

Finally we briefly discuss the relative stability of the axial and equatorial lone-pair conformers of piperidine derivatives in terms of the extended Hückel calculations. The total electronic energies calculated are summarized

in Table IX. It is evident that the equatorial lone pair is preferred for NH piperidine and the axial lone pair for N-methyl piperidines. These results are consistent with our experimental conclusions.

The Stereospecific Addition of Carbon and Nitrogen Nucleophiles to Dicyclopentadieneplatinum and -palladium Complexes¹

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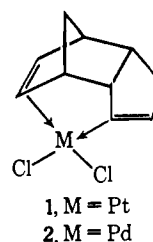
Abstract: The nucleophilic additions of acetylacetonate, ethyl acetoacetate, diethyl malonate, or benzylamine to the double bond of dichloro(*endo*-dicyclopentadiene)platinum(II) and of thallos acetylacetonate to dichloro(*endo*-dicyclopentadiene)palladium(II) produced platinum- and palladium-carbon σ -bonded complexes. The *trans* additions take place at the 5,6-double bond without skeletal rearrangement of the dicyclopentadiene moiety; the nucleophile is attached *exo* with the metal *endo* and coordinated to the 2,3-double bond.

The addition of oxygen nucleophiles to the carbon-carbon double bond of olefin-platinum and -palladium complexes has received wide attention,³⁻⁶ yet there is little information concerning the reactions of other nucleophiles with coordinated cyclic diolefins. More recently, the chemistry of the additions of other nucleophiles such as β -diketones,⁷ diethyl malonate,⁸ and amines^{6,9} to diolefins have been reported. In these cases the addition to diolefin complexes of the general formula [(diene) - MX₂], where M is platinum or palladium, has taken place with the formation of carbon-carbon or carbon-nitrogen σ bonds and a metal-carbon σ bond. Usually only one of the two double bonds suffers addition; the remaining double bond provides coordination to the metal.

Results and Discussion

Because of the success in determining the stereochemical pattern⁴ of the addition of oxygen nucleophiles to the rigidly cupped diolefins containing the bicyclo-[2.2.1] skeleton, the dichloro(*endo*-dicyclopentadiene)platinum(II) and -palladium(II) complexes, **1** and **2**, respectively, were employed in this work. As in the case of addition of methanol to complexes **1** and **2**,⁴

it was expected that the addition of other nucleophiles would take place at the more reactive norbornene double bond.



Carbon Nucleophiles. Acetylacetonate. The addition of acetylacetonate to dichloro(*endo*-dicyclopentadiene)platinum(II) was effected by stirring a suspension of the complex in acetylacetonate in the presence of sodium carbonate. Prior preparation of the thallium salt is not necessary.^{7b} When dichloro(*endo*-dicyclopentadiene)palladium(II) was treated similarly with acetylacetonate, decomposition to metallic palladium occurred during the isolation procedure. However, a stable complex was prepared by allowing dichloro(*endo*-dicyclopentadiene)palladium(II) to react with thallos acetylacetonate at 0°. Both compounds had the general formula (C₁₀H₁₂)M(C₅H₇O₂)₂. This is the general formula reported previously for the platinum complex, but the elucidation of the structure of the complex by the identification of the isomer obtained (of many possible) was not carried out.^{7b}

The hydrogenation of the platinum complex to form **3** showed that the addition of acetylacetonate to complex **1** had occurred at an olefinic bond by formation of a new carbon-carbon bond. The complex, suspended in methanol, was readily decomposed by hydrogen without the presence of an external catalyst; the double bond in the dicyclopentadiene ring is probably reduced by a platinum hydride species formed *in situ*. The 100-MHz nmr spectrum of **3** contains a well-resolved doublet centered at τ 6.65 (H_X). Although it was not

(1) For a preliminary report of this work see J. K. Stille and Dale B. Fox, *Inorg. Nucl. Chem. Lett.*, **5**, 157 (1969).

(2) Abstracted in part from the Ph.D. Thesis of D. B. Fox, University of Iowa, Iowa City, Iowa, August 1969.

(3) (a) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957); (b) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *ibid.*, 3413 (1957).

(4) (a) J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Amer. Chem. Soc.*, **87**, 3282 (1965); (b) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966), and references contained therein.

(5) (a) Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, *Tetrahedron Lett.*, 633 (1968); (b) Y. Fujiwara, I. Moritani, and M. Matsuda, *Tetrahedron*, **24**, 4819 (1968).

(6) G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).

(7) (a) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *Chem. Commun.*, 117 (1966); (b) B. F. G. Johnson, J. Lewis, and M. S. Subramanian, *J. Chem. Soc.*, **A**, 1993 (1968).

(8) (a) Jiro Tsuji and Hidetaka Takahashi, *J. Amer. Chem. Soc.*, **87**, 3275 (1965); (b) J. Tsuji and H. Takahashi, *ibid.*, **90**, 2387 (1968).

(9) R. Palumbo, A. De Renzi, A. Panunzi, and G. Paiaro, *ibid.*, **91**, 3874 (1969).

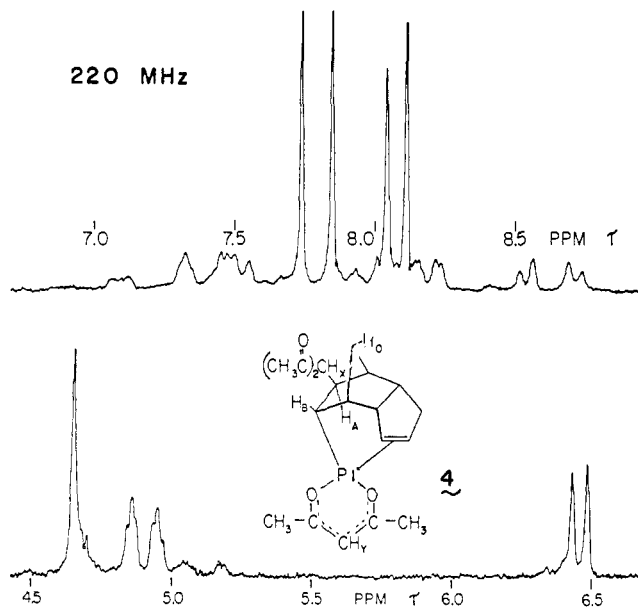
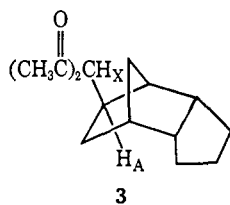
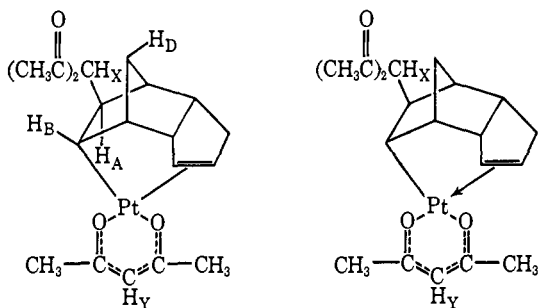


Figure 1.

possible to locate H_A , a comparison with the 60-MHz spectrum showed $J_{AX} = 12$ Hz.



One of the more important signals in the nmr spectrum (at 220 MHz) of the platinum complex was a well-resolved doublet at τ 6.46 (Figure 1) which may be assigned to the proton H_X . Proton H_A was located at τ 7.49 by irradiation (Varian HR 220) of H_X , $J_{AX} = 12$ Hz. The peak for H_A (Figure 2) obtained from this decoupling was poorly resolved (peak width at half-height = 5 Hz), indicating residual coupling to H_B and possibly H_D . This poorly resolved peak is clearly not a result of a coupling to a vicinal proton having a 0° dihedral angle ($J \approx 7-9$ Hz), but a result of small coupling(s) to H_D ($J_{AD} \approx 2-3$ Hz) and H_B for which the coupling constant would be that expected¹⁰ for a 120° dihedral angle ($J_{AB} \approx 2$ Hz). The platinum-carbon (5 position) bond must be *endo* so that platinum can remain coordinated to the 2,3-double bond (and hence, provide stability for the complex); the acetylacetonate



(10) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963), and references therein.

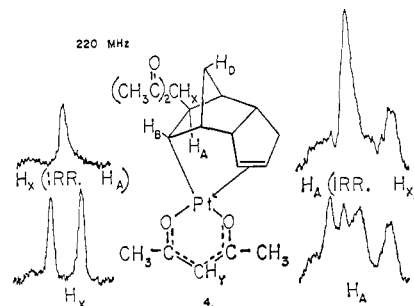
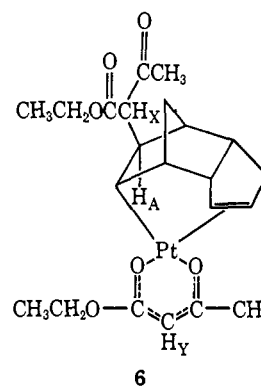


Figure 2.

moiety is, therefore, *exo*. Similarly, the stereochemistry of the addition of acetylacetonate to the corresponding palladium complex was established and the platinum and palladium complexes were assigned structures **4** and **5**, respectively.

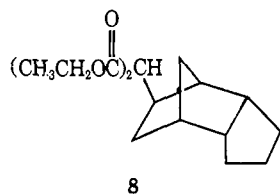
Ethyl Acetoacetate. The addition of ethyl acetoacetate to dichloro(*endo*-dicyclopentadiene)platinum(II) was effected by stirring a suspension of the complex in ethyl acetoacetate in the presence of sodium carbonate to give a product with the general formula $C_{10}H_{12}Pt(C_6H_9O_3)_2$. That a bond had been formed between the carbon atom of ethyl acetoacetate, which is α to both carbonyl groups, and a carbon atom of the dicyclopentadiene ring, was evidenced by the presence of a well-resolved doublet in the nmr spectrum centered at τ 6.79 assigned to H_X . The two peaks of the doublet were 12 Hz apart in both the 60- and 100-MHz spectra, indicating coupling to a proton labeled H_A , $H_{AX} = 12$ Hz.

Although *cis,trans* isomers of the complex **6** are possible, only one has been depicted since the 100-MHz spectrum indicates that only one isomer is present. Unfortunately, the spectrum does not provide the information necessary to determine which isomer was obtained.

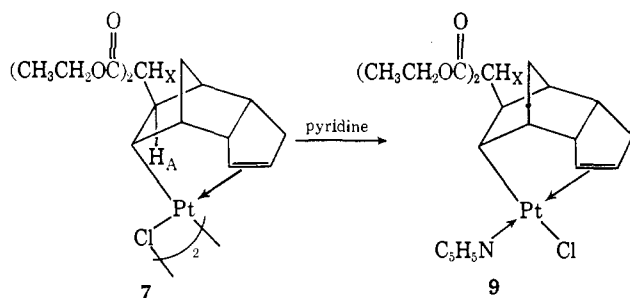


Diethyl Malonate. The addition of diethyl malonate to dichloro(*endo*-dicyclopentadiene)platinum(II) was effected by stirring a suspension of the complex in diethyl malonate in the presence of sodium carbonate to give $[C_{10}H_{12}(C_7H_{10}O_4)PtCl]_2$, **7**. The preparation of **8** through hydrogenation of the complex showed that the addition of diethyl malonate to complex **1** had occurred at a double bond by formation of a new carbon-carbon bond.

The integration of the nmr spectrum of complex **7**, as well as the elemental analysis and the molecular weight data, confirmed the presence of only one diethyl



malonate moiety per platinum, and suggested that a dimer was formed through chloro bridging. Chloro-bridged dimers are readily split by amines without alteration of the remainder of the complex.^{3,4} On treatment of **7** with pyridine, the corresponding monomeric complex, **9**, was obtained.



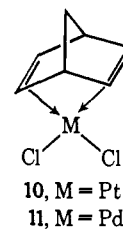
It has been shown^{8b} that the reaction of dichloro(*endo*-dicyclopentadiene)palladium(II) with a stoichiometric amount of diethyl malonate does not afford the palladium analog of **7**; our own results using sodium carbonate as a base confirm this report. In addition, treatment of **2** with a crude sample of thallium diethylmalonate did not afford addition of the nucleophile to the complex.

Deuterium Exchange Studies. The protons labeled H_Y in the complexes **4**, **5**, and **6** have been assigned to peaks appearing in the nmr spectra at τ 4.67, 4.91, and 5.28, respectively. When a deuteriochloroform solution of either the platinum(II) complexes **4** or **6** was treated with deuterium oxide which had been made basic with sodium carbonate, the peak assigned to H_Y disappeared from the nmr spectrum. It is surprising that proton H_Y in the palladium complex **5** did not undergo deuterium exchange, since facile electrophilic substitution reactions at the corresponding carbon in Pd(acetylacetonyl)₂ take place.¹¹ The failure of H_X to undergo deuterium exchange in complexes **4**, **5**, **6**, and **7** may be due to a combination of steric hindrance to proton removal and the inability of the β -diketonyl group to become sufficiently planar in order to form an enolate, because of the steric compression against the proton in the 7-*syn* position. The two methyl groups (in the acetylacetonate moiety attached to the dicyclopentadiene ring) are magnetically nonequivalent in **4** (see Figure 1) and **5**. The same is true with the ethyl groups in **7**.

Reactions with Norbornadiene Complexes. When either dichloro(norbornadiene)platinum(II), **10**, or dichloro(norbornadiene)palladium(II), **11**, was stirred with acetylacetonate, ethyl acetoacetate, or diethyl malonate in the presence of sodium carbonate, metallic platinum or palladium was formed. Complexes **10** or **11** reacted with thallos acetylacetonate at 0° without decomposition. However, when the reaction mixture filtrate was concentrated, even below 0°, the materials readily turned black and no meaningful analytical data

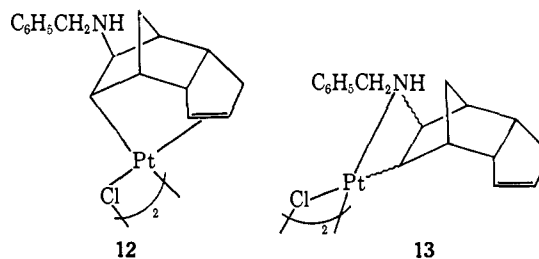
(11) A. Kasahara, K. Uji-ie, and K. Tanaka, *Bull. Chem. Soc. Jap.*, **39**, 2227 (1966).

were obtained. These results are contrary to an earlier report that the addition compounds could be obtained.^{7a}



Nitrogen Nucleophile. Benzylamine. Although the addition of various amines to diolefin-platinum and -palladium complexes has been reported⁹ recently, the isomerism in the product and the stereochemistry of the addition was only inferred. The reaction of **1** and **2** with benzylamine provided the opportunity to elucidate the stereochemistry of this addition. A solution of dichloro(*endo*-dicyclopentadiene)platinum(II), **1**, in methylene chloride, reacted with benzylamine to form a crystalline solid [C₁₀H₁₂(C₇H₅N)PtCl]_n. This is contradictory to the observation⁹ that rigid diolefin (1,5-cyclooctadiene, norbornadiene) complexes of platinum did not give a stable reaction product on reaction with amines. The solid was too insoluble in suitable solvents to determine a molecular weight or to obtain a nmr spectrum at 100 MHz, although the nmr spectrum after forty scans with the computer of average transients did indicate the presence of a phenyl group. Structures having a platinum-chlorine terminal bond may be ruled out for the complexed benzylamine adduct, since there was no absorption in the 270–340 cm⁻¹ region of the far-infrared spectrum; terminal platinum-chlorine vibrations have been assigned^{7b} to absorptions at 312 and 314 cm⁻¹.

Assuming that the platinum in the new complex remained divalent with a coordination number of four, the structures **12** and **13** may be considered. An uncoordinated double bond as in **13** is possible, but is less likely, since alkyl platinum(II) complexes are generally stable only when some other ligand (such as an olefinic bond) is present which affords large crystal field split-



ing.¹² For the same reason this type of chloro-bridged structure is the preferred one resulting from the addition of amines to other platinum complexes.⁹ Complexed carbon-carbon double bonds are known to have infrared absorptions at lower frequencies than similar uncomplexed olefinic bonds.^{13,14} However, it was not

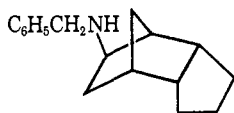
(12) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966).

(13) Kazuo Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, p 228.

(14) (a) J. R. Doyle and H. B. Jonassen, *J. Amer. Chem. Soc.*, **78**, 3965 (1956); (b) H. B. Jonassen and J. E. Field, *ibid.*, **79**, 1275 (1957); (c) P. E. Slade and H. B. Jonassen, *ibid.*, **79**, 1277 (1957); (d) H. B. Jonassen and W. B. Kirsh, *ibid.*, **79**, 1279 (1957).

possible to distinguish unambiguously between structures **12** and **13** due to interfering absorptions.

When the complex (**12**–**13**) was treated with either pyridine or *p*-toluidine,³ only the unchanged complex was isolated. When triphenylphosphine⁶ was allowed to react with the complex (**12**–**13**), the dicyclopentadiene moiety was displaced from the complex, as evidenced by the elemental analysis and infrared data of the product. Treatment of the complex with thallos acetylacetonate did not give identifiable products. The hydrogenation of complex (**12**–**13**) to form **14** showed that the addition of benzylamine to complex **1** had occurred at an olefinic bond by formation of a new carbon–nitrogen bond. The structure of **14** was established by its nmr spectrum.



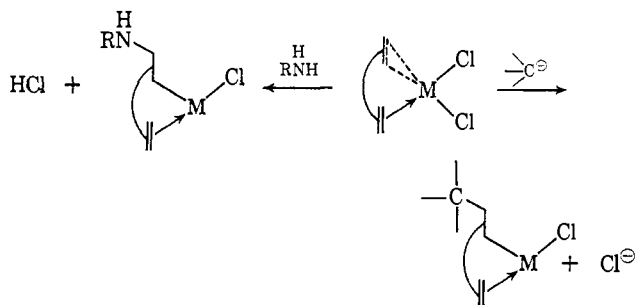
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Dichloro(*endo*-dicyclopentadiene)palladium(II), **2**, was also treated with benzylamine. The reaction mixture, even at 0° under a nitrogen atmosphere, turned black within 10 min due to decomposition to metallic palladium. When dichloro(*norbornadiene*)palladium(II), **11**, was treated with benzylamine, the reaction mixture turned dark. This is apparently in agreement with the report⁹ which noted an instability of the product of treatment of the *norbornadiene* complexes **10** and **11** with primary amines.

Conclusion

The reactions of stabilized carbanions (of the 1,3-dicarbonyl type) and amines with *endo*-dicyclopentadiene complexes occur to give stable products when the ligand is a diolefin which has the proper geometry to maintain coordination through a π bond. The stereochemical pattern is an overall *trans* addition, with the metal *endo* (or inside), and the reaction occurs without rearrangement of the carbon skeleton. Addition takes place at the more reactive *norbornene* double bond. These reactions provide a new route to stereospecific syntheses of hydrocarbons. This is the same stereochemical pattern as that followed by the oxymetallation reactions of platinum- and palladium-diolefin complexes, although oxymetallations, in general, give higher yields. The reactions of the carbon and amine nucleophiles with platinum- and palladium-*norbornadiene* complexes apparently afford products which are too unstable for isolation under the ordinary conditions.

These reactions with nucleophiles undoubtedly proceed by attack at the double bond on the side opposite from that which faces the metal. Susceptibility of the



double bond to nucleophilic attack is enhanced by its coordination to the metal.

Experimental Section

[*exo*-6-(1-Acetylacetylonyl)-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5 σ ,(2-3) π](2,4-pentanedionato)platinum(II) (**4**). A heterogeneous mixture of 10.08 g (25.4 mmol) of dichloro(*endo*-dicyclopentadiene)palladium(II), 13.51 g (143 mmol) of sodium carbonate, and 156 g (1.56 mol) of acetylacetonate was allowed to stir at room temperature under a nitrogen atmosphere for 4 days. The sodium carbonate was collected on a filter and washed with acetylacetonate. The excess acetylacetonate was distilled at reduced pressure from the yellow filtrate and the combined washings to give 11.67 g (87.4%) of the crude product. Purification was effected by passing a methylene chloride solution of the product over a column of silica gel followed by recrystallization from methylene chloride to give a 55.1% yield of **4** (mp 130–132°; lit.^{7b} mp 118–120°). The sodium fusion–silver nitrate test for halide was negative. The nmr spectra are shown in Figures 1 and 2. The ir spectrum showed maxima at 1700 cm^{-1} (C=O, uncoordinated) plus 1585 and 1515 cm^{-1} (C=O, coordinated).

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{Pt}$: C, 45.71; H, 4.99; N, 525.5. Found: C, 45.61; H, 4.91; M (benzene), 534.

Hydrogenation of Complex 4. 3-(Hexahydro-4,7-methanoindan-5-yl)-2,4-pentanedione (**3**). A suspension of 6.99 g (13.3 mmol) of **4** in 100 ml of dry methanol was shaken in a Paar hydrogenation apparatus at 50 psi until hydrogen absorption ceased. The free platinum was collected on a filter and washed with methanol. The filtrate was concentrated by removing part of the solvent at reduced pressure. Preparative gas–liquid chromatography (10-ft 10% Apiezon L on Chromosorb P) was used to isolate 85 mg (2.7%) of the >99% pure, white, saturated product, mp 70–71°. The prominent absorptions in the nmr spectrum at 100 MHz were a strong peak at τ 7.84 corresponding to 6 protons, and a doublet centered at τ 6.65 assigned to H_X . The important bands in the ir spectrum were at 1715 and 1720 cm^{-1} (C=O).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.88; H, 9.46. Found: C, 76.76; H, 9.35.

[*exo*-6-(1-Acetylacetylonyl)-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5 σ ,(2-3) π](2,4-pentanedionato)palladium(II) (**5**). A 2.00-g (6.47 mmol) sample of dichloro(*endo*-dicyclopentadiene)palladium(II) was stirred with 500 ml of chloroform at 15° for 1 hr. The small amount of insoluble material which did not dissolve was removed by filtration. Likewise, a 3.94-g (12.96 mmol) sample of thallos acetylacetonate was stirred with 500 ml of chloroform for 1 hr before the insoluble material was removed by filtration. The two filtrates were combined at 0° by slow addition of the thallos salt solution to the stirred solution of the palladium complex. The mixture was stirred for 4 hr at 0° before the precipitate was collected on a filter. The weight of the dried thallos chloride indicated that both of the chloride ligands had been displaced from the platinum complex. The filtrate was concentrated to a yellow oil at 5° under reduced pressure. Recrystallization from chloroform–Skellysolve F gave 0.57 g (21.0%) of the complex **5**, mp 102–107° dec. The sodium fusion–silver nitrate test for halide was negative. The prominent absorptions in the nmr spectrum at 100 MHz were peaks at τ 8.15, 8.08, 7.83, and 7.75 assigned to methyl groups, a doublet centered at τ 6.45 assigned to H_X , and a single peak at τ 4.91 assigned to H_Y . The ir spectrum showed maxima at 1650 cm^{-1} (C=O, uncoordinated) and at 1590 and 1515 cm^{-1} (C=O, coordinated).

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_4\text{Pd}$: C, 54.99; H, 6.00; Pd, 24.36; M, 436.9. Found: C, 55.12; H, 6.00; residue, 21.99; M (chloroform), 454.

[*exo*-6-(1-Carboethoxyacetylonyl)-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5 σ ,(2-3) π](hydrogen acetoacetato)platinum(II) Ethyl Ester (**6**). A heterogeneous mixture of 10.08 g (25.3 mmol) of dichloro(*endo*-dicyclopentadiene)palladium(II), 13.25 g (125 mmol) of sodium carbonate, and 185 g (1.42 mol) of ethyl acetoacetate was stirred at room temperature under a nitrogen atmosphere for 4 days. The sodium carbonate was collected on a filter and washed with ethyl acetoacetate. The solvent was distilled from the yellow filtrate and the combined washings under reduced pressure to leave a yellow oil. A methylene chloride solution of the oil was passed over a silica gel column and the solvent was removed from the eluate at reduced pressure. A 2.62-g (16.0%) yield of white, fine needles of **6** (mp 135–136°) was obtained after two recrystallizations of this yellow residue from pentane. The sodium fusion–silver nitrate test for halide was negative. The prominent

absorptions in the nmr spectrum at 100 MHz were two triplets centered at τ 8.80 and 8.75 as well as two quartets centered at τ 6.04 and 5.88 assigned to two ethyl ester groups, two peaks at τ 8.06 and 7.67 assigned to methyl groups, a doublet centered at τ 6.79 assigned to H_X , and a peak at τ 5.28 assigned to H_Y . The important bands in the ir spectrum were at 1730 and 1710 cm^{-1} (uncoordinated ester and ketone $\text{C}=\text{O}$), at 1605 cm^{-1} (ester $\text{C}=\text{O}$, coordinated), and at 1525 cm^{-1} (ketone $\text{C}=\text{O}$, coordinated).

Anal. Calcd for $\text{C}_{22}\text{H}_{30}\text{O}_6\text{Pt}$: C, 45.13; H, 5.16; M, 585.6. Found: C, 45.01; H, 5.31; M (benzene), 562.

Di- μ -chlorobis[*exo*-6-(biscarboethoxymethyl)-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene-*endo*-5 σ , (2-3) π]diplatinum(II) (7). A heterogeneous mixture of 11.59 g (29.2 mmol) of dichloro(*endo*-dicyclopentadiene)platinum(II), 10.54 g (99.5 mmol) of sodium carbonate, and 211 g (1.32 mol) of diethyl malonate was allowed to stir for 3 days at room temperature under a nitrogen atmosphere. The sodium carbonate was collected on a filter and washed with diethyl malonate. The excess diethyl malonate was distilled at reduced pressure from the yellow filtrate and the combined washings. Purification was effected by passing a benzene solution of the product over a column of silica gel; the eluate was concentrated to about 15 ml and washed with 100 ml of pentane. The resulting light yellow solid was recrystallized from benzene-pentane to obtain 4.14 g (27.1%) of **7**, mp 280° dec. A sodium fusion-silver nitrate test for halide was positive. The prominent absorptions in the nmr spectrum at 100 MHz were two quartets centered at τ 5.87 and 5.86 as well as two triplets centered at τ 8.76 and 8.74 assigned to two ethyl ester groups, a doublet centered at τ 6.98 assigned to H_X , and absorption centered at τ 4.87 assigned to vinyl protons. The ir spectrum showed carbonyl absorptions in the 1720-1733 cm^{-1} region.

Anal. Calcd for $\text{C}_{34}\text{H}_{46}\text{O}_8\text{Pt}_2\text{Cl}_2$: C, 39.12; H, 4.44; M, 1044. Found: C, 38.91; H, 4.24; M (benzene), 1028.

Chloro[3a,4,5,6,7,7a-hexahydro-*exo*-6-(biscarboethoxymethyl)-*endo*-4,7-methanoindene-*endo*-5 σ , (2-3) π](pyridine)platinum(II) (9). A 2.01-g (1.93 mmol) sample of complex **7** dissolved in methylene chloride was allowed to stir with 0.37 g (4.68 mmol) of pyridine for 9 hr. The solvent and excess pyridine were removed by distillation at reduced pressure. Washing the residue with benzene gave 1.97 g (85%) of **9**. White crystals, mp 161-163°, were obtained by recrystallization from methylene chloride-pentane. The prominent absorptions in the nmr spectrum at 60 MHz were two triplets centered at τ 8.68 and 8.64 as well as two quartets centered at τ 5.73 and 5.72 assigned to two ethyl ester groups, and multiple peaks in the region of τ 2.2 and 1.1 assigned to complexed pyridine. The ir spectrum showed maxima at 1720-1740 cm^{-1} ($\text{C}=\text{O}$), 1600 cm^{-1} (pyridine), and 760 cm^{-1} (pyridine).

Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_4\text{ClPt}$: C, 43.97; H, 4.70; N, 2.33; Cl, 5.90; M, 601. Found: C, 44.06; H, 4.65; N, 2.42; Cl, 5.88; M (chloroform), 583.

Hydrogenation of Complex 7. Diethyl Hexahydro-4,7-methanoindan-5-malonate (8). A suspension of 6.22 g (5.93 mmol) of complex **7** and 0.99 g (12.0 mmol) of sodium acetate in 150 ml of dry methanol was shaken in a Paar hydrogenation apparatus at 50 psi until hydrogen absorption ceased. The product was isolated in the same manner as **3**. The integration of the nmr spectrum of the product of hydrogenation corresponded to structure **8** with the following prominent peaks: a triplet centered at τ 8.68, a quartet centered at τ 5.75, and a doublet centered at τ 6.80.

Anal. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_4$: C, 69.36; H, 8.90. Found: C, 69.78; H, 8.97.

Deuterium Exchange in Complexes 4, 5, 6, and 7. The nmr spectrum of 100 mg of complex **4** dissolved in deuteriochloroform was obtained for use as a reference. To this solution was added several drops of deuterium oxide and the heterogeneous mixture (which was maintained at 25°) was shaken occasionally. After 3 days the nmr spectrum of this material was no different than the reference spectrum. The pH of the deuterium oxide was then adjusted to 10 with sodium carbonate and the mixture was shaken occasionally at 25°. After standing overnight, the nmr spectrum indicated that the peak formerly at τ 4.67 had disappeared.

When complex **6** was treated similarly with basic deuterium oxide, no deuterium exchange was apparent after 3 hr. After 4 days at 25°, the peak formerly at τ 5.28 was no longer present in the nmr spectrum. No deuterium exchange was noted when complexes **5** (after 7 days) and **7** (after 4 days) were treated in the same manner.

Reaction of Benzylamine with Dichloro(*endo*-dicyclopentadiene)platinum(II) (1). A 4.04-g (36.7 mmol) sample of benzylamine was added to a stirred solution of 7.26 g (18.2 mmol) of dichloro(*endo*-dicyclopentadiene)platinum(II) in 110 ml of methylene chloride. After about 10 min a fine precipitate formed. The mixture was allowed to stir at room temperature under a nitrogen atmosphere for 5 hr. The white solid was collected on a filter. The solid was stirred with 100 ml of water at room temperature overnight. The product was collected on a filter, air dried for 6 hr, and then dried for 15 hr under reduced pressure in the presence of phosphorus pentoxide. The weight of this material indicated a quantitative reaction to produce **12** or **13**. After recrystallization from chloroform-pentane, the white, crystalline product melted in the range 210-211° dec. The sodium fusion-silver nitrate test for halide was positive. The ir spectrum corresponded to structure **12** with bands at 700 and 740 cm^{-1} ($\text{C}-\text{H}$ bend, monosubstituted benzene) but the product was too insoluble to obtain a well-resolved nmr at 100 MHz after 40 scans with the computer of average transients. The far-ir spectrum had no absorption in the 270-340 cm^{-1} region indicating the absence of platinum-chlorine terminal bonds.¹¹

Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{N}_2\text{Cl}_2\text{Pt}_2$: C, 43.55; H, 4.30; N, 2.99; Cl, 7.56; Pt, 41.61. Found: C, 43.26; H, 4.24; N, 3.22; Cl, 7.81; residue, 39.13.

Hydrogenation of Complex (12-13). N-Benzylhexahydro-4,7-methanoindan-5-amine (14). A suspension of 3.93 g (4.19 mmol) of **12-13** in 100 ml of dry methanol was shaken in a Paar hydrogenation apparatus at 50 psi until hydrogen absorption ceased. The free platinum was collected on a filter and washed with methanol. The filtrate was concentrated by removing the solvent at reduced pressure. The residue was extracted with several portions of pentane and then dried over sodium sulfate. The pentane was removed (30° (2 mm)) to give 1.5 g (74.3%) of **14**. The integration of the nmr spectrum (neat) of the hydrocarbon corresponded to structure **14** with prominent peaks at τ 2.84 (5 protons) and at 6.44 (2 protons).

Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{N}$: C, 84.59; H, 9.60; N, 5.80. Found: C, 84.48; H, 9.50; N, 6.02.

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