

- (7) J. F. Villa, R. T. Curran, and G. C. Toralballa, *Russ. J. Inorg. Chem.*, **20**, 3026–3028 (1975).
 (8) J. F. Villa, R. F. Doyle, H. C. Nelson, and J. C. Richards, *Inorg. Chim. Acta*, **25**, 49–54 (1978).
 (9) P. F. Knowles, D. Marsh, and H. W. E. Rattle, "Magnetic Resonance of Biomolecules", Wiley, New York, N.Y., 1976, Chapter I.
 (10) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes", Chapman Hall, London, 1973, Chapter 3.
 (11) W. Wojciechowski, *Inorg. Chim. Acta*, **1**, 319–323 (1967).
 (12) C. L. Angell, *J. Chem. Soc.*, 504–508 (1961).
 (13) N. L. Alpert, W. E. Keiser, and H. A. Szymanski, *IR—Theory and Practices of Infrared Spectroscopy*, Plenum Press, New York, N.Y., 1970, p 271.

Juan F. Villa,* Joel Gelber
 Ngarling Khoe, Jose Cepeda

Department of Chemistry
 Herbert H. Lehman College of the
 City University of New York, Bronx, New York 10468

Received February 21, 1978

Enantiomer Recognition and Conformational Equilibria in Platinum(0) Complexes of 2,3-Isopropylidene-2,3-*trans*-dihydroxy-1,4-bis(diphenylphosphino)butane (diop)

Sir:

We report that the asymmetric chelating ligand (*R,R*)-diop (**1**) forms a mononuclear platinum(0) complex (**2**) which exhibits conformational isomerism observable by ^{31}P NMR. This is pertinent to the role of diop complexes in asymmetric homogeneous catalysis¹ and particularly to their optical efficiency when compared with chelate complexes derived from chiral diphosphinoethane derivatives.² Furthermore there is considerable stereoselectivity in ligand binding favoring the optically active bis(diop) complex over its meso diastereomer in solution.

Bis(cyclooctadiene)platinum(0)³ reacts with (*R,R*)-**1** in C_6H_6 or C_7D_8 giving complex **2**, isolable as a yellow crystalline solid. Anal. ($\text{C}_{62}\text{H}_{64}\text{O}_4\text{P}_4\text{Pt}$) C, H, P. Mol wt: obsd, 1132; calcd, 1191. The ^{31}P NMR spectrum of **2** (Figure 1) in C_7D_8 is a sharp singlet at $\delta -11.3$ ppm⁴ above 320 K with clearly defined platinum satellites ($J_{\text{P-Pt}} = 3751$ Hz); no rapid intermolecular exchange process is seen in the presence of free

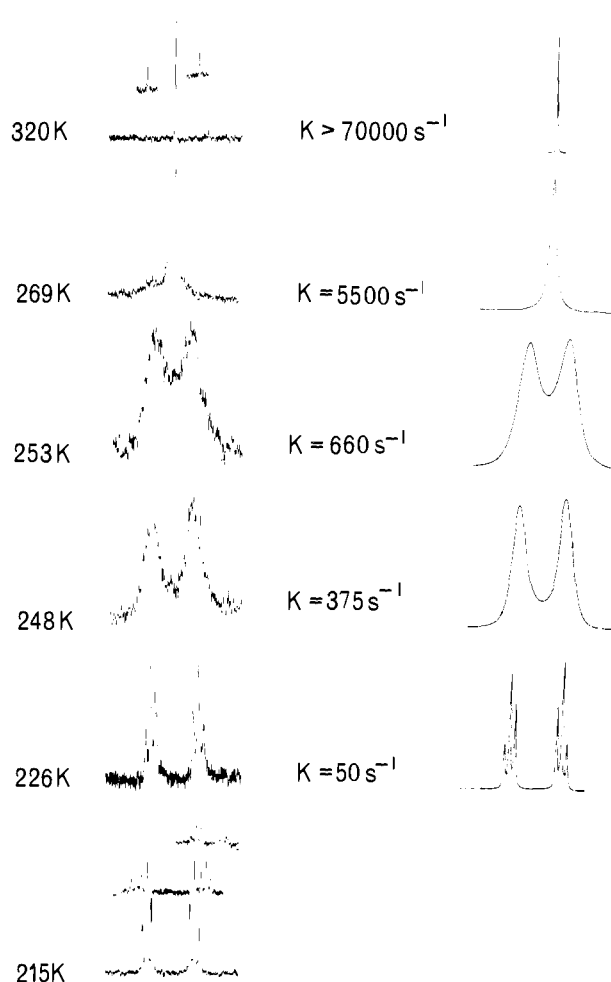
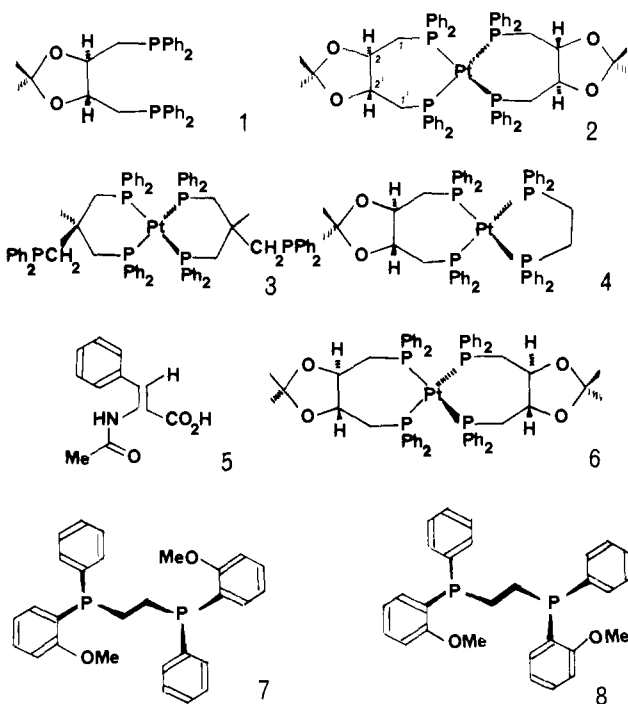


Figure 1. Variable-temperature proton-decoupled ^{31}P NMR spectra of **2** in C_7D_8 at stated temperatures, 36.43 MHz. Platinum-coupled satellites are inset where appropriate.

phosphine.⁵ Cooling the solution causes first broadening of the signals and then resolution into an $\text{AA}'\text{XX}'$ multiplet ($\delta_{\text{PA}} -5.2$, $\delta_{\text{PX}} -19.1$ ppm ($J_{\text{PA-Pt}} = 3983$, $J_{\text{PX-Pt}} = 3521$, $J_{\text{PA-PX}} = J_{\text{PA-PX}'} = 50$ Hz)). This dynamic process, for which $\Delta G^\ddagger_{250} = 48$ kJ mol^{-1} ,⁶ must be intramolecular in a monomeric complex because of the sharpness of the platinum satellite signals, even at 370 K. All other mechanisms would lead to satellite broadening by the process $\text{Pt}(I = 1/2) \rightleftharpoons \text{Pt}(I = 0)$ and the *minimum* free-energy of activation for this is 83 kJ mol^{-1} . Furthermore, line shapes are independent of concentration, or of added **1**, and the dynamic processes leading to broadening of both satellite peaks have similar rate constants⁶ to the dynamic process leading to broadening of the main peak.

Dynamic equilibria have previously been observed in the bis complex **3**⁷ owing to site exchange in the six-membered chelate. When this complex is static on the NMR time scale, the two bound phosphines of a single ligand are inequivalent and the observed low-temperature spectrum approximates to an A_2X_2 pattern because $J_{\text{AX}} = J_{\text{AX}'}$. The phenomenon observed with **2** is different and stems from equivalencing of two bound ligand geometries rather than equivalencing of an intrinsically different pair of phosphorus atoms within the same ligand. This interpretation is supported by the observation that the mixed complex **4**, prepared in situ by addition of an equimolar quantity of $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ to a solution of **2** in C_7D_8 at 300 K, shows a sharp A_2X_2 ^{31}P NMR spectrum throughout the range 220–320 K ($\delta_{\text{PA}} 25.9$, $\delta_{\text{PX}} -6.6$ ppm ($J_{\text{PA-Pt}} = 3471$, $J_{\text{PX-Pt}} = 3996$, $J_{\text{PA-PX}} = 56$ Hz)), requiring that the two phosphines of diop in **4** are equivalent.

Inspection of molecular models reveals two low-energy

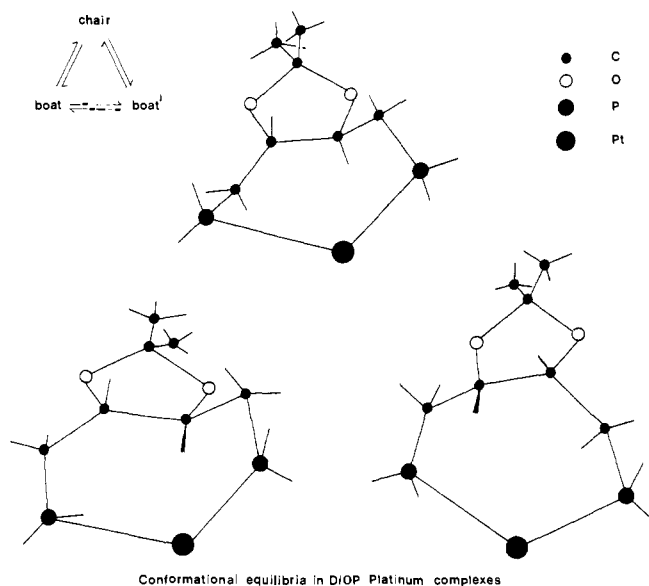


Figure 2. Conformational isomerism in diop-metal complexes; drawings are based on Dreiding models.

conformations for a tetrahedrally bound diop ligand (Figure 2) which approximate to chair and boat geometry.⁸ The former has C_2 symmetry (ignoring rotameric forms of the aromatic rings) but the latter is dissymmetric. There are, however, two boat conformations which may be interconverted by pseudorotation about $C_1C_2C_1C_2$, and this low-energy operation⁹ establishes C_2 symmetry. We believe¹⁰ that one diop ligand in **2** takes up the chair conformation and the other the boat conformation, and the observed dynamic process involves their interconversion. The activation energy is in part derived from the intrinsic boat-chair barrier in seven-membered rings (34 KJ mol^{-1} for cycloheptane)⁹ and in part from increased Ph-Ph nonbonded interactions at the transition state.

The existence of this conformational equilibrium has important implications for the catalytic specificity of diop complexes. Typically the optical yield in reduction of enamides such as **5** by rhodium diop complexes is 80%¹ but can be as high as 99% when asymmetric phosphines which form five-membered chelate rings are employed.² In diop complexes, the asymmetric center is four bonds removed from the site of binding of a prochiral olefin ligand, and, to achieve the observed stereoselection,^{1c} it must control the orientation of the phosphorus-bound phenyl rings. In the chair form (cf. Figure 2) two of the P-Ph bonds are axial and two equatorial; their relative stereochemistry is reversed on going to the boat form. Since the two conformations provide locally enantiomeric environments at the metal atom, they will encourage the binding of a prochiral ligand in opposite stereochemical senses. Conformational isomerism is clearly an undesirable feature in ligands for asymmetric catalysis.

The formation of bis(diop)platinum(0) complexes is also stereoselective. An equimolar mixture of **2** and its enantiomer derived from (*S,S*)-diop gave a ^{31}P spectrum in C_7D_8 identical with that derived from either pure enantiomer, but mixing equimolar quantities of bis(cyclooctadiene)platinum(0), (*R,R*)-diop, and (*S,S*)-diop in C_7D_8 at room temperature gave a solution which has a different spectrum at 250 K, 30% of the signal being due to a sharp singlet at -11.6 ppm ($J_{\text{P-Pt}} = 3743$ Hz). The spectrum of this species is unchanged over the range 210–280 K implying that both diop ligands adopt the same (boat or chair) geometry or that interconversions of boat and chair forms are still rapid on the NMR time scale at 210 K. Comparison with other observations suggests the latter to be unlikely; a study of molecular models suggests that a chair-chair geometry is favored. If a small quantity of **1** is added to

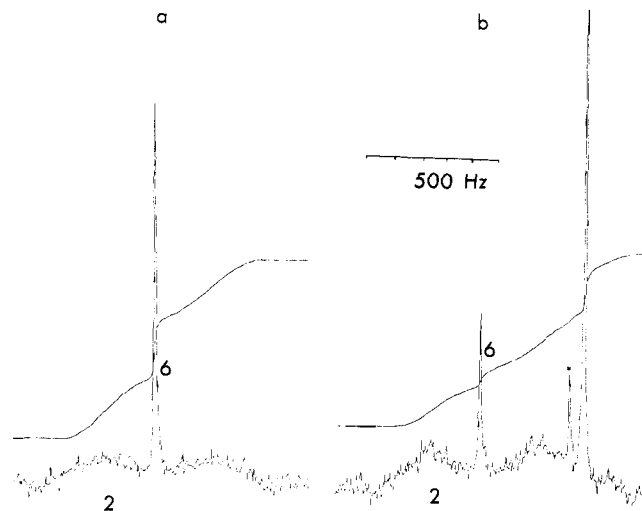


Figure 3. (a) ^{31}P NMR spectrum of the reaction product from bis(cyclooctadiene)platinum and equimolar quantities of (*R,R*)-**1** and (*S,S*)-**1** in C_7D_8 recorded at 250 K. (b) Sample after addition of further racemic **1** and brief heating at 340 K, again recorded at 250 K; *, 1-oxide.

either racemic solution, followed by brief heating to 340 K, the sharp singlet then accounts for only 5% of the total signal (Figure 3). We interpret these observations to demonstrate that 30% of the meso complex **6** is formed under conditions of kinetic control but only 5% under conditions of thermodynamic control.¹¹ This implies a high degree of stereoselectivity in ligand binding, presumed to be due to less favorable Ph-Ph interactions in **6** than in **2**. Although stereoselectivity has previously been noted in the formation of platinum-olefin complexes,¹² this appears to be the first example of its observation in a diphosphine complex.

The asymmetric ligand (*R,R*)-**7** (dipamp) introduced by Knowles and co-workers,^{2a} forms a bis(phosphine)platinum(0) complex whose ^{31}P NMR spectrum is unaltered between 200 and 305 K. Racemization and epimerization of **7** (C_7H_8 , 373 K, 12 h) gave an equimolar mixture of racemic **7** and **8**. This mixture reacted with bis(cyclooctadiene)platinum(0) in C_7D_8 to give all the possible mixed complexes with low specificity. Owing to the much tighter binding of **7** to platinum, conditions of thermodynamic control were not affected.

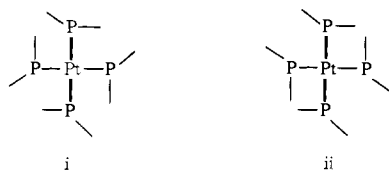
Acknowledgments. We thank IBM for a Fellowship (to P.A.C.) and Drs. J. L. Spencer and W. S. Knowles for gifts of chemicals. Lady Richards was most helpful in the determination of NMR spectra.

References and Notes

- (1) (a) H. B. Kagan and T.-P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972); (b) D. Sinou and H. B. Kagan, *J. Organomet. Chem.*, **114**, 325 (1976), and intervening papers; (c) J. M. Brown and P. A. Chaloner, *J. Chem. Soc., Chem. Commun.*, 321 (1978).
- (2) (a) B. D. Vineyard, W. S. Knowles, M. J. Sabacky, G. L. Bachman, and D. J. Weinkauff, *J. Am. Chem. Soc.*, **99**, 5946 (1977); (b) M. D. Fryzuk and B. Bosnich, *ibid.*, **99**, 6262 (1977).
- (3) M. Green, J. A. K. Howard, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 3 (1975); *J. Chem. Soc., Dalton Trans.*, 271 (1977).
- (4) Chemical shifts are quoted in parts per million downfield from H_3PO_4 .
- (5) J. Chatt, R. Mason, and D. W. Meek, *J. Am. Chem. Soc.*, **97**, 3826 (1975), have demonstrated slow interphosphine exchange for chelating phosphine-platinum(0) complexes.
- (6) Spectra were subjected to complete line-shape analysis using the program DNMR5 of Atlas Computer Program Library; G. Binsch, *J. Am. Chem. Soc.*, **91**, 1304 (1969).
- (7) F. C. March, R. Mason, D. W. Meek, and G. R. Scollary, *Inorg. Chim. Acta*, **19**, L25 (1976).
- (8) X-ray determination of the structure of diop complexes support a chair-like geometry in the solid state: S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan, *J. Organomet. Chem.*, **114**, 225 (1976); V. Gramlich and Ch. Saloman, *ibid.*, **73**, C61 (1974).
- (9) J. B. Hendrickson, *J. Am. Chem. Soc.*, **89**, 7047 (1967); D. F. Bocian, H. M. Pickett, T. C. Rounds, and H. L. Strauss, *ibid.*, **97**, 687 (1975); W. M. J. Flapper and C. Romers, *Tetrahedron*, **31**, 1701 (1975).
- (10) The ^{31}P NMR spectrum of cyclooctadiene(diop)rhodium(I) $^+\text{BF}_4^-$ shows

dynamic behavior below 210 K and has two separate rhodium-103 coupled signals in a 4:1 ratio at 190 K. These are attributed to conformational isomers in which the ligands exist in chair or boat form: P. A. Chaloner, unpublished work.

- (11) The reasons for preference of a boat-chair conformation in **2** but a chair-chair conformation in **6** must be quite subtle. Both correspond to the schematic orientation i rather than ii and molecular models suggest that the latter suffers more extensive H-H repulsive interactions.



- (12) R. Lazzaroni, P. Salvadori, C. Bertucci, and C. A. Veracini, *J. Organomet. Chem.* **99**, 475 (1975); S. Shinoda, Y. Sudo, Y. Yanaguchi, T. Iwayanagi, and Y. Saito, *ibid.*, **121**, 93 (1976); cf. H. Boucher and B. Bosnich, *J. Am. Chem. Soc.*, **99**, 6253 (1977).

John M. Brown,* Penny A. Chaloner*

Dyson Perrins Laboratory, South Parks Road
Oxford, OX1 3QY, England

Received November 7, 1977

Anionic Oxy-Cope Rearrangements with Aromatic Substrates in Bicyclo[2.2.1]heptene Systems. Facile Synthesis of *cis*-Hydrindanone Derivatives, Including Steroid Analogues¹

Sir:

Recently Evans² has greatly increased the usefulness of the oxy-Cope rearrangement, originally developed by Berson³ and Viola⁴ as a highly thermal process, by reporting that the rate of the [3,3]-sigmatropic shift is enhanced by up to a factor of 10¹⁷ by reaction of the anion of the allylic alcohol rather than the neutral compound. Similar rate enhancements have been observed in analogous reaction types.⁵ We now report the base-catalyzed oxy-Cope rearrangement in highly substituted norbornene systems in which one of the olefinic components is an aromatic ring. The use of a naphthyl substituent in this procedure affords a very rapid synthesis of 18,19-bis norsteroids.

The bicyclic enone **3** is readily available in four steps from vinyl acetate **1** and dimethoxytetrachlorocyclopentadiene **2** in an overall yield of 67% (Scheme I).⁶ To test the possibility of oxy-Cope rearrangements in these norbornenyl systems, **3** was reacted with vinylmagnesium bromide to afford only the

exo alcohol **4** (NMR (CDCl₃) δ 6.12 (2 H, m), 4.9–5.9 (3 H, vinyl H), 4.47 (1 H, s), 3.33 (3 H, s), 3.20 (3 H, s), 3.0 (1 H, m), 2.63 (1 H, m), 1.75 (2 H, m); IR (liquid film) 3500 cm⁻¹) in 98% yield.^{7,8} The exclusive endo attack of the organometallic reagent is expected since exo attack is sterically hindered by the *syn*-7-methoxy group. Treatment of **4** with KH in tetrahydrofuran (THF) at 25 °C or with NaH in THF at 66 °C for a few minutes afforded cleanly (presumably via the enolate **5**) the rearranged ketone **6** in 72% isolated yield after purification by filtration chromatography on neutral activity III alumina: NMR (CCl₄) δ 5.82 (2 H, br s), 3.12 (3 H, s), 3.08 (3 H, s), 1.5–2.6 (8 H, m); IR (liquid film) 1710 cm⁻¹; mass spectrum (70 eV) *m/e* 196 (M⁺), 164 (M – MeOH), 150 (M – MeOMe). This is the first instance of the oxy-Cope rearrangement in bicyclo[2.2.1]heptene systems of this type. Although the structurally similar bicyclo[2.2.2]octene systems are well-known substrates in this process,^{2,3} one might have expected some difficulties in reaching the transition state for rearrangement in the norbornenyl systems due to ring and angle strain. However, this does not appear to be the case.

With the demonstration of the feasibility of this type of anionic rearrangement in simple norbornenyl systems accomplished, attention was then directed to the possibility of utilizing aromatic rings as the olefinic component (Scheme II). At the outset of this research, there was only one example of the Cope rearrangement on an aromatic system in the literature, namely the pioneering work of Doering and Bragole.⁹ Reaction of **3** with 1-naphthylmagnesium bromide¹⁰ afforded the exo alcohol **7a** in 90% yield: mp 97–99 °C; NMR (CDCl₃) δ 7.2–7.8 (7 H, m), 6.0 (2 H, t, *J* = 2 Hz), 5.05 (1 H, s), 3.43 (3 H, s), 3.29 (3 H, s), 3.0 (2 H, m), 2.4–3.5 (2 H, m); IR (liquid film) 3400 cm⁻¹. The desired rearrangement was best effected by refluxing a mixture of **7a** and NaH in THF for 1 h. In this manner one can isolate (presumably via the enolate **8a**) a 75% yield of the tetracyclic ketone **9a**, which is again purified by filtering through neutral activity III alumina: NMR (CDCl₃) δ 6.9–7.3 (4 H, m), 5.8–6.3 (4 H, m), 3.17 (3 H, s), 3.09 (3 H, s), 2.3–3.5 (6 H, m); IR (liquid film) 1710 cm⁻¹; mass spectrum (70 eV) *m/e* 296 (M⁺), 264 (M – MeOH), 262 (M – MeOH – H₂). Although we have not yet been able to definitely assign the stereochemistry of the C-8 and C-9 hydrogens (steroid numbering) in ketone **9a**,¹¹ we believe that it is probably the all-*cis* isomer shown. Examination of molecular models of the likely transition state indicates that the C-8 hydrogen should be *syn* to the hydrogens at the juncture of the six- and five-membered rings (C-13 and C-14). One would expect the hydrogen at C-9 to be mainly *cis* to that

Scheme I

