rev.*, **4**, 155

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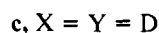
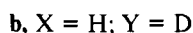
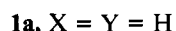
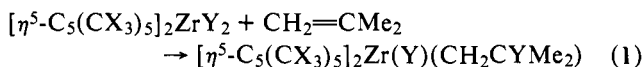
### Reductive Elimination of Isobutane from an Isobutyl Hydride Derivative of Bis(pentamethylcyclopentadienyl)zirconium

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.<sup>1</sup> In several cases such intermediates have been characterized in solution,<sup>1,2</sup> but there appear to be very few hydridoalkyl metal complexes which are sufficiently stable for their isolation at room temperature.<sup>3–7</sup> 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 H<sub>2</sub>, olefins, or donor ligands.

The paucity of stable hydridoalkyl compounds has been recognized by Norton,<sup>6</sup> 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, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub>,<sup>8</sup> and dimethyl derivative, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(CH<sub>3</sub>)<sub>2</sub>,<sup>9</sup> are stable for weeks at 100 °C, the isobutyl hydride complex, (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>) (**1**),<sup>9</sup> 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 H<sub>2</sub> (–15 °C). The relatively high thermal stability of **1**, the ease with which regiospecific deuterium labeling of **1** can be accomplished,<sup>10,11</sup> 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.

[η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>Zr(H)(CH<sub>2</sub>CHMe<sub>2</sub>) (**1a**), [η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>Zr(D)(CH<sub>2</sub>CDMe<sub>2</sub>) (**1b**), and [η<sup>5</sup>-C<sub>5</sub>(CD<sub>3</sub>)<sub>5</sub>]<sub>2</sub>Zr(D)(CH<sub>2</sub>CDMe<sub>2</sub>) (**1c**) are obtained quantitatively (NMR) via treatment of benzene solutions of [η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>ZrH<sub>2</sub>, [η<sup>5</sup>-C<sub>5</sub>(CH<sub>3</sub>)<sub>5</sub>]<sub>2</sub>ZrD<sub>2</sub>, and [η<sup>5</sup>-C<sub>5</sub>(CD<sub>3</sub>)<sub>5</sub>]<sub>2</sub>ZrD<sub>2</sub>, 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, <sup>1</sup>H NMR,<sup>9</sup> and molecular weight data<sup>12</sup> 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		
<b>1a</b>	C <sub>7</sub> D <sub>8</sub>	CH <sub>3</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ( <b>2a</b> )
<b>1b</b>	C <sub>7</sub> D <sub>8</sub>	CH <sub>3</sub> CD(CH <sub>3</sub> ) <sub>2</sub> ( <b>2b</b> )
<b>1c</b>	C <sub>7</sub> H <sub>8</sub>	CH <sub>2</sub> D <sub>2</sub> CD(CH <sub>3</sub> ) <sub>2</sub> ( <b>2c</b> )
<b>1a + 1c</b>	C <sub>7</sub> H <sub>8</sub>	<b>2a + 2c</b>
Reaction with H <sub>2</sub>		
<b>1a</b>	C <sub>6</sub> D <sub>6</sub>	<b>2a</b>
<b>1b</b>	C <sub>7</sub> D <sub>8</sub>	<b>2b</b>
<b>1c</b>	C <sub>7</sub> D <sub>8</sub>	<b>2b</b>
Reaction with D <sub>2</sub>		
<b>1a</b>	C <sub>7</sub> H <sub>8</sub>	(CH <sub>2</sub> D)CH(CH <sub>3</sub> ) <sub>2</sub> ( <b>2d</b> )
<b>1b</b>	C <sub>7</sub> D <sub>8</sub>	<b>2c</b>
Reaction with C <sub>2</sub> H <sub>4</sub>		
<b>1a</b>	C <sub>6</sub> D <sub>6</sub>	<b>2a</b>
<b>1b</b>	C <sub>7</sub> D <sub>8</sub>	<b>2b (+2c)</b> <sup>a</sup>
Reaction with C <sub>2</sub> D <sub>4</sub>		
<b>1a</b>	C <sub>7</sub> D <sub>8</sub>	<b>2a + 2d</b> <sup>b</sup>

<sup>a</sup> Not detected; large excess of C<sub>2</sub>H<sub>4</sub> used. <sup>b</sup> See text.

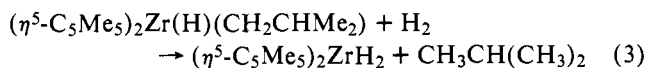
dergo further reaction(s) and the final products have not all been identified.<sup>13</sup> Nonetheless, the rate of disappearance of **1** and the rate of appearance of isobutane, monitored by <sup>1</sup>H NMR spectrometry (benzene-*d*<sub>6</sub>), are in very good agreement and obey a first-order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

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

with  $k_{1a} = (7.2 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$  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 ( $k_{1b} = (7.7 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ ), whereas **1c** decomposes roughly half as fast ( $k_{1c} = (3.8 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$ ).

The isotopic distributions for the isobutanes obtained on pyrolysis of **1a**, **1b**, and **1c** were determined by a combination of IR and mass spectrometry<sup>14a</sup> 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 H<sub>2</sub> (1 atm) in toluene at –15 °C ( $t_{1/2} \approx 5 \text{ min}$ ) to give (η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ZrH<sub>2</sub> 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 H<sub>2</sub>, 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 H<sub>2</sub>. 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<sup>14b</sup> 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