

# Molecular Asymmetry. IX. The Partial Resolution and Asymmetric Synthesis of 1,2-Cyclonadiene<sup>1</sup>

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**Abstract:** The diastereomeric platinum complexes of 1,2-cyclonadiene,  $[(\pm\text{C}_9\text{H}_{14})\text{PtCl}_2(\text{Am}^*)]$  where  $\text{Am}^*$  represents either optically active  $\alpha$ -methylbenzylamine or  $p$ -nitro- $\alpha$ -methylbenzylamine have been prepared and partially separated by fractional crystallization. Optically active 1,2-cyclonadiene having an optical purity of ca. 44% has been isolated from the treatment of a complex enriched in one diastereoisomer with aqueous sodium cyanide. Both enantiomers of optically active *trans*-cyclooctene were converted to the corresponding optically active dibromocarbene adducts which upon treatment with methyl lithium afforded 1,2-cyclonadiene having a high optical purity.

The resolution of *trans*-cycloalkenes has recently been accomplished by the formation of coordination complexes with platinum.<sup>3,4</sup> The olefins were resolved by separating the diastereomeric platinum(II) complexes  $[(\pm \text{olefin})\text{PtCl}_2(\text{amine})]$  employing optically active  $\alpha$ -methylbenzylamine. This method has more recently been utilized in the resolution of ethyl-*p*-tolyl sulfoxide.<sup>5</sup> In this study, we have examined the extension of this method to the resolution of allenes.

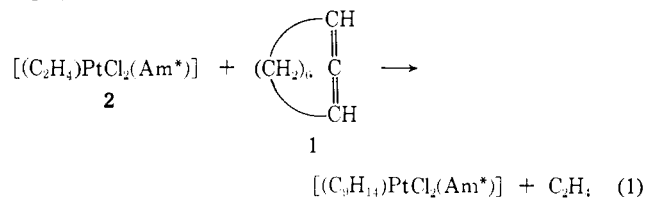
A number of optically active allenes have been obtained either by asymmetric syntheses or by classical resolution techniques.<sup>6-8</sup> In general, the latter have required that the allene be substituted with a functional group which could serve as a handle in forming a diastereomeric pair by reaction with an optically active reagent. A useful asymmetric synthesis has been devised by Jones and coworkers who have prepared optically active ethyl *N*-nitroso-*N*-(*trans*-2,3-disubstituted cyclopropyl)carbamates with bases.<sup>9</sup> This reaction generates the corresponding diazocyclopropanes which readily decompose to allenes, at least in part *via* cyclopropylidene intermediates. Until recently, only modest success had been achieved with several methods for preparing optically active allene hydrocarbons by asymmetric induction (summarized in ref 9b), but the report by Waters, Linn, and Caserio<sup>10</sup> appears to be a promising exception. They obtained partially resolved 1,3-dimethylallene by selective reduction of the racemic allene with an optically active dialkylborane.

The approach to resolution of an allene *via* platinum complexes discussed in this paper does not require any

functional substituents on the allene. The resolution simply utilizes the principle of attaching both racemic allene and the optically active amine to the (square planar) platinum(II) to form a pair of diastereoisomers which, hopefully, can be separated by fractional crystallization. The optically active allene can then be displaced from a diastereoisomer by treatment with aqueous sodium cyanide.

At the outset of this work no platinum complexes of allene had been reported. Palladium complexes of allenes, but in which the allene moiety has been converted to an allyl group, had been prepared from alkylallenes.<sup>11</sup> A current flurry of activity has produced a variety of allene-transition metal complexes, including those of iron,<sup>12</sup> platinum,<sup>13</sup> and rhodium.<sup>14</sup>

Preliminary experiments were carried out with 1,3-diethylallene and 1,3-diphenylallene but work on these systems was abandoned because we could not obtain the platinum complexes as well-defined crystalline solids which could be fractionally recrystallized. Our efforts were then turned toward resolution of 1,2-cyclonadiene which was found to give several crystalline complexes which could be prepared by the procedure employed for the platinum complex of *trans*-cyclooctene<sup>3</sup> (eq 1).



a,  $\text{Am}^* = (+)\text{-C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NH}_2$

b,  $\text{Am}^* = (-)\text{-C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{NH}_2$

c,  $\text{Am}^* = (+)\text{-}p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2$

d,  $\text{Am}^* = (-)\text{-}p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{NH}_2$

e,  $\text{Am}^* = (+)\text{-C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2$

(1) (a) R. G. Schultz, *Tetrahedron*, **20**, 2809 (1964); (b) M. S. Lupin and B. L. Shaw, *Tetrahedron Lett.*, 883 (1964).

(2) R. Ben-Shoshan and R. Pettit, *J. Am. Chem. Soc.*, **89**, 2231 (1967).

(3) (a) S. Otsuka, A. Nakamura, and K. Tani, *J. Organometal. Chem.*, **14**, P30 (1968); (b) K. Vrieze, H. C. Volger, M. Gronert, and A. P. Praat, *ibid.*, **16**, P19 (1969).

(4) (a) T. G. Hewitt, K. Anzenhofer, and J. J. de Boer, *Chem. Commun.*, 312 (1969); (b) T. Kashiwagi, N. Yasuoka, N. Kasai, and M. Kukudo, *ibid.*, 317 (1969); (c) P. Racanelli, G. Pantini, A. Immirzi, G. Allegra, and L. Porri, *ibid.*, 361 (1969).

(1) (a) Supported in part by the National Science Foundation (GP-6222) and the Army Research Office (Durham, DA-31-124-ARO-D435). (b) For the previous papers in this series see A. C. Cope and B. A. Pawson, *J. Am. Chem. Soc.*, **90**, 636 (1968).

(2) (a) Deceased, June 4, 1966. (b) To whom inquiries may be addressed. (c) National Institutes of Health Predoctoral Fellow, 1964-1967.

(3) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

(4) A. C. Cope, K. Banholzer, H. Keller, J. J. Whang, B. A. Pawson, and H. J. S. Winkler, *ibid.*, **87**, 3644 (1965).

(5) A. C. Cope and E. A. Caress, *ibid.*, **88**, 1711 (1966).

(6) E. L. Eliel, "Stereochemistry of Carbon Compounds," W. A. Benjamin, Inc., New York, N. Y., 1962.

(7) K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, Inc., New York, N. Y., 1966.

(8) D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967).

(9) (a) W. M. Jones, J. W. Wilson, Jr., and F. B. Tutwiler, *J. Am. Chem. Soc.*, **85**, 3309 (1963); (b) J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *ibid.*, **90**, 2895 (1968).

(10) W. L. Waters, W. S. Linn, and M. C. Caserio, *ibid.*, **90**, 6741 (1968).

Addition of racemic 1,2-cyclononadiene to a methylene chloride solution of (the optically pure) complex **2a** led to ready displacement of ethylene. Evaporation of the solvent afforded the allene complex **3a**, a mixture of diastereoisomers, as a yellow crystalline solid.<sup>15</sup> The complex was recrystallized repeatedly, first from methylene chloride-pentane and then from carbon tetrachloride-hexane. The rotation of the lead fraction became increasingly negative but after a few recrystallizations, the change became very small. The maximum rotation observed (after 13 recrystallizations) for the less soluble fraction<sup>15b</sup> **3a'** was  $[\alpha]^{24D} - 61.6^\circ$  ( $\text{CHCl}_3$ ). This material was decomposed with aqueous sodium cyanide and the allene isolated by distillation was found to have  $[\alpha]^{24D} - 71^\circ$  (neat). Subsequent results established that this allene was only partially resolved; the optical purity was *ca.* 44%.<sup>16,17</sup> Since the rotation of **3a'** was not changing significantly with further recrystallization, it appeared that complete separation of diastereoisomers and thus complete resolution of the allene could not be achieved.

The view that the resolution had reached an impasse was substantiated when optically active allene became available by the synthetic method discussed later. Complex **3a'** was prepared from optically active 1,2-cyclononadiene,  $[\alpha]^{24D} - 132^\circ$  (neat), and complex **2a**. After several recrystallizations, **3a'** had a rotation of  $[\alpha]^{24D} - 118^\circ$  ( $\text{CH}_2\text{Cl}_2$ ), a value which was not changed by additional recrystallization. The allene was recovered from the platinum complex and found to be essentially unchanged in rotation,  $[\alpha]^{25D} - 129^\circ$  (neat). Similarly **3b'** (the enantiomer of **3a'**) was prepared from complex **2b** and dextrarotatory 1,2-cyclononadiene,  $[\alpha]^{25D} + 138^\circ$  (neat). After several recrystallizations to ensure chemical purity, complex **3b'** had a rotation of  $[\alpha]^{25D} + 123^\circ$  ( $\text{CH}_2\text{Cl}_2$ ), a value which was not raised upon further recrystallization.

We estimate that a pure diastereoisomer (**3a'** or **3b'**) would have a specific rotation with an absolute value of *ca.* 150%.<sup>18</sup> Thus, even though the complexes synthesized from optically active 1,2-cyclononadiene had rotations about twice that of the material obtained from the partial resolution described above and the rotations were not noticeably changing with recrystallization, we still had not obtained a pure diastereoisomer. The fact that separation of diastereoisomers (**3a'**-**3a''** or **3b'**-**3b''**) was stopped at two very different compositions apparently reflects some special, but unfortunate, crystal stabilization at these compositions which is reflected in the solubility behavior observed. When complex **3b'** was prepared<sup>19</sup> with a rotation of *ca.* 86°,

(15) (a) This material is a 1:1 mixture of dichloro[(-)-1,2-cyclononadiene][(+)- $\alpha$ -methylbenzylamine]platinum(II) (**3a'**) and dichloro[(+)-1,2-cyclononadiene][(+)- $\alpha$ -methylbenzylamine]platinum(II) (**3a''**). The chloro ligands are probably *trans* based on the structure established for the related complex derived from *trans*-cyclooctene.<sup>3</sup> (b) In each such pair of diastereoisomers, **3**, the less soluble isomer is designated by a single prime (*e.g.*, **3a'**) and the more soluble by a double prime (*e.g.*, **3a''**). Fractions enriched in one isomer will be designated according to the same system.

(16) We estimate that optically pure allene has a specific rotation of about 170–175° in  $\text{CH}_2\text{Cl}_2$  and 158–162° neat. This estimate, based on results obtained in dimerizing optically active **1**, is discussed elsewhere.<sup>17</sup>

(17) W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Am. Chem. Soc.*, **91**, 5918 (1969).

(18) This value is obtained by extrapolating the linear relation between the rotation of the complex and that of the allene obtained from it to the rotation we have estimated for optically pure allene.

indicating a composition between the values referred to above, recrystallization led to a decrease in rotation of lead fractions suggesting a retrogression to the composition obtained by the partial resolution.

During the course of the resolution, mutarotation of complex **3a'** was observed. In chloroform, the half-life for mutarotation, which appeared to be first order in the complex, was about 1 month at room temperature (*ca.* 25°) and a few hours at reflux (*ca.* 61°). Fortunately, a solution of **3a'** in methylene chloride did not show a measurable change in rotation when kept at 0° for 48 hr. As a consequence a recrystallization procedure could be employed which avoided mutarotation (Experimental Section).

The mutarotation is not due to racemization of the amine (which can be recovered unchanged) and it is not due to reversible dissociation of the complex and racemization of the free allene because 1,2-cyclononadiene is not detectably racemized at room temperature either neat or in methylene chloride solution. Allene-acetylene interconversion would effect racemization of the allene. Although base-catalyzed allene-acetylene interconversion has been achieved in this system and the allene predominates at equilibrium,<sup>20</sup> we believe that there is no basis for proposing some sort of platinum catalysis of this interconversion. Some support for this view is gained from the observation that when samples of **3a'** and **3a''** were allowed to mutarotate extensively and then were decomposed with sodium cyanide, the hydrocarbon which was recovered consisted of 1,2-cyclononadiene only; no cyclononyne was detected by glpc. Thus we believe that mutarotation reflects racemization of the allene while it is a ligand in the platinum complex.

Ben-Shoshan and Pettit have reported that the complex [(tetramethylallene)Fe(CO)<sub>4</sub>] exhibits three methyl singlets with a 1:1:2 ratio of intensities in the nmr spectrum at -60° as would be expected for a structure in which the iron is bonded to one double bond.<sup>12</sup> At room temperature the spectrum collapses to only one singlet, a result which they suggest indicates that the iron migrates from one double bond to the other, moving about the allene in a "quasihelical" fashion<sup>21</sup> with a barrier of about 9 kcal. Vrieze and coworkers have reported a similar behavior for [(tetramethylallene)PtCl<sub>2</sub>]<sub>2</sub> and [(tetramethylallene)PtCl<sub>2</sub>(Py)], where Py represents various substituted pyridines, but they found no temperature dependence for the nmr spectra of the related 1,1-dimethylallene complexes (in which the Pt was bonded to the C=CH<sub>2</sub> end only).<sup>18b</sup> While a "back-and-forth" migration might be occurring in the cyclononadiene-platinum complexes (**3**),<sup>22</sup> it would not affect the asymmetry of the allene and thus could not account for racemization. Clearly some other change must occur in which the allene part of the complex passes through a symmetrical intermediate or transition state. We can envision several mechanisms which accomplish this change but will restrict discussion to two.

(19) This sample was prepared by diluting a sample of **3b'**,  $[\alpha]^{25D} + 112^\circ$ , with **3b** prepared from racemic 1,2-cyclononadiene.

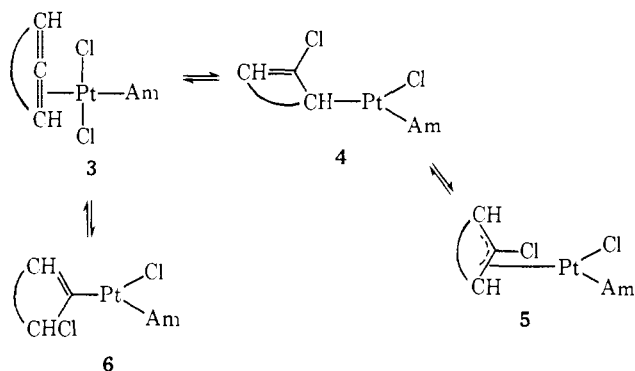
(20) W. R. Moore and H. R. Ward, *J. Am. Chem. Soc.*, **85**, 86 (1963).

(21) Refer to F. A. Cotton [*Accounts Chem. Res.*, **1**, 9 (1968)] for a discussion of this and other fluxional organometallic molecules.

(22) Such exchange was not occurring on the nmr time scale at room temperature.

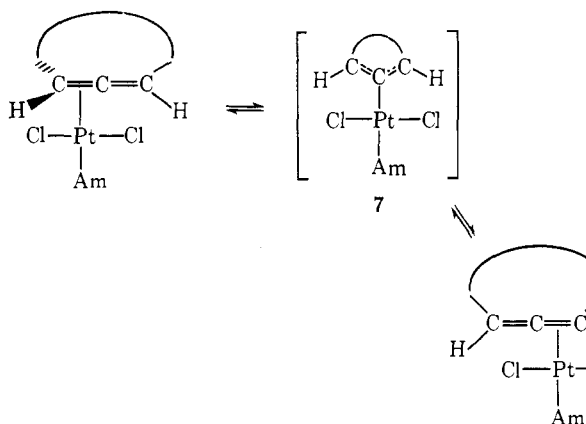
The reversible isomerization of the ( $\pi$ -allene)-platinum complex **3** to the  $\sigma$ -allyl complex **4** and/or the related  $\pi$ -allyl complex **5** or to the  $\sigma$ -vinyl complex **6** would result in racemization of the allene (Scheme I).<sup>23</sup>

Scheme I



Alternatively, the mutarotation could result from a "slow fluxional change" in which the ( $\pi$ -allene)-platinum complex is transformed to a species **7** (transition state or intermediate) with the platinum  $\sigma$  bonded to the central carbon atom of an allyl group. The latter, with only two electrons in the  $\pi$  system, would be formally equivalent to an allyl cation. Obviously transfer of a chloride ion from platinum to the allyl group would give the  $\sigma$ -vinyl species **6** shown in Scheme I. The idea introduced in Scheme II is that the configuration of the

Scheme II



allene may be inverted without any such ligand transfer.<sup>24</sup>

Since the art of resolution is still very much a matter of trial and error, another optically active amine was chosen in an effort to obtain a pair of diastereoisomers that could be separated more readily by crystallization. Although 1-phenyl-2-aminopropane (Dexedrine) has not proven to be a useful resolving agent for *trans*-cyclooctene,<sup>3</sup> its commercial availability prompted us to try it for the resolution of **1**. Complex **2e** was prepared from Zeise's salt and treatment with racemic 1,2-cyclononadiene afforded complex **3e** as a yellow solid. Attempts to recrystallize the complex were thwarted by the

(23) M. S. Lupin, J. Powell, and B. L. Shaw [*J. Chem. Soc., A*, 1687 (1966)] discuss the formation ( $\sigma$ - and  $\pi$ -allyl) and proposed intermediacy ( $\sigma$ -vinyl) of related palladium complexes derived from alkylallenes.

(24) It is worth noting that increased substitution on the allene should favor the process shown in Scheme II by stabilizing the (formal) allyl cation and that Scheme II represents a possible alternative explanation for the fluxional changes observed by Pettit<sup>12</sup> and Vrieze.<sup>13b</sup>

fact that **3e** was quite soluble in pentane and it was very difficult to obtain it in a crystalline form.

In an effort to prepare a diastereoisomer that would be less soluble in nonpolar hydrocarbon solvents, and would permit use of a broader range of more polar solvent systems for the resolution of **1**, the use of *p*-nitro- $\alpha$ -methylbenzylamine was investigated.

Racemic *p*-nitro- $\alpha$ -methylbenzylamine **8** was synthesized<sup>25</sup> and the dextrarotatory antipode (+)-**8**, obtained by resolution with *d*-10-camphorsulfonic acid,<sup>25a</sup> was converted to the platinum complex **2c** by treatment with Zeise's salt. Levorotatory amine (–)-**8** was prepared<sup>25</sup> from (–)- $\alpha$ -methylbenzylamine by acetylation, nitration, and hydrolysis and converted to the corresponding platinum complex **2d**.

Racemic 1,2-cyclononadiene was treated with complex **2c** in methylene chloride to give a mixture of diastereoisomers **3c** [ $[\alpha]^{25D} + 42^\circ$ ].

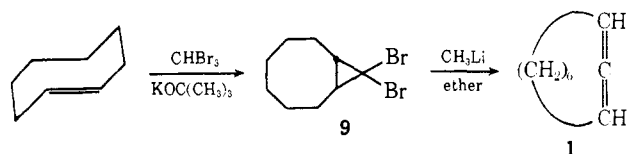
Recrystallization from benzene-cyclohexane led to a change in rotation, but after several recrystallizations the change was only a few degrees per step. After six recrystallizations the lead fraction, enriched in **3c'**, had a rotation of [ $\alpha$ ]<sup>23D</sup>  $- 13^\circ$ . This sample was treated with aqueous sodium cyanide and the 1,2-cyclononadiene recovered by distillation had a rotation of [ $\alpha$ ]<sup>27D</sup>  $- 56.7^\circ$  (*c* 1.5, CH<sub>2</sub>Cl<sub>2</sub>) showing that only partial resolution of the allene had been achieved.

Complex **3d**, [ $\alpha$ ]<sup>24D</sup>  $- 41^\circ$ , was prepared from **2d** and racemic 1,2-cyclononadiene and this material was recrystallized exhaustively until the rotation of the lead fraction of **3d'** had nearly levelled out at [ $\alpha$ ]<sup>24D</sup>  $+ 30^\circ$ , a value more than  $100^\circ$  below our estimate for the rotation of the pure diastereoisomer.<sup>26</sup> Thus complete resolution was again thwarted by unfortunate crystal properties. Clearly, however, the concept of resolving allenes *via* metal complexes is sound and is worthy of further study.

Although we had by no means exhausted all of the possible combinations of optically active amines with 1,2-cyclononadiene, we decided to synthesize **1** from optically active *trans*-cyclooctene. The route chosen was conversion of the olefin to the dibromocarbene adduct and utilization of the transformation of such cyclopropane derivatives to allenes by treatment with methyllithium.<sup>27</sup>

The synthesis of both enantiomers of 1,2-cyclononadiene followed the route shown in Scheme III. Treat-

Scheme III



ment of (–)-*trans*-cyclooctene with bromoform and potassium *t*-butoxide gave the optically active dibromide (+)-**9**, [ $\alpha$ ]<sup>25D</sup>  $+ 44.2^\circ$ , which upon treatment with methyllithium at 0° afforded the optically active allene

(25) (a) F. Nerdel and H. Liebig, *Ann.*, **621**, 21 (1963); (b) H. E. Baumgarten and J. M. Peterson, *J. Am. Chem. Soc.*, **82**, 459 (1960).

(26) A sample of optically active 1,2-cyclononadiene, [ $\alpha$ ]<sup>25D</sup>  $- 132^\circ$  (neat), synthesized as described below, was used to prepare a sample of **3c'** with a rotation of [ $\alpha$ ]<sup>25D</sup>  $- 110^\circ$  (CH<sub>2</sub>Cl<sub>2</sub>). Extrapolation from this point to optically pure allene gives an estimate of  $- 140^\circ$  for the specific rotation of **3c'** and thus  $+ 140^\circ$  for **3d'**.

(27) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **27**, 4179 (1962), and references therein.

(+)-1,  $[\alpha]^{25D} + 138^\circ$  (neat). Similarly, (+)-*trans*-cyclooctene led to the levorotatory dibromide (-)-9 which afforded (-)-1.

This method of adding  $\text{CBr}_2$  to *trans*-cyclooctene has been found to give a small amount of the *cis* (*meso*) adduct as well as the expected *trans* adduct **9** (the product of *cis* addition). Fortunately the latter is crystalline and can be freed of the liquid *cis* isomer by sufficient recrystallization. The origin of the *cis* adduct is of some interest because the addition of  $\text{CBr}_2$  to many (unstrained) olefins has been shown to be stereospecific *cis* process. If any *trans* addition to *trans*-cyclooctene did occur it could be interpreted as a reflection of the great strain in this olefin, possibly leading to a nonconcerted addition. However, we have found that under the conditions used for adding  $\text{CBr}_2$ , *trans*-cyclooctene undergoes partial isomerization to the *cis* isomer, suggesting that the latter is the source of the *cis* adduct.<sup>28</sup>

As examination of molecular models will show, the methylene chain of *trans*-cyclooctene screens one side of the double bond, thus addition can occur only from the "outside." As a result, the optical purity of a  $\text{CBr}_2$  adduct should be as high as that of the olefin employed,<sup>29</sup> which in the present case means at least very close to 100%. Thus if the reaction of the  $\text{CBr}_2$  adduct with methylolithium were completely stereospecific, the allene formed would also be essentially optically pure. In fact, based on our estimate<sup>16,17</sup> of the rotation of optically pure 1,2-cyclononadiene, the rotation of  $138^\circ$  referred to above indicates an optical purity of 85–88%. Higher optical purities have been obtained when the allene is formed at lower temperatures, but the price is a reduced yield of allene. We will discuss the stereochemical implications of these and other results in detail elsewhere.<sup>30</sup> At this time we wish to emphasize that the synthesis of 1,2-cyclononadiene from optically active *trans*-cyclooctene is a practical route to allene of high optical purity. Allene of lower optical purity can be obtained in fewer steps by direct partial resolution.

## Experimental Section<sup>31</sup>

**Resolution of  $\alpha$ -Methylbenzylamine.** This resolution, based on a modification of Ault's convenient procedure,<sup>32</sup> is described briefly since it affords large quantities of both enantiomers of this widely used amine optically pure.

**a. *l*- $\alpha$ -Methylbenzylamine.** A scaled-up version (using 200 g of amine) of Ault's procedure was followed with the change that the amine tartrate was collected in four crops (by concentration) which were carried through a fractional crystallization procedure<sup>33</sup>

(28) W. R. Moore and T. M. Ozretich, unpublished results. Significantly, *trans*-cyclooctene is not appreciably isomerized by either potassium *t*-butoxide or the 1:1 complex of potassium *t*-butoxide with *t*-butyl alcohol, but is isomerized under the conditions where bromoform reacts with potassium *t*-butoxide. The reactivity of the *trans*-olefin toward  $\text{CBr}_2$  is roughly three times that of the *cis* isomer.

(29) The resolved adduct melts about  $10^\circ$  higher than the racemic material, thus recrystallization could well raise the optical purity of the adduct; we have evidence that this occurs, W. R. Moore and T. M. Ozretich, unpublished observations.

(30) W. R. Moore and R. D. Bach, in preparation.

(31) Melting points of the platinum complexes were taken on a Kofler hot stage; all others are uncorrected capillary melting points. Analyses were performed by Dr. S. M. Nagy. Optical rotations were measured with a Zeiss photoelectric precision polarimeter. The rotations measured at 546.1 and 577.8 nm were used to calculate the value at the sodium D line (589.2 nm).

(32) A. Ault, *J. Chem. Educ.*, **42**, 269 (1965).

(33) The fractional recrystallizations referred to in this paper essentially followed the "double withdrawal" procedure described by R. S. Tipson in "Technique of Organic Chemistry," Vol. 3, Part 1, A. Weissberger, Ed., 2nd ed, Interscience Publishers, New York, N. Y., 1956,

employing 8:1 methanol-water, recrystallizing the first crop three times. A total of 167 g (74%) of crystalline tartrate was obtained which afforded 68 g of the distilled *l*-amine,  $[\alpha]^{25D} - 40.1^\circ$  (neat) (lit.<sup>34</sup>  $[\alpha]^{25D} - 40.3^\circ$  (neat)).

**b. *d*- $\alpha$ -Methylbenzylamine.** As described by Ault,<sup>32</sup> the *d*-amine sulfate (from combined preparations) was isolated from the recovered amine and converted to *d*-amine, 80 g (0.66 mole),  $[\alpha]^{25D} + 36.0$  (neat). The latter was treated with 85 g (0.64 mole) of *l*-malic acid in water<sup>35</sup> yielding the malate salt (two crops) which was fractionally recrystallized<sup>33</sup> once from water. Treatment of the combined crops with aqueous base, extraction, and distillation gave 41 g of *d*-amine,  $[\alpha]^{25D} + 40.1^\circ$  (neat) (lit.<sup>36</sup>  $[\alpha]^{15D} + 40.67$ ).

***l*-*p*-Nitro- $\alpha$ -methylbenzylamine, (-)-8.** The *N*-acetyl derivative of (-)- $\alpha$ -methylbenzylamine was prepared,<sup>25</sup> mp  $100-101.5^\circ$ ,  $[\alpha]^{25D} - 152.8$  (c 1.4, absolute ethanol) (lit.<sup>25a</sup>  $[\alpha]^{25D} - 149.6$  (ethanol)). Nitration<sup>25b</sup> gave (-)-*N*-acetyl-*p*-nitro- $\alpha$ -methylbenzylamine, mp  $132-134^\circ$ ,  $[\alpha]^{25D} - 131^\circ$  (c 1.1, absolute ethanol) which was hydrolyzed to afford the amine (-)-8, bp  $127^\circ$  (1.1 mm),  $[\alpha]^{25D} - 20.3^\circ$  (c 4.5,  $\text{CHCl}_3$ ).

***d*-*p*-Nitro- $\alpha$ -methylbenzylamine, (+)-8.** The racemic amine was resolved according to the procedure of Nerdel and Liebig<sup>25a</sup> except that higher optical purity was obtained when the *d*-camphorsulfonate salt was fractionally recrystallized<sup>33</sup> (the lead fraction was recrystallized six times) from water giving 137 g (56%) of salt in three crops of essentially constant purity: mp  $213-214^\circ$ ;  $[\alpha]^{25D} + 31.2^\circ$  (c 1.0, absolute ethanol),  $+27.4^\circ$  (c 0.9, 95% ethanol),  $+25.7^\circ$  (c 1.8, methanol) (lit.<sup>25a</sup>  $[\alpha]^{25D} + 26.7^\circ$  (ethanol)). Treatment of the salt with aqueous potassium hydroxide, extraction, and distillation gave the amine as a yellow oil,  $[\alpha]^{25D} + 16.7^\circ$  (neat) (lit.<sup>37</sup>  $[\alpha]^{25D} + 13^\circ$  (neat)).

**Recrystallization of Platinum Complexes of 1.** To avoid mutarotation, all recrystallizations were carried out by dissolving the complex in the chlorinated solvent ( $\text{CHCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ , or  $\text{CCl}_4$ ) at room temperature and adding the hydrocarbon cosolvent until the cloud point was reached. The solution was then stored in a refrigerator ( $0$  to  $-10^\circ$ ) overnight, permitting crystallization to occur slowly. In collecting the crystals, exposure to the air was minimized.

**(-)-Dichloro(1,2-cyclononadiene)( $\alpha$ -methylbenzylamine)platinum(II) (3a').** **a. From Racemic 1.** Racemic 1,2-cyclononadiene<sup>27</sup> (10.8 g, 0.088 mole) was added to a solution of 36 g (0.088 mole) of (+)-dichloro(ethylene)( $\alpha$ -methylbenzylamine)platinum(II),<sup>3</sup> **2a**, prepared from  $\alpha$ -methylbenzylamine with  $[\alpha]^{25D} + 40.1^\circ$  (neat), in 300 ml of methylene chloride. The reaction mixture was stirred overnight; then the solvent was evaporated under reduced pressure giving 46 g of a yellow solid,  $[\alpha]^{24,578} + 18^\circ$  (c 1.5,  $\text{CH}_2\text{Cl}_2$ ) which was fractionally recrystallized.<sup>33</sup> After six recrystallizations from methylene chloride-pentane, the lead fraction of the first crop had  $[\alpha]^{24,578} - 37^\circ$  (c 1.9,  $\text{CH}_2\text{Cl}_2$ ). After an additional seven recrystallizations from carbon tetrachloride-benzene, 1.1 g of **3a'** was obtained: mp  $125-126.5^\circ$ ;  $[\alpha]^{24,578} - 65.7^\circ$ ,  $[\alpha]^{24D} - 61.6^\circ$  (c 3.6,  $\text{CHCl}_3$ ). Treatment of this material with aqueous sodium cyanide followed by short-path distillation (see the procedure below) gave 0.19 g of 1,2-cyclononadiene,  $[\alpha]^{24D} - 71^\circ$  (neat).

Third and fourth crops of complex were carried only part way through the fractional crystallization procedure giving **3b'** of lower purity; third crop (nine recrystallizations), 4.3 g,  $[\alpha]^{24,578} - 44^\circ$  (c 1.8,  $\text{CH}_2\text{Cl}_2$ ); fourth crop (eight recrystallizations), 4.6 g,  $[\alpha]^{24,578} - 28^\circ$  (c 1.7,  $\text{CH}_2\text{Cl}_2$ ).

**b. From Optically Active 1.** Complex **3a'** was also prepared as above from **2a** and *l*-1,2-cyclononadiene,  $[\alpha]^{24D} - 132^\circ$  (neat), and recrystallized from carbon tetrachloride-hexane, mp  $121-122^\circ$ ,  $[\alpha]^{24D} - 118^\circ$  (c 3.9,  $\text{CHCl}_3$ ). Further recrystallizations did not change the rotation. The 1,2-cyclononadiene recovered from this complex (described below) had  $[\alpha]^{25D} - 129^\circ$  (neat).

p 490 ff. In brief, two or more crops were collected and the first crop was recrystallized from the solvent indicated. Following crops were recrystallized from the appropriate mother liquor of the preceding crop and finally from fresh solvent until the purity of the lead fraction of the first crop was attained. The number of recrystallizations refers to the first crop.

(34) W. Theilaker and H.-G. Winkler, *Chem. Ber.*, **87**, 691 (1954).

(35) The amount of acid taken is based on the amount of *d*-amine present; see A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1943, p 506.

(36) W. Leithe, *Monatsh. Chem.*, **51**, 385 (1929).

(37) A. P. Terentev and V. M. Potapoo, *Zh. Obshch. Khim.*, **27**, 1092 (1957).

*Anal.* Calcd for  $C_{17}H_{25}NCl_2Pt$ : C, 40.08; H, 4.95; Cl, 13.92; N, 2.75; Pt, 38.31. Found: C, 40.02; H, 5.15; Cl, 14.07; N, 2.79; Pt, 38.14.

(+)-Dichloro(1,2-cyclononadiene)( $\alpha$ -methylbenzylamine)platinum(II) (**3b'**). Complex **3b'** was prepared as above from complex **2b**,<sup>3</sup> which was made using *l*- $\alpha$ -methylbenzylamine having  $[\alpha]^{25D} -40.1^\circ$  (neat), and *d*-1,2-cyclononadiene,  $[\alpha]^{25D} +138^\circ$  (neat),  $+149^\circ$  (*c* 3.6,  $CH_2Cl_2$ ). The solid was recrystallized twice from chloroform-hexane giving **3b'**, mp 117–119°,  $[\alpha]^{25D} +124^\circ$  (*c* 2.0,  $CHCl_3$ ), which did not change in rotation upon additional recrystallization. The 1,2-cyclononadiene recovered from this complex had  $[\alpha]^{25D} +145^\circ$  (*c* 0.77,  $CH_2Cl_2$ ).

Complex **3b'** (0.55 g),  $[\alpha]^{27D} +112^\circ$  (*c* 3.3,  $CHCl_3$ ), prepared as above, and 0.13 g of complex **3b** prepared from racemic **1** and optically pure *d*- $\alpha$ -methylbenzylamine were dissolved in chloroform. Removal of the solvent gave a yellow solid,  $[\alpha]^{27D} +86^\circ$  (*c* 1.1,  $CHCl_3$ ). After two recrystallizations from chloroform-hexane the lead fraction had  $[\alpha]^{25D} +80^\circ$  (*c* 1.8,  $CHCl_3$ ). The decrease in rotation was also observed with a second crop, initially with  $[\alpha]^{25D} +90^\circ$  (*c* 2.6,  $CHCl_3$ ), which upon recrystallization gave a lead fraction with  $[\alpha]^{25D} +85^\circ$  (*c* 1.0,  $CHCl_3$ ) while the mother liquor yielded complex with  $[\alpha]^{25D} +92^\circ$  (*c* 1.4,  $CHCl_3$ ).

(+)-Dichloro(ethylene)(*p*-nitro- $\alpha$ -methylbenzylamine)platinum(II) (**2c**). A cooled solution of 20.8 g (0.125 mole) of *p*-nitro- $\alpha$ -methylbenzylamine,  $[\alpha]^{25D} +16.7^\circ$  (neat), in 250 ml of water acidified with dilute hydrochloric acid was added to a cooled solution of 46.2 g (0.125 mole) of potassium trichloro(ethylene)platinate(II), Zeise's salt,<sup>38</sup> in 500 ml of 3% aqueous potassium chloride containing 10 ml of 10% hydrochloric acid. With cooling and stirring, 5% potassium hydroxide solution was added slowly until pH 5 was reached. The yellow solid which formed was collected giving 51 g of **2c**, mp 92–100°,  $[\alpha]^{24D} +40.7^\circ$  (*c* 2.3,  $CH_2Cl_2$ ).

*Anal.* Calcd for  $C_{10}H_{14}N_2Cl_2O_2Pt$ : C, 26.09; H, 3.06; N, 6.09; Cl, 15.40; Pt, 42.41. Found: C, 26.00; H, 2.85; N, 6.02; Cl, 15.17; Pt, 42.24.

(-)-Dichloro(1,2-cyclononadiene)(*p*-nitro- $\alpha$ -methylbenzylamine)platinum(II) (**3c**). a. From Racemic **1**. Racemic 1,2-cyclononadiene (13.3 g, 0.11 mole) was added to 50 g (0.108 mole) of **2c** in 200 ml of methylene chloride. After 18 hr the solvent was evaporated (reduced pressure). The complex was triturated with pentane and then freed of solvent to give 53 g of **3c** as yellow crystals, mp 153–155°,  $[\alpha]^{24D} +42^\circ$  (*c* 2.3,  $CH_2Cl_2$ ).

*Anal.* Calcd for  $C_{17}H_{24}Cl_2N_2O_2Pt$ : C, 36.82; H, 4.36; Cl, 12.79; N, 5.05; Pt, 35.21. Found: C, 36.93; H, 4.48; Cl, 12.88; N, 4.81; Pt, 35.03.

Recrystallization of this material from benzene-cyclohexane resulted in a change of *ca.* 15° per step initially, but then the change decreased. After six recrystallizations complex **3c'** had mp 156.5–158°,  $[\alpha]^{23D} -13.3^\circ$  (*c* 2.2,  $CH_2Cl_2$ ). The 1,2-cyclononadiene obtained from this complex (in 78% yield) had  $[\alpha]^{27D} -57^\circ$  (*c* 1.5,  $CH_2Cl_2$ ),  $-49^\circ$  (*c* 0.7, heptane).

b. From Optically Active **1**. Complex **3c'** was prepared as above from *l*-1,2-cyclononadiene,  $[\alpha]^{24D} -132^\circ$  (neat), and complex **2c**. After recrystallization from benzene-hexane, the crystalline **3c'** had  $[\alpha]^{24D} -110^\circ$  (*c* 1.2,  $CH_2Cl_2$ ).

(+)-Dichloro(1,2-cyclononadiene)(*p*-nitro- $\alpha$ -methylbenzylamine)platinum(II) (**3d**). Complex **2d** was prepared (see **2c** above) from Zeise's salt and *l*-*p*-nitro- $\alpha$ -methylbenzylamine;  $[\alpha]^{25D} -43^\circ$  (*c* 1.0,  $CH_2Cl_2$ ). Following procedures used above, from 2.0 g (4.4 mmoles) of **2d** and 0.55 g (4.5 mmoles) of racemic 1,2-cyclononadiene, 1.73 g of **3d** was obtained,  $[\alpha]^{25D} -41^\circ$  (*c* 1.6,  $CH_2Cl_2$ ). This material was recrystallized repeatedly until the rotation of **3b'** was  $[\alpha]^{25D} +31^\circ$  (*c* 1.2,  $CH_2Cl_2$ ) and no further significant change occurred (the complex recovered from the mother liquor had essentially the same rotation).

Recovery of Optically Active 1,2-Cyclononadiene from Platinum Complexes. The procedure given for **3a'** was employed for all complexes. A chilled solution of 3.50 g (6.9 mmoles) of **3a'**,  $[\alpha]^{24D} -118^\circ$ , in 40 ml of methylene chloride was shaken with 50 ml of cold 15% aqueous sodium cyanide. When the yellow color (of **3a'**) had disappeared, the layers were separated and the aqueous layer was shaken with three 30-ml portions of pentane. The combined organic layers were washed with 10% hydrochloric acid, saturated sodium bicarbonate solution, and water. The solution

was dried ( $Na_2SO_4$ ) and concentrated without heating under reduced pressure (nitrogen bleed) using a rotary evaporator. Bulb-to-bulb reduced pressure distillation at 40–50° gave 0.55 g (66% of 1,2-cyclononadiene (glpc, 24 in. 20% SE-30 column, 90° indicated less than 0.2% of impurities),  $[\alpha]^{25D} -129^\circ$  (neat).

Although the allene probably is formed nearly quantitatively, the isolated yields of pure **1** ranged from 66 to 78%, reflecting losses in handling small quantities. Since **1** is fairly reactive toward oxygen, samples were handled under an inert atmosphere. When the optically active allene was collected by glpc, care was essential to avoid partial racemization by hot injection ports and detectors, particularly in metal systems. Best results were obtained using a home-made all-glass system. Samples of optically active **1** were identified by comparison of infrared spectra with the spectrum of an authentic sample.

Optically Active *trans*-Cyclooctene. *trans*-Cyclooctene was prepared by the pyrolysis of trimethylcyclooctylammonium hydroxide.<sup>39</sup> In the course of this work a convenient synthesis of the *N,N*-dimethylcyclooctylamine<sup>40</sup> required and an improved procedure for carrying out the elimination step<sup>41</sup> were developed. A scaled-up version of the original resolution of *trans*-cyclooctene<sup>3</sup> was followed with the modifications which follow. The [(*trans*-cyclooctene)PtCl<sub>2</sub>(amine)] complexes were formed as described, but the efficiency of the separation of diastereoisomers was improved by directly crystallizing the less soluble diastereoisomer (either *d*-olefin-*l*-amine or *l*-olefin-*d*-amine) from the reaction mixture (methylene chloride solution) either by simply cooling or by reducing the volume by about one-half. A nearly pure first crop and one or two additional crops were collected and carried through a fractional recrystallization procedure,<sup>33</sup> recrystallizing (the first crop) three or four times from carbon tetrachloride. The separation was also improved by recovering the *trans*-cyclooctene, enriched in one enantiomer, from the more soluble diastereoisomer (*e.g.*, *l*-olefin-*l*-amine) and using the enantiomeric amine (*d*-amine) to convert the olefin to the less soluble complex (*l*-olefin-*d*-amine). The separation then was carried out as above. The less soluble platinum complexes (*e.g.*, *d*-olefin-*l*-amine) were isolated in a pure state in yields of *ca.* 70% (based on *d*-olefin taken). The complexes were decomposed<sup>3</sup> to give optically active *trans*-cyclooctene in *ca.* 90% yields.

9,9-Dibromo-*trans*-bicyclo[6.1.0]nonane (**9**). Freshly distilled bromoform (8.3 g, 0.033 mole) was added dropwise to a stirred suspension of 3.7 g (0.033 mole) of potassium *t*-butoxide in a solution of 3.3 g (0.030 mole) of *trans*-cyclooctene,  $[\alpha]^{25D} +437^\circ$  (neat), in 75 ml of pentane maintained at  $-10^\circ$  under nitrogen. Water was added, the aqueous layer was shaken with pentane (three 75-ml portions), and the combined pentane extract was dried ( $Na_2SO_4$ ). Evaporation of the pentane gave a white solid which was recrystallized from methanol giving 4.1 g of (–)-**9**: white platelets; mp 51.5–52.5°;  $[\alpha]^{23D} -43.6^\circ$  (*c* 2.2,  $CH_2Cl_2$ ); ir (neat) (strong) 2925, 2855, 1460, 1450, 1440, 1055, 1000, 970  $cm^{-1}$ , (medium) 1355, 1205, 850, 715  $cm^{-1}$ ; nmr broad envelope  $\delta \sim 0.8$ –2.5. Processing the mother liquors gave an additional 2.1 g, mp 49–51° (combined, 73%).

*Anal.* Calcd for  $C_9H_{14}Br_2$ : C, 38.32; H, 5.00; Br, 56.68. Found: C, 38.24; H, 4.94; Br, 56.64.

(–)-*trans*-Cyclooctene gave (+)-**9**: mp 51.5–53°;  $[\alpha]^{25D} +44.2^\circ$  (*c* 2.5,  $CH_2Cl_2$ ). Racemic cyclooctene gave racemic **9**, long white needles, mp 43.5–44°.

Optically Active 1,2-Cyclononadiene from **9**. Methylolithium (9 ml, 1.6 *M* in ether) was added dropwise to a stirred solution of 3.5 g (1.24 mmoles) of (+)-**9**,  $[\alpha]^{25D} +44.2^\circ$ , in 75 ml of ether maintained at 0° under nitrogen. Water was added, the aqueous layer was shaken with ether, and the combined ether extracts were dried ( $Na_2SO_4$ ). Evaporation of the ether and bulb-to-bulb distillation gave 1.35 g (89%) of **1**:  $[\alpha]^{25D} +138^\circ$ ,  $[\alpha]^{25,578} +145^\circ$ ,  $[\alpha]^{25,546} +166^\circ$ ,  $[\alpha]^{25,436} +298^\circ$ ,  $[\alpha]^{25,405} +367^\circ$ ,  $[\alpha]^{25,365} +503^\circ$  (neat);  $[\alpha]^{25D} +150^\circ$  (*c* 3.6,  $CH_2Cl_2$ ). The infrared spectrum was identical with that of an authentic sample of **1**.

A sample of (–)-**9**<sup>42</sup> gave **1**,  $[\alpha]^{25D} -132^\circ$ .

(39) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(40) R. D. Bach, *J. Org. Chem.*, **33**, 1647 (1968).

(41) A. C. Cope and R. D. Bach, *Org. Syn.*, in press.

(42) This sample of **1** contained *ca.* 4% of the *cis*-dibromocarbene adduct, accounting for the slightly lower rotation of the allene.

(38) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).