

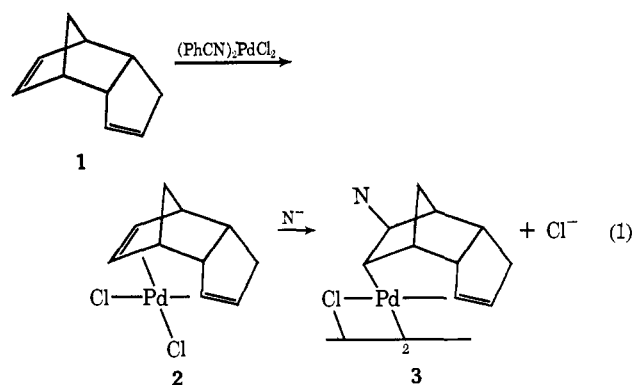
## Trans Addition of the Elements Pd-Cl to a Diene

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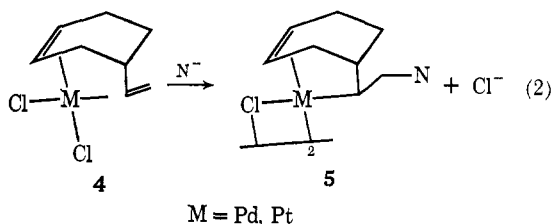
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**Abstract:** The first example of a stable  $\sigma$ -bonded palladium complex, resulting from the addition of the elements of Pd-Cl to a double bond is described. Trans addition takes place at the ring double bond of 5-vinyl-2-norbornene, with the palladium atom endo and coordinated to the endo vinyl group. Other nucleophilic additions to this diene in the presence of PdCl<sub>2</sub> are described. The stereochemistry, as well as the substitution pattern, is determined by nmr using Eu(dpm)<sub>3</sub>.

This research is part of a study to evaluate the effect of diene structure on nucleophilic additions to palladium-diene complexes. It has been shown that dicyclopentadiene (1) forms the monomeric  $\pi, \pi$  com-



plex 2, which is attacked by nucleophiles at the norbornene double bond giving the  $\sigma$ -bonded dimeric complex 3.<sup>1,2</sup> The palladium and platinum complexes of 4-vinylcyclohexane (4) also react with nucleophilic



reagents, but in this case reaction occurs at the acyclic double bond, as in 5.<sup>3</sup> From these and similar results,<sup>1</sup> it has been concluded that if the diene has an acyclic double bond, this is preferentially attacked.<sup>4</sup> In an effort to determine the causes of this preference we investigated reactions of 5-vinyl-2-norbornene (6), a diene which has both the strained norbornene double bond, and an acyclic double bond.

## Results

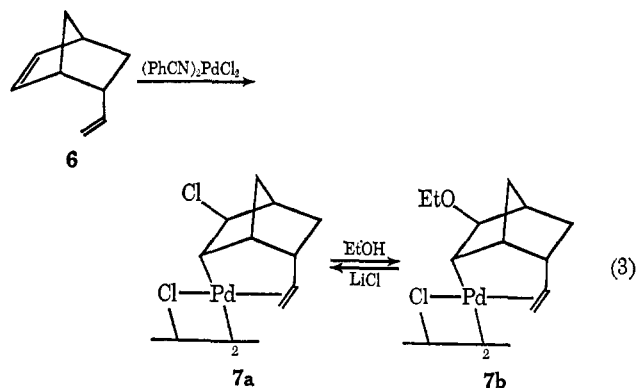
Diene complexes of palladium are often prepared by allowing an excess of the diene to react with a solution

(1) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 3413 (1957).

(2) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966).

(3) G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967). R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969).

(4) P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. 1, Academic Press, New York, N. Y., 1971.



of bis(benzonitrile)palladium dichloride [(PhCN)<sub>2</sub>Pd-Cl<sub>2</sub>] in benzene. The deep red color of the benzonitrile complex fades to a light yellow and the relatively insoluble  $\pi, \pi$  complex precipitates. However, when an excess of 5-vinyl-2-norbornene (6) is allowed to react under these same conditions, the red solution turns yellow, but no precipitate forms. Removal of the benzene leaves a pale yellow granular solid which can be recrystallized from CHCl<sub>3</sub>/ligroin. Elemental analysis indicates the empirical formula of this compound to be C<sub>9</sub>H<sub>12</sub>Cl<sub>2</sub>Pd, and osmometric molecular weight determination establishes this as a dimeric species. When this solid is stirred with a 1.5 M KCN solution in CCl<sub>4</sub>, one obtains a clear liquid which, on the basis of its nmr spectrum,<sup>5</sup> was identified as pure *endo*-5-vinyl-2-norbornene. These results indicate that selective complex formation has occurred with the *endo* isomer<sup>6</sup> of the diene resulting in the formation of a  $\mu$ -bridged dimeric species; we believe this species to have structure 7a because it has the solubility characteristics of a  $\sigma, \pi$  complex and because of the following additional evidence.

Initial attempts to purify the dimeric complex 7a by passing it through a silica gel column using CHCl<sub>3</sub>/EtOAc (8:1) as eluent resulted in the formation of a new dimeric complex 7b (empirical formula C<sub>10</sub>H<sub>15</sub>OClPd), whose nmr spectrum (Figure 1b) is very similar to that for complex 7a (Figure 1a) except that the chloride appears to have been replaced by an ethoxy group. Treatment of the ethoxy complex 7b with LiCl in methylene chloride containing a trace of HCl produced the chloro complex 7a (see eq 3). Treatment of 7a with NaBH<sub>4</sub> in toluene or diisobutyl aluminum hydride in

(5) R. V. Moen and H. S. Makowski, *Anal. Chem.*, **39**, 1860 (1967). Although these authors were unable to separate the *endo*-*exo* isomers, they distinguish between them by nmr.

(6) Commercial 5-vinyl-2-norbornene (Aldrich Chemical Co.) consists of a 76:24 *endo*/*exo* mixture.

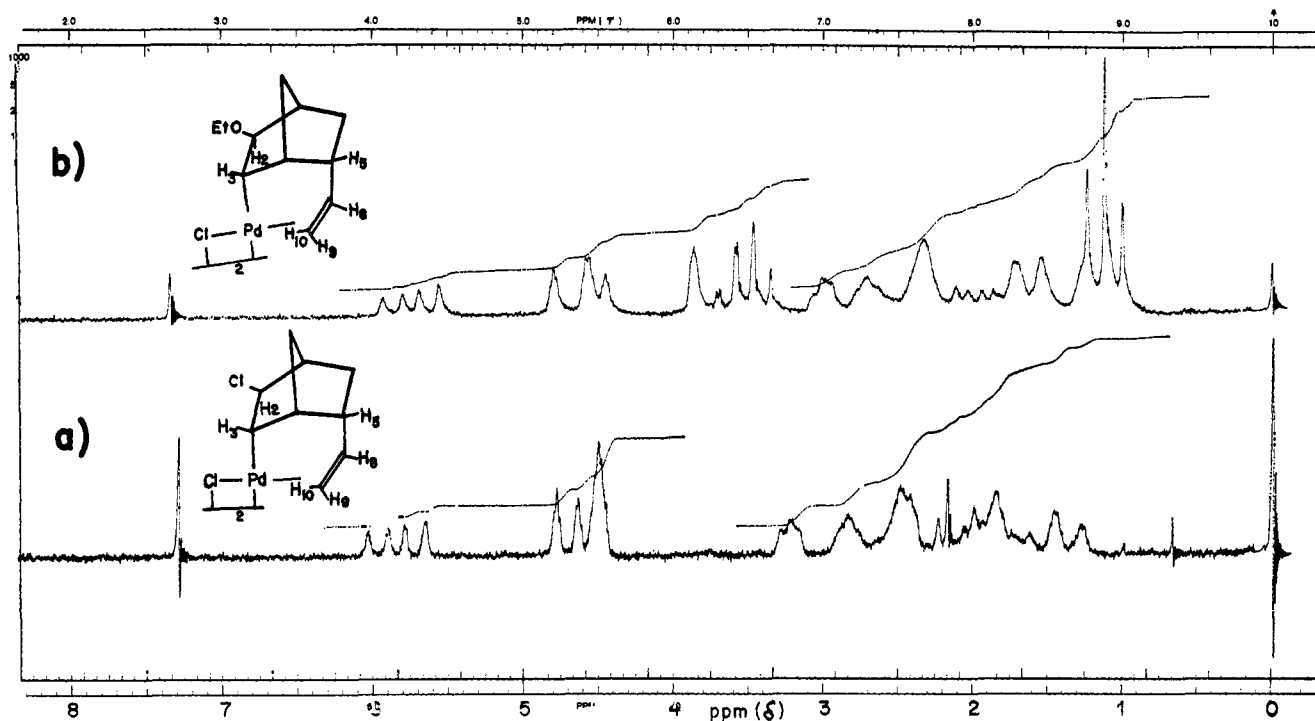
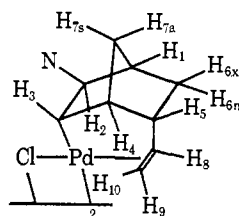


Figure 1. Nmr spectra (60 MHz) of (a) complex **7a** and (b) complex **7b** in  $\text{CDCl}_3$  with TMS as internal standard.

toluene or with hydrogen in benzene gave hydrocarbons which contained no halogen atoms.

In the nmr spectrum of complex **7a** the downfield



- 7a**, N = Cl  
**b**, N = OEt  
**c**, N = OMe  
**d**, N = OAc

doublet of doublets at  $\delta = 5.82$  ppm is assigned to  $\text{H}_3$ , which couples with  $\text{H}_9$  ( $J = 8$  Hz) and  $\text{H}_{10}$  ( $J = 14$  Hz). The latter protons appear as doublets at  $\delta 4.55$  and  $4.62$  ppm, respectively. These couplings are typical for a vinyl group.<sup>7</sup> The absorptions are shifted slightly from those of the parent diene as is expected upon coordination to the metal.<sup>8</sup> There is an additional absorption at  $\delta 4.55$  ppm which we assign to  $\text{H}_2$ ; this absorption shifts to higher field ( $\delta 3.85$  ppm) when the chloride group is replaced with the less electronegative ethoxy group.<sup>1,7</sup> The unresolved multiplet at  $\delta 3.25$  ppm is tentatively assigned to  $\text{H}_3$ , in agreement with the values found by other workers in related systems.<sup>2,9,10</sup> A similar multiplet at  $\delta 2.58$  ppm is thought to be the

(7) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Vol. 5, Pergamon Press, New York, N. Y., 1969.

(8) (a) For leading references, see M. L. Maddox, A. L. Stafford, and H. D. Kraesz, *Advan. Organometal. Chem.*, **3**, 1 (1965); (b) R. P. Hughes and J. Powell, *J. Organometal. Chem.*, **30**, C45 (1971); **60**, 387 (1973).

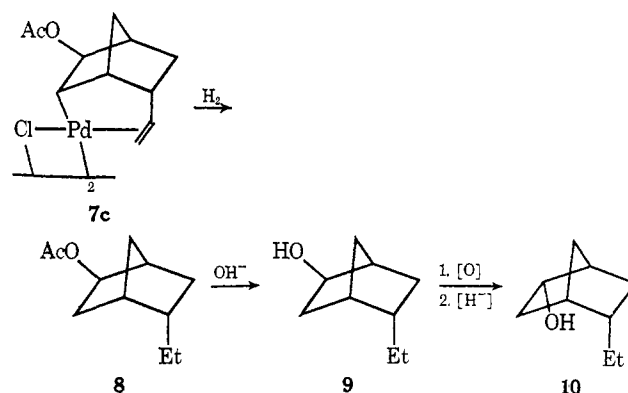
(9) S. J. Betts, A. Harris, R. N. Haszeldine, and R. V. Parish, *J. Chem. Soc. A*, 3699 (1971); H. Takahashi and J. Tsuji, *J. Amer. Chem. Soc.*, **90**, 2387 (1968).

(10) M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

allylic proton  $\text{H}_5$ ; the chemical shift of this proton varies very little within the range of nucleophiles studied, and Shooley's rules predict a value of  $\delta 2.81$  for an allylic, exo proton in an unperturbed system.<sup>7</sup>

The palladium must be in the endo position, otherwise intramolecular coordination with the vinyl group, which has been shown to be endo, would not be possible. Were the chloride in **7a** cis to the palladium, the  $\text{H}_2$ - $\text{H}_3$  coupling in the nmr would be 9-10 Hz.<sup>7,8b</sup> Since the width at half-height of  $\text{H}_2$  is only 5.5 Hz, we conclude that the Cl is trans to the Pd and thus exo, the same orientation of nucleophile as observed in other systems.<sup>2</sup>

Additional evidence for the exo orientation of the chlorine atom stems from comparison of the nmr spectra of **7a** and acetate complex **7d**. Complex **7d** was prepared from **7a** by treatment with NaOAc, or by reaction of diene **6** with  $\text{PdCl}_2$  (or  $\text{Na}_2\text{PdCl}_4$ ) in HOAc/NaOAc. Hydrogenation of **7d** afforded acetate **8**, which was hydrolyzed to alcohol **9**. Oxidation of alcohol **9** to the ketone followed by reduction of the ketone with  $\text{LiAlH}(\text{OCH}_3)_3$  afforded an alcohol (**10**)



different from **9**. The reduction of norbornane is

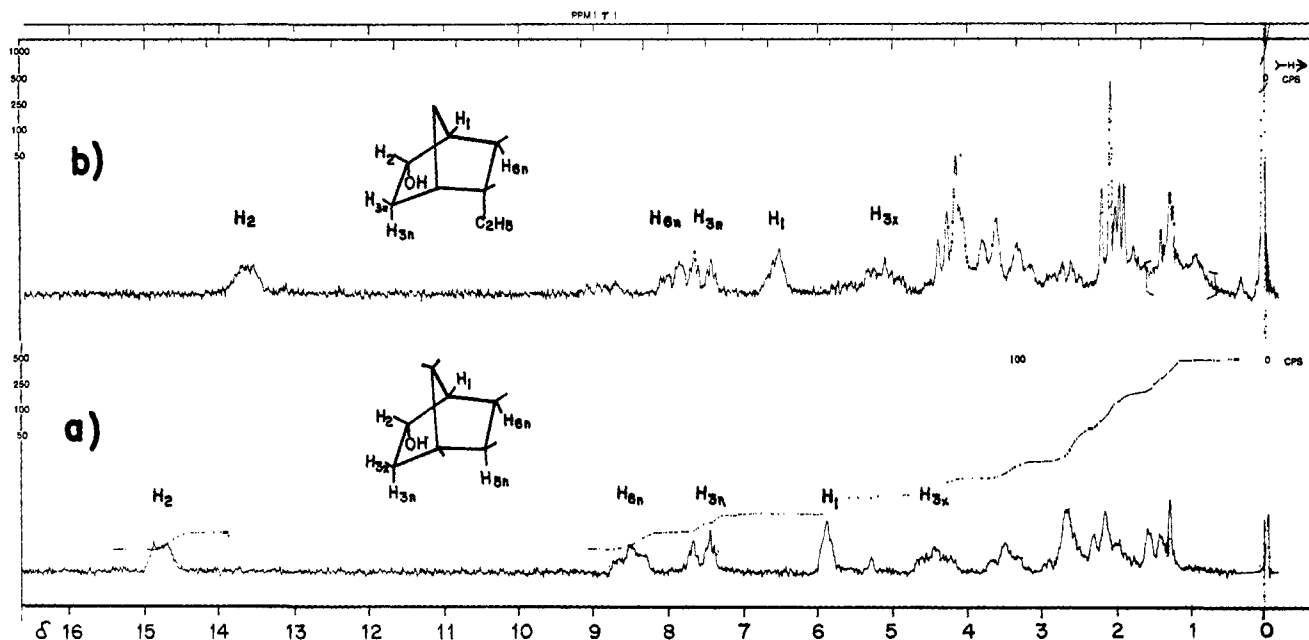


Figure 2. Nmr spectra (60 MHz) of (a) *endo*-norborneol in the presence of 0.54 mol of  $\text{Eu}(\text{dpm})_3$  and (b) alcohol **10** in the presence of 0.36 mol  $\text{Eu}(\text{dpm})_3$  in  $\text{CCl}_4$  with TMS as internal standard (mol of  $\text{Eu}(\text{dpm})_3 = [\text{Eu}]/[\text{alcohol}]$ ).

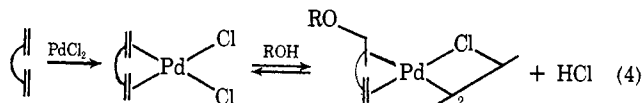
known to occur from the less congested side to give the *endo* alcohol as the major isomer,<sup>11</sup> therefore, alcohol **9** must be the *exo* isomer, and the complex from which it was derived must have been formed by nucleophilic attack from the *exo* side. The similarity between the nmr spectra of **7a** and **7d** (see Experimental Section) allows us to infer that the chlorine atom in **7a** is also *exo*.

The formation of **7d** from **7a** appears to occur by a dechloropalladation-acetoxypalladation reaction similar to the alkoxy exchange reactions observed by Stille in the dicyclopentadiene complex.<sup>2</sup> Since complex **7a** can also be obtained by exchange between  $\text{LiCl}$  and **7b** (eq 3) and since all the derivatives (**7**) seem to have the same *exo* orientation of the group N, it appears that the formation of complexes of general structure **7** are best explained by *exo* attack of a nucleophile on an intermediate diene complex. Clearly in the formation of **7a** from diene **6** the chloride comes from the palladium salt, but we note that the same product **7a** is obtained when external chloride ion is present. We interpret this to mean that the reaction begins by some nucleophile (water or trace chloride ion, etc.) attacking the intermediate diene  $\pi, \pi$  complex, ejecting a chloride ion (eq 1), which is free to attack another  $\pi, \pi$  complex, ejecting another chloride ion, in a chain reaction. Thus while the chloride ion is originally derived from the palladium salt, it attacks the double bond from outside the coordination sphere of the palladium in an intermolecular, *exo* attack trans to the palladium.

To establish the position of the nucleophile with respect to the vinyl group, alcohol **10** was subjected to a shift reagent study using  $\text{Eu}(\text{dpm})_3$ ,<sup>12</sup> with pure *endo*-norborneol as a model. The absorptions in the spectrum for *endo*-norborneol (Figure 2a) were assigned analogously with those of *endo*-norborneol (the latter

assignments were based on decoupling experiments).<sup>13</sup> The 6-*endo* proton,  $\beta$  to the hydroxyl group, is easily recognized since it is shifted less than  $\text{H}_2$ , but more than  $\text{H}_1$ . The spectrum of alcohol **10** (Figure 2b) shows an absorption which is shifted analogously to  $\text{H}_{6n}$ , indicating the presence of an *endo* proton B to the hydroxyl group. Therefore the hydroxyl group must be at C-2 as shown in **10**, for if it were at C-3, the absorption for an *endo* proton  $\beta$  to the hydroxyl group would be absent.

The ethoxy and methoxy complexes (**7b** and **7c**) could be prepared from the diene directly by reaction with  $\text{PdCl}_2$  in the appropriate alcohol. Under these conditions dicyclopentadiene similarly gave the  $\sigma, \pi$  complexes in high yield, but 1,5-cyclooctadiene and norbornadiene gave predominantly the  $\pi, \pi$  complexes (see eq 4). In the latter cases, complete conversion to



$\sigma, \pi$  complexes could be affected by the addition of base ( $\text{Na}_2\text{CO}_3$ ) to the reaction medium. Attempts to prepare the chloro complex of dicyclopentadiene (**3**,  $\text{N} = \text{Cl}$ ) by reaction of the methoxyl adduct **3** ( $\text{N} = \text{OMe}$ ) with  $\text{LiCl}$  and  $\text{HCl}$  gave only the  $\pi, \pi$  complex **2**.

## Conclusions

The two substrates, dicyclopentadiene (**1**) and 5-vinyl-2-norbornene (**6**), exhibit similar reactivity in their reaction with  $\text{PdCl}_2$  in methanol in the absence of base; in each case the methanol attacks the norbornene double bond, forming a  $\sigma, \pi$  complex. The relief of strain in the norbornyl system has been invoked to explain the site of nucleophilic attack in the dicyclo-

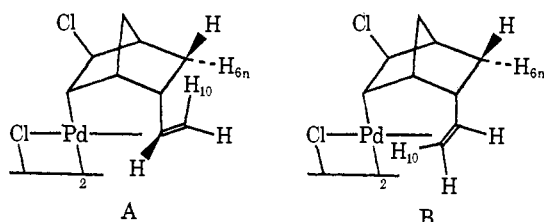
(11) W. T. Wipke and P. Gund, *J. Amer. Chem. Soc.*, **96**, 299 (1974); C. H. DePuy and P. R. Story, *J. Amer. Chem. Soc.*, **82**, 627 (1960).

(12) J. K. M. Sanders and D. H. Williams, *Chem. Commun.*, 422 (1970).

(13) J. Paasivirta, *Suom. Kemistilehti B*, **44**, 131 (1971); see also J. Paasivirta and P. J. Mätkönen, *ibid.*, **44**, 283 (1971); P. V. Demarco, T. K. Elzey, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, **92**, 5734 (1970).

pentadiene  $\pi, \pi$  complex (**2**),<sup>2</sup> and still appears to determine the site of reaction even when the competing double bond is acyclic. Norbornadiene and cyclooctadiene do not add methanol under neutral conditions owing to the greater stability and lower reactivity of the corresponding  $\pi, \pi$  complexes.<sup>14</sup> This increased stability results from the favorable parallel alignment of the double bonds, which affords maximum overlap between the d orbitals of the metal and the  $\pi$  orbitals of the diene.<sup>15</sup>

Although the two substrates, **1** and **6**, react similarly with  $\text{PdCl}_2$  in methanol, they react quite differently with  $(\text{PhCN})_2\text{PdCl}_2$  in benzene; dicyclopentadiene (**1**) forms the  $\pi, \pi$  complex **3**, but 5-vinyl-2-norbornene (**6**) forms the  $\sigma, \pi$  chloro complex **7a**. The question arises of how the difference in structure of **1** and **6** leads to this difference in reactivity. The lack of coupling between  $\text{H}_5$  and  $\text{H}_8$  in the nmr of **7a** suggests a dihedral angle between them of  $90^\circ$  ( $J = 8 \text{ Hz}$  in **6**).<sup>7</sup> There are two possible conformations having this dihedral angle, A and B. Conformation A involves severe steric



crowding of  $\text{H}_{10}$  with  $\text{H}_{6n}$  ( $1.4 \text{ \AA}$ ), whereas in conformation B this interaction is relieved. Thus it appears that the terminal methylene group in **7a-d** lies outside rather than under the norbornene ring system. This conformation of the diene would be poor for  $\pi, \pi$  complex formation, but good for  $\sigma, \pi$  complex formation.

Although the 5-vinyl-2-norbornene  $\pi, \pi$  complex could not be isolated, even at  $-40^\circ$  in methylene chloride, its existence can be implied from the fact that the ethoxy complex (**7b**) could be formed from the chloro complex (**7a**) and *vice versa* (eq 1). Similar exchange reactions have been observed by Stille<sup>2</sup> in the dicyclopentadiene complex, and by Anderson<sup>16</sup> in the 1,5-cyclooctadiene complex.

Addition of the elements of  $\text{Pd-Cl}$  to acetylenes,<sup>17</sup> allenes,<sup>18</sup> and cyclopropanes<sup>19</sup> are general organopalladation reactions, resulting in formation of stable chloropalladation adducts. Although many catalytic,<sup>20,21</sup> exchange and isomerization<sup>22</sup> reactions are

(14) W. Partenheimer, *Inorg. Chem.*, **11**, 743 (1972).

(15) J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953).

(16) C. B. Anderson and B. J. Burreson, *J. Organometal. Chem.*, **7**, 181 (1967).

(17) T. Hosokawa, I. Moritani, and S. Nishioka, *Tetrahedron Lett.*, 3833 (1969). See also: H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **92**, 2276 (1970); T. Yukawa and S. Tsutsumi, *Inorg. Chem.*, **7**, 1458 (1968).

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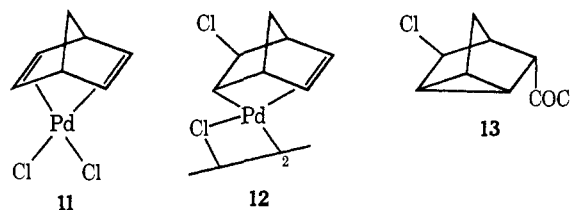
(19) G. Albelo and M. F. Rettig, *J. Organometal. Chem.*, **42**, 183 (1972); E. Vedejs, *J. Amer. Chem. Soc.*, **90**, 4751 (1968). See also: A. D. Ketley and J. A. Braatz, *J. Organometal. Chem.*, **9**, P5 (1967); A. D. Ketley, J. A. Braatz, and J. Craig, *Chem. Commun.*, 1117 (1970).

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(21) J. Tsuji, *Advan. Org. Chem.*, **6**, 109 (1969).

(22) J. F. Harrod and A. J. Chalk, *J. Amer. Chem. Soc.*, **86**, 1776 (1964); R. Cramer and R. V. Lindsey Jr., *ibid.*, **88**, 3534 (1966); K. Dunne and F. J. McQuillin, *J. Chem. Soc. C*, 2196 (1970); P. M. Henry, *Accounts Chem. Res.*, **6**, 16 (1974).

thought to proceed *via*  $\sigma$ -bonded chloro complexes, none of these intermediates has been isolated. In the carbonylation of **11**, the formation of **13** is thought to involve initial trans addition of  $\text{Pd-Cl}$  to give intermediate **12**.<sup>23,24</sup> The formation of chloro complex **7a**



from 5-vinyl-2-norbornene represents the first isolation of the product of trans addition of the elements of  $\text{Pd-Cl}$  to a diene, and, as such, supports mechanisms invoking these additions. Further work on this interesting system is continuing in these laboratories.

### Experimental Section

Melting points were taken on a Mel-temp apparatus and are uncorrected. Spectral measurements were made on the following instruments: ir, Perkin-Elmer Model 237B grating spectrophotometer; nmr, Varian Associates Model A-60; molecular weights, Melchrolab osmometer; vpc/mass spectra, Du Pont Model 21-490.<sup>25</sup> Elemental analyses were performed by either Schwarzkopf Microanalytical Lab, Woodside, N. Y., or Hoffmann-La Roche, Inc., Nutley, N. J.

Bis(benzonitrile)palladium dichloride was prepared by the method of Kharasch;<sup>26</sup> 2-*exo*-norborneol was prepared according to Brown;<sup>27</sup> 2-*endo*-norborneol was prepared according to Brown;<sup>28</sup> 5-vinyl-2-norbornene was purchased from Aldrich Chemical Co., and was used without further purification; the palladium salts were purchased from Englehart Industries.

**General Procedure for the Reaction of Diolefins with Palladium Salts.** The palladium salt and the solvent were placed in a 25-ml erlenmeyer flask, a serum cap was attached, and the flask was flushed with nitrogen. The diene was injected into the flask, and the contents were stirred until either a new solid had formed, or a color change indicated completion of reaction. The contents were filtered, and precipitate was washed with ligroin and dried. Additional solid could be obtained by diluting the solvent layer with ligroin and filtering as before.

***Di- $\mu$ -chloro-bis(2-*exo*-chloro-5-*endo*-vinyl-3-norbornyl)dipalladium (7a).*** From Bis(benzonitrile)palladium Dichloride. The general procedure was followed using 0.2145 g (0.56 mmol) of  $(\text{PhCN})_2\text{PdCl}_2$  and 0.5 ml of the diene in 5 ml of benzene. The red color faded, but no solid formed. The solvent was evaporated under reduced pressure to give a pale green solid, which was recrystallized from  $\text{CHCl}_3$ /ligroin to afford 0.1513 g (91%) of **7a** as a tan, granular solid; the solid darkened at  $180^\circ$  but did not decompose until  $220^\circ$ ; ir (KBr)  $\nu$  1560 (w, coordinated  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ ; mol wt (toluene) 588 (calcd, 595.02). When the above reaction was repeated using acetone as solvent, a copious precipitate formed immediately. This had identical ir and nmr spectra with the above compound. Reaction in acetone at  $-60^\circ$  gave identical results.

*Anal.* Calcd for  $\text{C}_{18}\text{H}_{24}\text{Cl}_4\text{Pd}_2$  (595.02): C, 36.33; H, 4.06; Cl, 23.84; Pd, 35.76. Found: C, 36.55; H, 3.97; Cl, 23.30 (Hoffmann-La Roche #91760).

**B. From  $\text{Na}_2\text{PdCl}_4$ .** The general procedure was followed using 0.2850 g (1.0 mmol) of  $\text{Na}_2\text{PdCl}_4$  and 0.2 g of the diene in 10 ml of acetone. After the mixture was stirred for 4 hr, 0.2357 g (80%) of a pale yellow solid was collected after work-up. This solid was identified as **7a** on the basis of ir and nmr spectra.

(23) L. F. Hines and J. K. Stille, *J. Amer. Chem. Soc.*, **94**, 485 (1972).

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(25) This equipment was purchased through funds made available by NSF (GP-32826).

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(27) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1524 (1967); H. C. Brown, J. H. Kawakami, and S. Ikegami, *ibid.*, **89**, 1525 (1967).

(28) H. C. Brown and P. M. Weismann, *J. Amer. Chem. Soc.*, **87**, 5614 (1965).

**C. From PdCl<sub>2</sub>.** The general procedure was followed using 0.190 g (1.1 mmol) of PdCl<sub>2</sub> and 0.25 g of the diene in 10 ml of benzene. This was stirred for 8 hr, during which time the brown solid gradually turned yellow. After normal work-up, 0.304 g (93%) a yellow solid was found, which gave ir and nmr spectra identical with **7a** prepared above.

**Di- $\mu$ -chloro-bis(2-*exo*-ethoxy-5-*endo*-vinyl-3-norbornyl)dipalladium (7b).** The general procedure was followed using 0.3610 g (2.0 mmol) of PdCl<sub>2</sub> and 0.5 g of the diolefin in 15 ml of ethanol. The mixture was stirred for 3 days, during which time the color changed from a muddy brown to a pale yellow. This solid was isolated as usual to give 0.5249 g (91%) of complex **7b**: mp 153–154° dec; ir (KBr)  $\nu$  1515 (w, coordinated C=C) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>) see Figure 1b.

*Anal.* Calcd for C<sub>20</sub>H<sub>30</sub>Cl<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub> (586.17): C, 40.98; H, 5.16; Cl, 12.10; Pd, 36.30. Found: C, 41.17; H, 5.20; Cl, 12.28; Pd, 36.13 (Schwarzkopf #347319).

Complex **7b** was also formed by passing complex **7a** through a short silica gel column using CHCl<sub>3</sub>/EtOAc as eluent; or by stirring a chloroform solution of **7a** with ethanol. These products were identified by comparison of their nmr spectra.

**Reaction of Ethoxy Complex 7b with LiCl and HCl.** The ethoxy complex **7b** (0.043 g, 0.07 mmol) and 0.03 g (0.7 mmol) of LiCl was stirred in 10 ml of CH<sub>2</sub>Cl<sub>2</sub> containing a drop of concentrated HCl. After 1 hr, the mixture was washed with water and the organic layer dried over MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give 0.034 g of a yellow solid, the nmr of which was identical with that of complex **7a**. The solid started to darken at 170°, and decomposed over a broad temperature range.

**Di- $\mu$ -chloro-bis(2-*exo*-methoxy-5-*endo*-vinyl-3-norbornyl)dipalladium (7c).** The general procedure was followed using 0.3532 g (2.0 mmol) of PdCl<sub>2</sub> and 0.5 g of the diene in 15 ml of methanol. After 2 days a yellow solid was isolated and recrystallized from methanol to give 0.4334 g (74%) of complex **7c** as yellow platelets: mp 142–144° dec; ir (KBr)  $\nu$  1520 (w, coordinated C=C) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  5.63 (1 H, d of d,  $J_{8,10} = 14$  Hz,  $J_{8,9} = 8$  Hz, H<sub>8</sub>), 4.73 (1 H, doublet, H<sub>10</sub>), 4.45 (1 H, doublet, H<sub>9</sub>), 3.69 (1 H, broad singlet, H<sub>2</sub>), 3.24 (3 H, singlet, OCH<sub>3</sub>), 2.88 (1 H, mound, H<sub>5</sub> or H<sub>3</sub>), 2.68 (1 H, mound, H<sub>5</sub> or H<sub>3</sub>), 1.0–2.5 (6 H, complex band) ppm.

*Anal.* Calcd for C<sub>20</sub>H<sub>30</sub>Cl<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub> (586.17): C, 40.98; H, 5.16; Cl, 12.10; Pd, 36.30. Found: C, 41.17; H, 5.20; Cl, 12.28; Pd, 36.13 (Schwarzkopf #347319).

This complex (**7c**) was also obtained in 46% yield by reaction of the diene with Na<sub>2</sub>PdCl<sub>4</sub> in methanol.

**Di- $\mu$ -chloro-bis(2-*exo*-acetoxy-5-*endo*-vinyl-3-norbornyl)dipalladium (7d).** The general procedure was followed using 0.177 g (1.0 mmol) of PdCl<sub>2</sub>, 0.20 g (2.4 mmol) of NaOAc, and 0.5 g of the diene in 15 ml of acetic acid. After the mixture was stirred for 5 days, a yellow solid was isolated. Recrystallization from CHCl<sub>3</sub>/ligroin gave 0.2960 g (92%) of complex **7d**: mp 189° dec; ir (KBr)  $\nu$  1710 (s, C=O) and 1510 (w, coordinated C=C) cm<sup>-1</sup>; nmr (CDCl<sub>3</sub>)  $\delta$  5.93 (1 H, d of d,  $J_{8,10} = 14$  Hz,  $J_{8,9} = 8$  Hz, H<sub>8</sub>), 4.62 (1 H, doublet, H<sub>10</sub>), 4.57 (1 H, doublet, H<sub>9</sub>), 5.24 (1 H, broad singlet, H<sub>2</sub>), 3.0 (1 H, mound, H<sub>5</sub> or H<sub>3</sub>), 2.78 (1 H, mound, H<sub>5</sub> or H<sub>3</sub>), 1.97 (3 H, singlet, OCOCH<sub>3</sub>), 0.9–2.16 (6 H, complex band) ppm.

*Anal.* Calcd for C<sub>23</sub>H<sub>30</sub>Cl<sub>2</sub>O<sub>2</sub>Pd<sub>2</sub> (642.18): C, 41.15; H, 4.71; Cl, 11.05. Found: C, 41.39; H, 4.71; Cl, 11.63 (Hoffmann-La Roche #91944).

**Decomposition of 7a with KCN.** The complex (0.2 g) was stirred for 1 hr with a solution 1.5 M KCN (5 ml) and 5 ml of CCl<sub>4</sub>. The clear solution was separated and the organic phase dried over MgSO<sub>4</sub>. Evaporation of the solvent gave 0.0512 g of a clear liquid, identified by nmr as pure 5-*endo*-vinyl-2-norbornene.<sup>5</sup>

**Reaction of 1,5-Cyclooctadiene with PdCl<sub>2</sub> in Methanol.** The general procedure was followed using 0.188 g (1.06 mmol) of PdCl<sub>2</sub> and 0.5 g of 1,5-cyclooctadiene in 10 ml of methanol. After 8 hr, a gold-colored precipitate had formed. This was isolated (0.238 g) and identified as (1,5-cyclooctadiene) PdCl<sub>2</sub>, mp 210° dec (lit.<sup>19</sup> mp 210–215° dec). The methanol layer was evaporated to leave 0.0169 g of a pale yellow solid, identified as di- $\mu$ -chloro-bis(2-methoxycyclooct-5-enyl)dipalladium, mp 130–140° dec (lit.<sup>1</sup> mp 136–140° dec).

When the above procedure was repeated using 0.2 g (2.0 mmol) of Na<sub>2</sub>CO<sub>3</sub>, a gray solid formed after 5 hr. The methanol was removed under reduced pressure, and the residue was taken up in 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. This was washed with water, treated with Norit, and dried over MgSO<sub>4</sub>. The solvent was evaporated to leave 0.1237 g (88%) of di- $\mu$ -chloro-bis(2-methoxycyclooct-5-enyl)dipalladium, mp 126–136°.

**Reaction of Dicyclopentadiene with PdCl<sub>2</sub> in Methanol.** The general procedure was followed using 0.175 g (1.0 mmol) of PdCl<sub>2</sub> and 0.25 g of the diene in 10 ml of methanol. The mixture was stirred for 24 hr, resulting in the formation of a pale yellow solid. This was isolated in the usual manner to give 0.2756 g (91%) of a yellow powder, identified as the methoxy adduct **3** (N = OMe) on the basis of nmr<sup>2</sup> and melting point data, mp 165–180° (lit.<sup>1</sup> mp 166–170° dec).

**Reaction of Norbornadiene with PdCl<sub>2</sub> in Methanol.** The general procedure was followed using 0.177 g (1.0 mmol) of PdCl<sub>2</sub> and 0.25 g of the diene in 10 ml of methanol. The mixture was stirred for 8 hr, and the dark golden solid which had formed was isolated in the usual manner to give 0.2560 g (94%) of a solid identified as (norbornadiene) PdCl<sub>2</sub>, mp 180–210° dec (lit.<sup>2</sup> mp 190–200° dec).

When the above reaction was repeated with the addition of 0.2 g (2.0 mmol) of Na<sub>2</sub>CO<sub>3</sub> in 50 ml of methanol, a muddy solid was formed. The solvent was evaporated under reduced pressure, and the resulting mixture taken up in 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. This was washed with water, treated with Norit, and filtered while hot. Evaporation of the solvent left 0.1187 g of a yellow solid identified as the methoxy adduct of (norbornadiene) PdCl<sub>2</sub>, mp 125° dec (lit.<sup>2</sup> mp 134–137° dec).

**Hydrogenation of 7d.** A solution of acetoxy complex **7d** (1.28 g, 2.0 mmol) in 100 ml of acetone was hydrogenated on a Paar apparatus for 1 hr at 30 psi. The product was filtered and the acetone removed under reduced pressure. The residue was taken up in ether, washed with 10 ml of 5% NaHCO<sub>3</sub>, and dried over MgSO<sub>4</sub>. The solvent was evaporated to leave 0.485 g (67%) of 2-*exo*-acetoxy-5-*endo*-ethylnorbornane (**8**) as a clear, sweet smelling liquid: ir (CCl<sub>4</sub>)  $\nu$  1735 (s, C=O) cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  4.43 (1 H, multiplet, CHOAc), 1.92 (3 H, singlet, OCOCH<sub>3</sub>), 0.5–2.3 (14 H, complex band) ppm; mass spectrum (peaks  $\geq$  50% intensity) *m/e* (rel intensity) 184 (M<sup>+</sup> + 2, 1), 183 (M<sup>+</sup> + 1, 2), 139 (50), 122 (70), 95 (75), 94 (90), 93 (75), 79 (60), 67 (68), 66 (100), 55 (62), 43 (88); no parent peak was visible.

*Anal.* Calcd for C<sub>11</sub>H<sub>18</sub>O<sub>2</sub> (182.3): C, 72.49; H, 9.95. Found: C, 72.15; H, 9.43 (Hoffmann-La Roche #92335).

**Hydrolysis of 8.** Acetate **8** (0.5 g, 2.75 mmol) was refluxed with 0.5 g of KOH in 10 ml of 95% ethanol for 1 hr. The solution was poured into 10 ml of water and the ethanol was removed under reduced pressure. The aqueous solution was extracted with ether, and the ether layer was washed with 10 ml of 5% HCl and dried over MgSO<sub>4</sub>. The solvent was evaporated to leave 0.35 g (92%) of 2-*exo*-hydroxy-5-*endo*-ethylnorborane (**9**) as a clear, viscous liquid: ir (CCl<sub>4</sub>)  $\nu$  3610 (w, free OH) and 3320 (m, broad, associated OH) cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  3.55 (1 H, unresolved multiplet, CHOH), 2.60 (1 H, singlet, OH), 2.0 (2 H, mound, bridgehead H), 0.7–2.0 (12 H, complex band) ppm.

**Oxidation of 9.** Alcohol **9** (0.205 g, 1.46 mmol) and 5 ml of ether were placed in a 50-ml round-bottomed flask, which was immersed in an ice bath. The solution was stirred rapidly while 5 ml of "Brown's oxidant"<sup>29</sup> (4 N Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>/H<sub>2</sub>SO<sub>4</sub>) was added through a dropping funnel. After 5 min, a green color persisted and an additional 5 ml of the oxidant was added. This mixture was stirred at 0° for 1 hr. The layers were separated and the aqueous layer was extracted with ether. The ether layers were combined, washed with 10 ml of 5% NaHCO<sub>3</sub> solution followed by 10 ml of water, and dried over MgSO<sub>4</sub>. Evaporation of the solvent left 0.14 g (71%) of 5-*endo*-ethylnorbornanone as a clear liquid: ir (CCl<sub>4</sub>)  $\nu$  1755 (s, C=O) cm<sup>-1</sup>; nmr (CCl<sub>4</sub>)  $\delta$  0.7–2.6 (complex band) ppm; mass spectrum (peaks  $\geq$  40% intensity) *m/e* (rel intensity) 139 (M<sup>+</sup> + 1, 6), 138 (M<sup>+</sup>, 46), 109 (40), 95 (63), 94 (100), 81 (63), 79 (60), 67 (78), 55 (50), 41 (76).

**Reduction of 5-*endo*-Ethylnorbornanone.** The ketone (0.142 g, 1.03 mmol) was added to a previously prepared solution of LiAl(OCH<sub>3</sub>)<sub>3</sub>H (0.0105 g, 0.275 mmol, of LiAlH<sub>4</sub>) and 0.0264 g, 0.825 mmol, of methanol<sup>28</sup> in 10 ml of THF at 0°. This mixture was stirred for 1 hr, and the excess hydride was hydrolyzed with 1 ml of water. The solution was extracted with ether, and the ether layer was dried over MgSO<sub>4</sub>. Evaporation of the solvent left a slightly cloudy mixture. This was passed through a short alumina (Woelm, neutral) column and eluted with pentane followed by ether. The ether portion was evaporated to leave 0.128 g (89%) of 2-*endo*-hydroxy-5-*endo*-ethylnorbornane (**10**) as a clear viscous liquid: ir (CCl<sub>4</sub>)  $\nu$  3610 (w, free OH) and 3330 (m, broad, associated OH)

(29) H. C. Brown, C. P. Garg, and K. T. Liu, *J. Org. Chem.*, **36**, 387 (1971).

cm<sup>-1</sup>; nmr (CCl<sub>4</sub>) δ 4.10 (1 H, d of d of d,  $J_{1,2} = 4$  Hz,  $J_{2,3a} = 5$  Hz,  $J_{2,3x} = 10$  Hz, CHOH), 2.60 (1 H, singlet, OH), 0.9–2.3 (14 H, complex band) ppm.

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## Effects of Base Association and Strength upon Base-Promoted Syn Eliminations

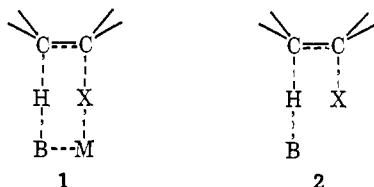
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**Abstract:** Primary deuterium isotope effects and Hammett  $\rho$  values for syn E2 reactions of *trans*-2-arylcyclopentyl tosylates promoted by associated and dissociated alkoxide ion bases have been determined. More carbanionic transition states are observed for a dissociated base than the corresponding associated base. Transition states with greater carbanionic character and C<sub>β</sub>-H bond rupture are found for a stronger dissociated alkoxide ion base in an alcoholic solvent of lower polarity.

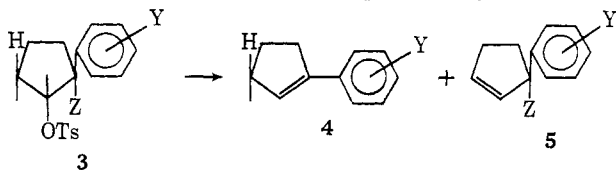
Base association has been postulated to facilitate transition states for base-promoted syn eliminations by allowing simultaneous coordination of the counterion with the base and leaving group as depicted in **1**, where X is the leaving group, B is the base, and M



is the counterion.<sup>2,3</sup> In order to assess transition-state differences for syn eliminations induced by (a) *associated* and *dissociated* alkoxide base species, **1** and **2**, respectively, and (b) *dissociated* alkoxide ion bases of varying strength, the following investigation was conducted.

### Results and Discussion

Reactions of *trans*-2-arylcyclopentyl tosylates **3**, with



	Y	Z
a	H	H
b	H	D
c	<i>m</i> -Cl	H
d	<i>p</i> -Cl	H
e	<i>m</i> -Me	H
f	<i>p</i> -Me	H
g	<i>p</i> -OMe	H

various bases produce 1-arylcyclopentene **4**, by activated syn elimination and 3-arylcyclopentene, **5**, by unactivated anti elimination.<sup>4–6</sup> Formation of **5** by unactivated syn elimination is unimportant.<sup>6</sup> Since rates of anti elimination producing **5** should be insensitive to variation of Y<sup>7</sup> or substitution of deuterium for hydrogen at Z in **3**, relative rates of formation of **4** may be determined with reference to the internal standard **5** by product analysis.

**Associated and Dissociated Alkoxide Ion Bases.** The relative proportions of **4a** and **5a** obtained from reactions of **3a** with 0.10 M *t*-BuOK-*t*-BuOH in the absence and presence of two crown ethers<sup>8</sup> are presented in Table I. Addition of the strong potassium ion

Table I. Effect of **6** and **7** upon the Relative Proportions of Isomeric Phenylcyclopentenes Formed in Reactions of 0.025 M **3a** with 0.10 M *t*-BuOK-*t*-BuOH at 50.0°

Crown ether	[Crown ether], M	Total phenylcyclopentenes, %	1-Phenylcyclopentene	3-Phenylcyclopentene
		89.2 ± 0.5 <sup>a</sup>	10.8 ± 0.5	
<b>6</b>	0.031	46.5 ± 0.3 <sup>a</sup>	53.5 ± 0.3	
<b>6</b>	0.049	33.0 ± 0.2 <sup>a</sup>	67.0 ± 0.2	
<b>6</b>	0.10	30.1 ± 0.7 <sup>a,b</sup>	69.9 ± 0.7	
<b>6</b>	0.17	29.5 ± 0.3 <sup>a</sup>	70.5 ± 0.3	
<b>6</b>	0.22	30.8 ± 0.4 <sup>a</sup>	69.2 ± 0.4	
<b>7</b>	0.10	90.7 ± 0.4 <sup>a</sup>	9.3 ± 0.4	

<sup>a</sup> Standard deviation from repetitive analysis of product mixture.

<sup>b</sup> Average of values from three runs conducted by three different investigators.

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(7) Rates of formation of **5** in reactions of **3a** and **3f** with *t*-BuOK-*t*-BuOH<sup>4</sup> are the same within experimental error.

(8) Macrocyclic polyethers. For a review, see C. H. Pederson and H. K. Frensdorff, *Angew. Chem., Int. Ed. Engl.*, **11**, 16 (1972).

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