Contribution from the Istituto Chimico dell'Università,
Centro Nazionale di Chimica delle Macromolecole
del C.N.R. Sez. VII, Via Mezzocannone, 4, 80134 Naples, Italy

Resolution of *endo*-Dicyclopentadiene and Interaction of DL-*sec*-Butyl Alcohol with Enantiomeric *endo*-Dicyclopentadiene in Platinum and Palladium Chloride Complexes[1]

A. Panunzi, A. De Renzi and G. Paiaro

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Resolution of endo-*dicyclopentadiene has been accomplished through fractional crystallization of chloro (3a, 4, 7, 7a, tetrahydro*-exo-6-*methoxy*-endo-4,7-*methanoindene*-endo-$5\sigma,2\pi$)(*S*-α-*methylbenzylamine*)*platinum*-(*II*). *Elimination of amine and methoxyl group by boiling in concentrated hydrochloric acid and decomposition with sodium cyanide yielded optically active* endo-*dicyclopentadiene. The enantiomeric dichloro*(endo-*dicyclopentadiene*)*platinum*(*II*) *and -palladium(II) complexes react with an excess of dl*-sec-*butyl alcohol to give the corresponding dicyclopentadiene* sec-*butoxy chloride complexes. The unreacted alcohol was recovered and was found to be optically active. This indicates the existence of asymmetric induction in the butoxylation reaction. In the most favorable run, the degree of stereoselectivity, calculated from experimental data, was about 18%.*

Introduction

Studies concerning the stereochemistry of transition metal complexes of simple monoolefins have previously been reported.[2] The main purpose of these studies was to examine the stereochemical behaviour of this type of complexes as a model of a possible π-intermediate in the stereospecific polymerization of α-olefines. A meanigful feature of this behaviour is the connection between the configuration achieved by an unsaturated carbon atom, when coordinated in a π-complex, and the reactivity of this atom toward an asymmetric center.

The only type of complexes that appear to be well-suited for this study are the known diene complexes of Pt^{II} and Pd^{II}. In these complexes a π-coordinated double bond is known to react by addition of an alkoxy groups,[3] β-diketones[4] and ethylmalonate[5] with formation of a carbon-metal bond. In contrast, very few addition reactions to the double bond of a simple monoolefin in a π-complex occur without departure of the coordinate ligand.[6] NMR measurements have shown[7] both for palladium(II) and platinum(II)-diolefin complexes that the addition of the methoxy group is stereospecific. In these case of *endo*-dicyclopentadiene complexes the product is the *exo*-6-methoxy derivative, with the metal in *endo* position.

In the present investigation the stereochemistry of the reaction of dicyclopentadiene-platinum(II) and -palladium(II) monomeric complexes, involving attack of an asymmetric alkoxy group on carbon atom 6 (norbornene bond) was examined (Figure 1). The substrate for this reaction was one of the two enantiomers of the diene complex, **h** or **i** in Chart I, in which carbon atom 6 clearly has a specific configuration.

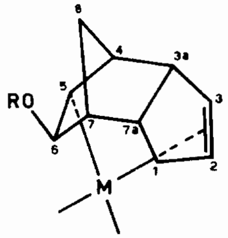

Figure 1. Alkoxy derivative of *endo*-dicyclopentadiene coordinated to metal atom. R = CH_3, $CH(CH_3)C_2H_5$; M = Pt, Pd.

With the isolation of these two enantiomers, the resolution of the intrinsically asymmetric endo-dicyclopentadiene has been achieved. The enantiomeric olefin can be obtained by treatment of an aqueous suspension of the complex with cyanide ion. Optical data at different wavelengths and in different solvents of the resolved diene (**j**, **k**) will also be reported here.

Experimental Section

In the preparation and isolation procedures, all operations were carried out under nitrogen. The

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[1] Preliminary account: G. Paiaro, A. Panunzi and A. De Renzi, *Tetrah. Lett.*, 3905 (1966).

[2] (a) G. Paiaro, P. Corradini, R. Palumbo and A. Panunzi, *Makrom. Chem.*, *71*, 184 (1964); (b) G. Paiaro and A. Panunzi, *J. Am. Chem. Soc.*, *86*, 5148 (1964); (c) A. Panunzi and G. Paiaro, *ibid.*, *88*, 4843 (1966); (d) G. Paiaro and R. Palumbo, *Gazz. Chim. It.*, *97*, 265 (1967).

[3] (a) K. A. Hoffmann and J. V. Narbutt, *Chem. Ber.*, *41*, 1625 (1908); (b) J. Chatt, L. M. Vallarino and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957); (c) J. Chatt, L. M. Vallarino and L. M. Venanzi, *ibid.*, 3413 (1957).

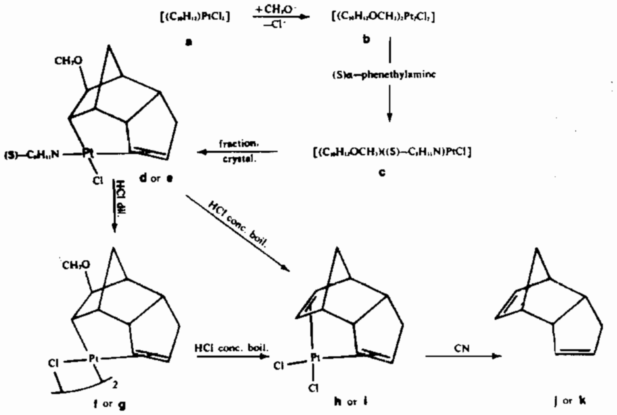
[4] B. F. G. Johnson, J. Lewis and M. S. Subramanian, *Chem. Comm.*, 117 (1966).

[5] J. Tsuji and M. Tatahashi, *J. Am. Chem. Soc.*, *87*, 3275 (1965).

[6] See, for instance, M. L. Green and P. L. I. Nagy, *J. Am. Chem. Soc.*, *84*, 1310 (1962).

[7] (a) J. K. Stille, R. A. Morgan, D. D. Whitehyrst and J. R. Doyle, *J. Am. Chem. Soc.*, *82*, 535 (1960); (b) J. K. Stille and R. A. Morgan, *ibid.*, *88*, 5135 (1966).

Chart I. Scheme of the resolution of dicyclopentadiene. The portion of the schema illustrated by structural drawings is concerned with the products **d**, **f**, **h** and **j** or **e**, **g**, **i** and **k** according to the actual (not yet known) absolute configuration.



optical measurements were made with a Perkin-Elmer mod. 141 polarimeter, with a reading accuracy of ±0.002. The liquid volume in 100-mm tubes was 1 ml. Infrared spectra were recorded with a Beckman IR9 spectrophotometer. Melting points were taken on a Kofler hot stage. Some of the elemental analyses were performed in this laboratory, and others by Mikroanalytisches Laboratorium of the Max Planck Institut für Köhlenforschung, Mülheim.

Materials. Fluka tecnical grade dicyclopentadiene was purified by the procedure of Waring, *et al.*,[8] and had mp 32°. The S-α-methylbenzylamine was obtained from the racemic amine by the Theilacker and Winkler[9] method and had $[\alpha]^{25}_{D}$ -40.3 (neat, usind d^{25} 0.9531). Sodium tetrachloroplatinate(II) tetrahydrate was prepared by evaporating to dryness a solution of tetrachloroplatinic(II) acid, after neutralization with aqueous sodium carbonate. Reagent grade chloroform was distilled through a fractionation column and stored and handled in nitrogen. The other chemicals used were of Analar grade.

Dichloro(endo-*dicyclopentadiene*)*platinum*(*II*) (**a**) was prepared according to the modification by Chatt, *et al.*,[3b] of the Hoffmann and Narbutt procedure. This complex had mp 210-220° (dec) (lit. 210-210° dec).

Di-μ-chlorobis(*3a,4,7,7a,tetrahydro*-exo-*6-methoxy*-endo-*4,7-methanoindene*-endo-*5σ,2π*)*diplatinum*(*II*) (**b**) was also prepared by the method of Chatt, *et al.*[3b] This complex had mp 210-220° (dec) (lit. 210-220° dec).

Chloro(*3a,4,7,7a,tetrahydro*-exo-*6-methoxy*-endo-*4,7-methanoindene*-endo-*5σ,2π*)(*S-α-methylbenzylamine*)-*platinum*(*II*) (**c**). A solution of 5.575 g (46 mmoles) of S-α-methylbenzylamine in 30 ml of chloroform was added slowly with stirring to an ice-cold solution of 18.12 g (23 mmoles) of **b** in 300 ml of chloroform. After standing at 0° for 0.5 hr, the solution was evaporated to dryness in vacuo. The oily residue was washed with petroleum ether and vacuum dried (0.1 mm). This material was dissolved in 80 ml of ether. By cooling the solution at 0° a small dark colored oily fraction separated and was removed. Evaporation to dryness of the ether solution gave the crude diastereoisomeric mixture **c** (19.5 g, 82.3% yield) as a white vetrous solid. Optical activity: $[\alpha]^{25}_{D}$ -8.5, $[\alpha]^{25}_{546}$ -10.4, $[\alpha]^{25}_{436}$ -20.0 (c 0.5, methylene chloride).

Anal. Calcd. for $C_{19}H_{26}ONClPt$: C, 44.31; H, 5.09; N, 2.72. Found: C, 44.52; H, 5.33; N, 2.95.

Resolution of the diastereoisomeric pair (**c**). A solution of 18.0 g of **c** in 60 ml of a 1:2 mixture of carbon tetrachloride and cyclohexane was placed in a refrigerator (−5°) for 24 hr. After this time, 3.5 g of white crystal having $[\alpha]^{25}_{D}$ -85 (c 0.5, methylene chloride) was collected. The mother liquor was evaporated in vacuo and the residue was dissolved in 50 ml of toluene. After 48 hr at 0° a second crop, weighing 2.8 g, $[\alpha]^{25}_{D}$ -85, was collected. Three additional fractions, which had $[\alpha]^{25}_{D}$ $+85$ (4.2 g), $[\alpha]^{25}_{D}$ -81 (1.8 g) and $[\alpha]^{25}_{D}$ $+77$ (3.2 g) respectively, were collected in the following days from the solution, increasingly concentrated. The combined levorotatory fractions were crystallized three from a methylene chloride-cyclohexane mixture, until a constant rotation was achieved, to give 6.5 g (36.1% yield) of pure diastereoisomer **d** mp 160-175° (dec), $[\alpha]^{25}_{D}$ -114, $[\alpha]^{25}_{578}$ -119, $[\alpha]^{25}_{546}$ -138, $[\alpha]^{25}_{436}$ -266, $[\alpha]^{25}_{365}$ -446 (c 0.5, methylene chloride).

Anal. Calcd. for $C_{19}H_{26}ONClPt$: C, 44.31; H, 5.09; N, 2.72. Found: C, 44.33; H, 5.15; N, 2.80.

Several crystallizations from an acetone-ether mixture of the combined dextrorotatory fraction gave 5.7 g (31.7% yield) of this diasteroisomer (**e**), mp 120-121° (dec), $[\alpha]^{25}_{D}$ $+107$, $[\alpha]^{25}_{578}$ $+113$, $[\alpha]^{25}_{546}$ $+132$, $[\alpha]^{25}_{436}$ $+251$, $[\alpha]^{25}_{365}$ $+414$.

Anal. Calcd. for $C_{19}H_{26}ONClPt$: C, 44.31; H, 5.09; N, 2.72. Found: C, 44.41; H, 5.17; N, 2.85.

Enantiomers of di-μ-chlorobis(*3a,4,7,7a,tetrahydro*-exo-*6-methoxy*-endo-*4,7 methanoindene*-endo-*5σ,2π*)-*diplatinum*(*II*) (**f**, **g**). To a stirred ice-cold solution of 6.03 g (11.7 mmoles) of the diastereoisomer **d** in 60 ml of methanol, 25 ml of a 5N methanolic solution of HCl was added dropwise.

The precipitate was collected and after crystallization from a chloroform-ether mixture 4.3 g of a material **f** were obtained having identical IR spectrum and melting point with those of *b*, $[\alpha]^{25}_{D}$ $+25.4$, $[\alpha]^{25}_{578}$ $+27$, $[\alpha]^{25}_{546}$ $+33$, $[\alpha]^{25}_{436}$ $+97$ (c 0.5, methylene chloride).

With the same procedure the other enantiomer *g*, having IR spectrum, melting point and absolute value of the rotation identical with those of **f**, was obtained from **e**.

Enantiomers of Dichloro(endo-*dicyclopentadiene*)-*platinum*(*II*) (**h**, **i**). According to the known procedure,[3a] a stirred suspension of 4.01 g (5.1 mmoles) of **f** in 300 ml of 5N HCl was refluxed 3 hr. After cooling the solid was filtered off, washed with water, and dried. Crystallization from a mixture of chloroform-ether gave 3.2 g (77,1%) of a material **h** having melting point and IR spectrum identical with

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[8] C. E. Waring, E. E. Kern and W. A. Blann, *J. Am. Chem. Soc.*, 63, 1767 (1941).

[9] W. Theilacker and H. G. Winkler, *Chem. Ber.*, 87, 690 (1954).

those of **a**, $[\alpha]_D^{25}$ +26.2, $[\alpha]_{578}^{25}$ +28.3, $[\alpha]_{546}^{25}$ +34, $[\alpha]_{436}^{25}$ +98 (*c* 0.5, methylene chloride).

The other enantiomer was obtained in one step by refluxing for 3 hr a suspension of **e** (5.0 g, 9.7 mmoles) in 300 ml of 5N HCl. Crystallization of the crude product from chloroform-ether afforded 2.6 g (67.2% yield) of a product **i** having melting point, IR spectrum and absolute value of the rotation identical with those of **h**. This one step procedure is equivalent to that which involves the intermediate μ complex (see Chart I).

Enantiomers of endo-*dicyclopentadiene* (**j**, **k**). To a stirred suspension of 3.0 g (7.5 mmoles) of **h** in 30 ml of water, a solution of 2.2 g (45 mmoles) of sodium cyanide was added. After 20 minutes of stirring the olefin was extracted with four 10 ml portions of pentane, and the combined extracts were washed with water. After drying on calcium sulphate the pentane extract was concentrated to about 1 ml and 5 ml of absolute ethanol were added. The separate crystalline olefin **j** weighed 215 mg (yield 21.6%); mp 30.5°, $[\alpha]_D^{25}$ +13.3, $[\alpha]_{578}^{25}$ +11.7, $[\alpha]_{546}^{25}$ +14.0, $[\alpha]_{436}^{25}$ +38.3, $[\alpha]_{365}^{25}$ +87.7 (*c* 0.5, methylene chloride), $[\alpha]_D^{25}$ +11.7, $[\alpha]_{578}^{25}$ +11.2, $[\alpha]_{546}^{25}$ +14,3, $[\alpha]_{436}^{25}$ +37.1, $[\alpha]_{365}^{25}$ +86.0 (*c* 0.5, pentane).[10] The olefin was identified by the IR spectrum, identical with that of the racemic compound.

In the manner above described for the levorotatory enantiomer the dextrorotatory *endo*-dicyclopentadiene **k** was obtained from **i**, showing IR spectrum and absolute values of rotation identical with those of the other optical antipod. Both the enantiomer **j** and **k** displayed no change in specific rotation when they were kept at room temperature for 5 days in solution of ethyl alcohol.

Reaction of **i** *with racemic 2-butanol.* To a suspension of 0.199 g (0.5 mmoles) of **i** in 1.852 g (25 mmoles) of DL-2-butanol, 0.123 g (0.75 mmoles) of sodium acetate was added and the mixture was stirred at 85° for 0.5 hr. The alcohol was quantitatively collected by distilling into a cold trap under vacuum and had n_D^{25} 1.3970 (lit. n_D^{25} 1.3975), $[\alpha]_{436}^{25}$ +0.041, (neat, using d^{25} 0.803).

From the values of the optical activity reported in literature,[11] ($[\alpha]_{436}^{25}$ +27.2) for the enantiomeric 2-butanol the optical purity of the sample was determined to be about 0.15%. Assuming that the alkoxylation of **i** was quantitative and multiplying this value by the ratio moles of the alcohol in excess over moles of the complex, we calculated a degree of stereoselectivity for this reaction of about 7%.[12]

The solid residue was crystallized from chloroform-ether to give 0.118 g (54.1%) of di-μ-chlorobis (3,4,7, 7a,tetrahydro-*exo*-6-*sec*-butoxy-*endo*-4,7 methanoindene-*endo*-5σ,2π)diplatinum(II) **l** having $[\alpha]_D^{25}$ −28.4 (*c* 0.5, methylene chloride).

Anal. Calcd for $C_{28}H_{42}O_2Cl_2Pt_2$: C, 38.58; H, 4.86. Found: C, 38.65; H, 4.80.

This material was again heated (85°, 0.5 hr) with 2-butanol in presence of sodium carbonate: no rotation was observed in the isolated alcoholic phase.

Enantiomeric Dichloro (endo-*dicyclopentadiene*) *palladium(II)* (**m**). The reaction of 2.0 g (5.0 mmoles) of the product **i** with aqueous sodium cyanide gave the enantiomeric olefin which was extracted with pentane. To the dried pentane extract 5 ml of benzene were added and the major part of the pentane carefully removed. To the resulting solution, a solution of 1.92 g (5 mmoles) of dichlorobis(benzonitrile)-palladium(II)[3c] in 100 ml of benzene was added and the mixture was allowed to stand at room temperature for 3 days. The orange crystals were filtered off, washed with benzene and dried. A crystallization from chloroform-ether gave 1.1 g (71% yield) of a material **m** with $[\alpha]_D^{25}$ +20.6 (*c* 0.48 in methylene chloride) having identical IR spectrum with that of the product prepared from an authentic sample of racemic olefin with the same procedure.

Alkoxylation of **m** *in presence of undissolved solid.* To a suspension of 0.186 g (0.6 mmoles) of **m** in 1.778 g (24 mmoles) of DL-2-butanol, a small amount of sodium carbonate was added. This solution was slightly acid. The solution was allowed to stand at room temperature until neutral (5 hr), and the butanol as collected by vacuum distillation.

The alcohol had n_D^{25} 1.3970 and rotation $[\alpha]_{436}^{25}$ +0.121, (neat using d^{25} 0.803), corresponding to an optical purity of this sample of about 0.45%. The stereoselectivity of the reaction calculated as in the case of the corresponding reaction with the platinum complex, was about 17%. The solid residue was dissolved in 10 ml of chloroform, placed on a silica gel column, and eluted with ether-petroleum ether. After evaporation to dryness of the eluate, the residue was crystallized from chloroform-ether, affording 0.155 g (74.5%) di-μ-chlorobis (3a,4,7,7a,tetrahydro-*exo*-6-*sec*-butoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) **n** having rotation $[\alpha]_D^{25}$ +279 (*c* 0.45 in methylene chloride). This product can be retransformed into the starting material **m** by boiling it with 5N HCl.

Anal. Calcd. for $C_{28}H_{42}O_2Cl_2Pd_2$ C, 48.44; H, 6.10. Found: C, 48.25; H, 6.02.

When 0.3 mmoles of **n** was stirred with DL-2-butanol in presence of sodium carbonate for 24 hr, the isolated alcohol from this mixture was inactive.

Alkoxylation of **m** *in solution.* To a solution of 0.310 g (1 mmole) of **m** in 20 ml of chloroform, 0.741 g (10 mmoles) of DL-2-butanol and a small quantity of sodium carbonate were added. The solution was allowed to stand at room temperature until neutral (about 75 hr). Both chloroform and 2-butanol were distilled and collected together. The chloroform was removed in vacuum until the residual liquid had n_D^{25} 1.3972.

This residue (0.253 g) was diluted with 0.885 g of racemic 2-butanol. The rotation of this sample was $[\alpha]_{436}^{25}$ +0.068, corresponding to an optical purity of about 0.25%. The degree of stereoselectivity, cal-

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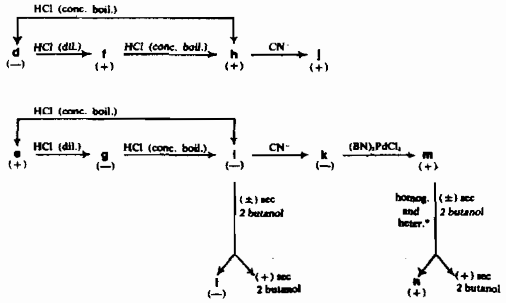
[10] The value of $[\alpha]_D^{25}$ in carbon disulphide which was reported in our preliminary note as +60 should read +36.0. The refined values was $[\alpha]_D^{25}$ +35.2, $[\alpha]_{546}^{25}$ +43.1, $[\alpha]_{436}^{25}$ +95.4 (*c* 0.6).

[11] J. Kenyon, H. Phillips and V. P. Pittmann, *J. Chem. Soc.* 1077 (1935).

[12] It should be noted that no change in rotation was detected when an authentic sample of optically active 2-butanol (74% optical purity) was heated at 80° for 0.5 hr in presence of sodium acetate and collected by distillation.

Chart II. Scheme of the reactions paths followed and of the sign of optical rotations of the various products



BN = benzonitrile. * This reaction was accomplished both in solution and in the presence of undissolved solid.

culated as above, was about 11%. The solid residue, purified by chromatography on silica gel, gave, after crystallization from chloroform-ether, 0.276 g (79.4% yield) of a product identical by IR spectrum with **n**.

Results

It was reported in our preliminary note[1] that the reaction of the alkoxy derivative of **a** (see Chart I) with an optically active amine resulted in the formation of only one diastereoisomeric pair **c**.

It was however possible to achieve the resolution of the pair **c** by fractional crystallization. The difference in fractionating ability displayed in this separation by aromatic solvents and mixtures of chlorinated and saturated cyclic hydrocarbons is noteworthy. From toluene or xylene consecutive fractions having alternating sign of the rotation were obtained, while from the latter solvents after the collection of the first crop the major part of the complex separated as a 1:1 mixture of the two diastereoisomers. The fractionating ability of non aromatic solvents can find an explanation in the inability of these solvents to weaken the intermolecular interaction of the type previously discussed[13] between the methoxy groups of **c** and the π-electron cloud of the phenyl groups of other molecules of **c** which lead to a stabilization of the racemate.

Indication of a similar type of interaction has also been found[14] in solid state by x-ray analysis of the *cis*-dichloro(*trans*-2-butene)-(S)-(α-methylbenzylamine)-platinum(II). The aromatic solvent would compete for this interaction allowing one diastereoisomer to separate preferentially.

From the isolated diastereoisomers **d**, **e** the optical antipodes **f**,**g** of the dimeric methoxy derivative can be obtained by removing the amine with a mineral acid. At this stage use can be made of the reversibility, earlier described by Hoffmann and Narbutt,[3a] of the alkoxylation in presence of concentrated HCl. It is then possible to restore the monomeric complex **h**,**i** as pure enantiomer.

One of the two antipodes of the palladium complex was obtained by direct coordination of the olefin resolved according to the Chart I, without attempting to perform a similar separation. In all investigated range of wavelength the sign of the enantiomeric palladium complex **m** is opposite to that of the enantiomeric platinum complex **i** containing the same antipode of the diene. For instance, $[\alpha]_D^{25}$ +20.5 for the former, $[\alpha]_D^{25}$ −26.1 for the latter.

Both the palladium and the platinum enantiomeric complexes were allowed to react with DL-2-butanol. After completion of the reaction, the unreacted alcohol was separated from the reaction mixture and the rotation of the collected sample was measured. From these data a stereoselectivity about 7% for the Pt^{II} complex and about 18% for the Pd^{II} complex was calculated from the restrictive hypothesis of a quantitative yield.

Discussion

In previous papers experimental evidence was presented for the influence of the asymmetry of the environment on the configuration achieved by an olefin upon coordination in a π complex. This appeared of interest in connection with a requirement common to most of the proposed mechanisms of stereospecific heterogeneous catalysis of polymerization of α-olefin. For instance it was pointed out[15] that the process «leads to a stereoregular polymer if each monomer addition assumes the same orientation». Also in the Cossee mechanism[15] the production of isotactic polymer follows from the pre-orientation of the monomer (together with the migration of the growing chain). The cited results[2a,b] showed that also for a very simple model and in absence of a rigidly hindering layer structure, the chemical potentials of the two diastereoisomeric π-complexes, corresponding to the two different orientations of the coordinated monomer, were rather different. On the other hand, if the pre-orientation of the monomer could not account for the activation energy difference between the two possible steric paths of the insertion, this difference would very likely be due to substantial interaction between the last asymmetric carbon atom of the growing chain and the potentially asymmetric carbon of the coordinating monomer double bond. This hypothesis appears particularly reasonable in view of the asymmetric induction effect reported here for the butoxylation of dichloro (*endo*-dicyclopentadiene)Pt^{II} and Pd^{II}.

However, before reaching any conclusion on the argument both the stereochemistry of the attack on the resolved uncoordinated diene and the mechanism of the addition must be elucidated. In regard to the latter point the study of the addition of nucleophiles other than alkoxy groups is now in progress in our laboratory.

Acknowledgments. We are indebted to Professor P. Corradini and Professor V. Crescenzi for helpful discussions.

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[13] See, for instance, A. A. Sandoval and M. w. Hanna, *J. Phys. Chem.*, *70*, 1203 (1966).
[14] C. Pedone, private communication.
[15] H. W. Coover Jr., *J. Pol. Sci.*, Part C, 1511 (1963).
[16] P. Cossee, *J. of Catal.*, *3*, 80 (1964).