Stereochemistry of Carbonylation of Some Diene–Palladium(II) Complexes and Their Corresponding Carbon–Palladium(II) σ-Bonded Oxymetallation Products[1]

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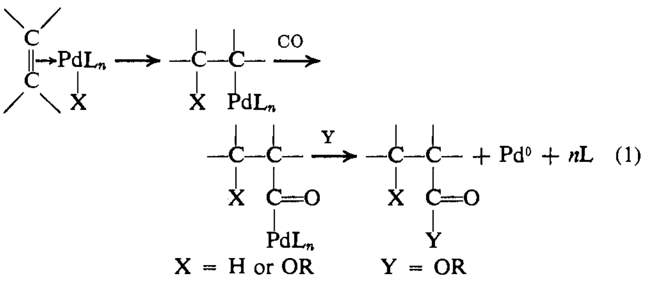
Abstract: The carbonylations of σ-bonded methoxy adducts derived from the oxymetallation reaction of dichloro-(norbornadiene)palladium(II), dichloro(1,5-cyclooctadiene)palladium(II) and dichloro(*endo*-dicyclopentadiene)-palladium(II) in methanol afforded esters. Elucidation of the stereochemistry of the product esters showed that the ester moiety had replaced palladium with retention of configuration at the carbon to which the palladium was σ bonded.

The carbonylation of olefins in the presence of palladium(II) in alcohol solvents produces saturated esters[3] or β-alkoxy esters,[4] depending on the reaction conditions. In these reactions, palladium–carbon σ-bonded complexes, resulting from the formal addition of PdX to the olefin, have been postulated[5] as intermediates which subsequently undergo an intramolecular rearrangement to acyl complexes; the acyl complexes decompose to afford the observed products. The essential features of this mechanism which have been adopted in order to explain the observed products are contained in eq 1.

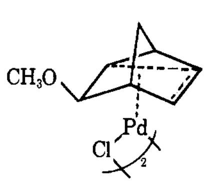


$$\mathrm{C{=}C}\rightarrow\mathrm{PdL}_n \longrightarrow -\underset{\mathrm{X}}{\mathrm{C}}-\underset{\mathrm{PdL}_n}{\mathrm{C}}- \xrightarrow{\mathrm{CO}} -\underset{\mathrm{X}}{\mathrm{C}}-\underset{\underset{\mathrm{PdL}_n}{\mathrm{C{=}O}}}{\mathrm{C}}- \xrightarrow{\mathrm{Y}} -\underset{\mathrm{X}}{\mathrm{C}}-\underset{\underset{\mathrm{Y}}{\mathrm{C{=}O}}}{\mathrm{C}}- + \mathrm{Pd}^0 + n\mathrm{L} \qquad (1)$$

X = H or OR   Y = OR

In these reactions, no intermediate alkyl or acyl complexes actually have been isolated or observed; however, in many other studies involving carbonylation reactions, alkyl and acyl complexes are easily observed, and their interconversions have been studied in some detail.[6]

Until recently,[1,7] little attention has been given to the stereochemistry of the carbonylation reaction at the carbon bearing the metal σ bond. The work reported here is a study of the carbonylation of some palladium(II) complexes in which particular emphasis has been placed on the elucidation of the stereochemical consequences at this carbon. The compounds employed for this study were the σ-bonded complexes **1**,[8] **2**, and **3**, as well as the corresponding diene complexes **4**, **5**, and **6**.



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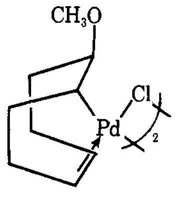

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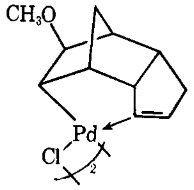

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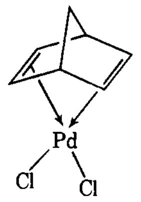

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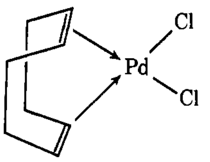

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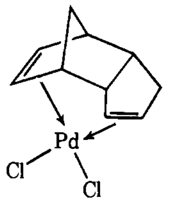

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The σ-bonded alkoxy complexes are easily prepared by the reaction of methanol with the particular diene complex in the presence of a weak base. Investigations[8,9] of the structure of these adducts or their platinum(II) analogs have shown that the addition takes place in an overall trans fashion with the methoxy group exo and the metal endo or "inside" in each case. These σ complexes closely resemble the intermediates which are thought to be involved in the carbonylation of olefins promoted by palladium(II).

Results and Discussion

The carbonylation of **1** was effected by treatment of a mixture of the complex and absolute methanol

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(1) For a preliminary report of this work see J. K. Stille and L. F. Hines, *J. Amer. Chem. Soc.*, **92**, 1798 (1970).

(2) Abstracted in part from the Ph.D. Thesis of L. F. Hines, University of Iowa, Iowa City, Iowa, August 1971.

(3) (a) J. Tsuji, M. Morikawa, and J. Kiji, *Tetrahedron Lett.*, 1437 (1963); (b) J. Tsuji, S. Hosaka, T. Susuki, and J. Kiji, *Bull. Chem. Soc. Jap.*, **39**, 141 (1966).

(4) J. Tsuji, M. Morikawa, and J. Kiji, Japanese Patent 19,940 (1965); *Chem. Abstr.*, **63**, 16219 (1965).

(5) J. Tsuji, in "Advances in Organic Chemistry," E. C. Taylor and H. Wynberg, Ed., Vol. 6, Interscience Publishers, New York, N. Y., p 109.

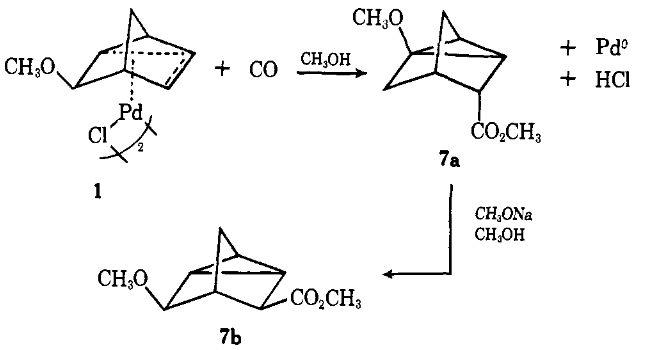
(6) (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, p 578, and references therein; (b) M. C. Baird, J. T. Mague, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc.*, *A*, 1347 (1967); (c) M. Kubota and D. M. Blake, *J. Amer. Chem. Soc.*, **93**, 1368 (1971).

(7) The reaction of π-cyclopentadienyldicarbonyliron *threo*-3,3-dimethylbutyl-*1,2-d*$_2$ with triphenylphosphine to yield π-cyclopentadienylcarbonyltriphenylphosphineiron *threo*-4,4-dimethyl-pentanoyl-*2,3-d*$_2$ proceeds with *retention* of configuration at carbon: G. M. Whitesides and D. J. Boschetto, *J. Amer. Chem. Soc.*, **91**, 4313 (1969).

(8) It has been suggested the complex **1** is best formulated as a π-homoallylic system on the basis of nmr evidence: M. Green and R. I. Hancock, *J. Chem. Soc. A*, 2054 (1967).

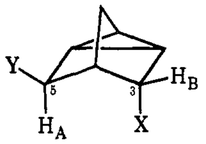
(9) (a) J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, **88**, 5135 (1966); (b) W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966); (c) C. Panattoni, G. Bombieri, E. Forsellini, B. Crociani, and U. Belluco, *ibid.*, 187 (1969); (d) C. B. Anderson and B. J. Burreson, *J. Organomet. Chem.*, **7**, 181 (1967).

with carbon monoxide (1 or 50 atm) at room temperature. The reaction produced metallic palladium, hydrogen chloride, and a single organic product, the evidence for which was in agreement with 3-*endo*-carbomethoxy-5-*exo*-methoxynortricyclene (**7a**). The geometry at the 3 and 5 positions of the carbonylation product was established on the basis of nmr chemical shift data. It has been shown,[10] that exo substituents at the 3 position have little or no effect on the chemical shift of an exo- or endo-5 proton, while an endo-3 substituent produces a paramagnetic shift in a 5-endo-proton. The nmr data contained in Table I reveal that the proton on the 5 carbon (H_A) in **7a** has experienced a downfield shift relative to the corresponding proton in the parent ether (δ H_A = ~3.4, Y = OCH_3, X = H). The proton on the 3 carbon (H_B) in **7a** has essentially the same chemical shift found for H_B in the parent ester (δ H_B = ~2.5, Y = H, X = CO_2R). Treatment of **7a** with sodium methoxide produced a mixture of **7a** and its epimer. The nmr spectrum of the epimer was in good agreement with that expected for 3-*exo*-carbomethoxy-5-*exo*-methoxynortricyclene (**7b**, δ H_A = 3.39). The proton on the carbon bearing the methyl ester group experienced almost no change in chemical shift (δ H_B = 2.46).



1 **7a** **7b**

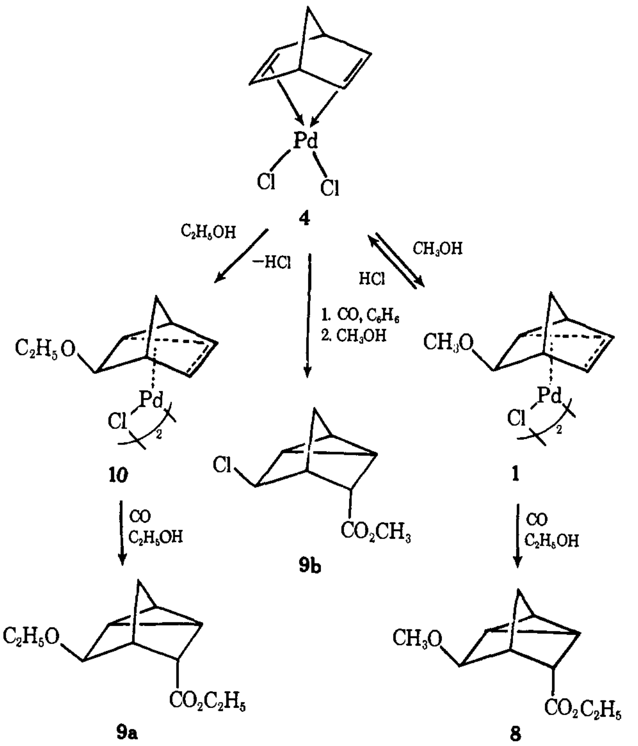
Table I. Chemical Shift Data for Substituted Nortricyclenes[a]



	Structure	δ, ppm	
		H_A	H_B
	X = H; Y = OCH_3	3.39	1.15
	X = CO_2R; Y = H	1.1-1.2	2.5
7a	X = CO_2CH_3; Y = OCH_3	3.75	2.51
8	X = $CO_2C_2H_5$; Y = OCH_3	3.71	2.48
9a	X = $CO_2C_2H_5$; Y = OC_2H_5	3.80	2.48
9b	X = CO_2CH_3; Y = Cl	4.23	2.58
	X = H; Y = Cl	3.87	~1.2-1.3

[a] 60 MHz; $CDCl_3$.

Rapid exchange of alkoxy or acetoxy groups has been observed in complexes similar to **1**.[9a,d] The reaction can be initiated by trace amounts of acid, and probably proceeds by a deoxymetallation–reoxymetallation path. Under certain conditions, complex **1** is converted to the diene complex **4** by the action of hydrogen chloride. Since hydrogen chloride was generated in the production of **7a** from **1** it was of interest to determine the amount of exchange that had occurred under the conditions of the carbonylation experiment. This was investigated by carrying out the carbonylation of **1** in ethanol. The reaction afforded a product mixture consisting of 93% 3-*endo*-carboethoxy-5-*exo*-methoxynortricyclene (**8**) and only 7% 3-*endo*-carboethoxy-5-*exo*-ethoxynortricyclene (**9a**) in a total yield of 86%. From this result, it was apparent that the methoxy group of **1** was not particularly labile under the reaction conditions. However, since it appeared that an oxymetallation reaction (**4** → **10**) had taken place under the conditions of the carbonylation reaction, it seemed likely that the diene complex **4** could be carbonylated directly under the same conditions as those employed for **1**. The carbonylation of **4** in methanol provided a 40% yield of **7a**; in a similar manner a 39% yield of **9a** was realized in ethanol. In another experiment it was found that **4** could be converted to **7a** in 56% yield in methanol which had been saturated with dry hydrogen chloride.[11]



4 **10** **9b** **1** **9a** **8**

Carbonylation of **4** in benzene gave a product resulting from an initial trans addition of Cl-Pd to the coordinated double bond. The acid chloride which was obtained was converted to the methyl ester, 3-*endo*-carbomethoxy-5-*exo*-chloronortricyclene (**9b**).[12]

Methoxy complex **2** was observed to behave quite differently than **1** during carbonylation in methanol. Carbonylation of **2** resulted in an 50% conversion to the diene complex **5**; appreciable amounts of metallic palladium were also formed and only minor amounts of organic products were recovered. Vpc analysis of the organic material showed it to consist of at least six components. Ir analysis of this mixture showed

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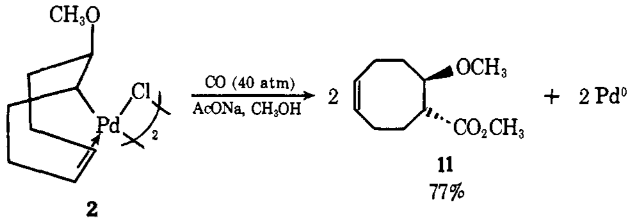
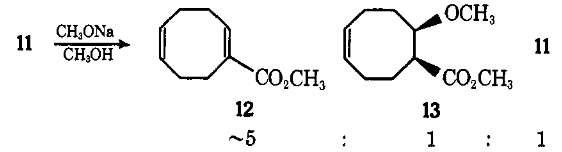
[10] D. R. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969), and references therein.

[11] The stereochemical assignments of **8**, **9a**, and **9b** are based on nmr chemical shift data as contained in Table I. The yields of esters from the various reactions discussed above merely reflect differences in reaction times. Unchanged complex accounted for most of the material balance in the individual experiments.

[12] J. Tsuji and S. Hosaka, *Polymer Lett.*, **3**, 703 (1965).

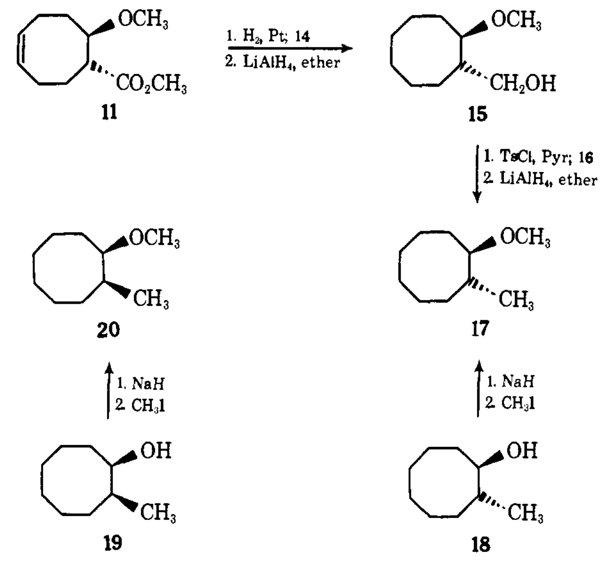
weak carbonyl absorption. The composition of this mixture was not investigated. The carbonylation of **2** in methanol was effected, however, by carrying out the reaction in the presence of sodium acetate. Under these conditions, **2** was converted to metallic palladium and a single organic product[13] *trans*-methyl 8-methoxy-4-cyclooctenecarboxylate, **11**, whose structure was assigned from the following evidence. Treatment of **11** with sodium methoxide in methanol gave three products, one of which had identical retention times to those of the starting material on various vpc columns. The remaining two components were purified by preparative vpc. Analytical and spectral data of these two components were consistent with the structures methyl 1,5-cyclooctadienecarboxylate **12** and *cis*-methyl 8-methoxy-4-cyclooctenecarboxylate (**13**). A comparison of the nmr spectra of **11** and **13** did not allow an evaluation to be made concerning their stereochemical assignments.



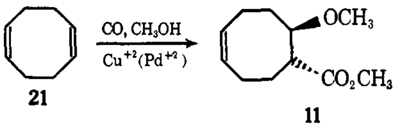


The carbonylation product, **11**, was converted to an ether by the reaction sequence shown in Scheme I. The structure of this material was assigned *trans*-1-methyl-2-methoxycyclooctane (**17**). Authentic *trans*- and *cis*-2-methylcyclooctanol, **18** and **19**, were prepared[14] and were converted to their corresponding methyl ethers **17** and **20**. The nmr spectra of these two isomers were easily distinguishable. The nmr spectrum of the methyl ester, **17**, derived from **11** was identical with that of the ether obtained from *trans*-2-methylcyclooctanol, **18**.

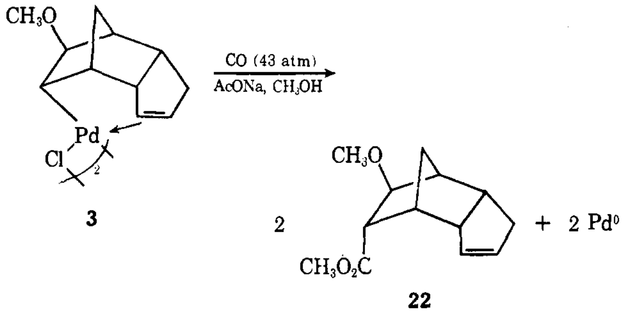
Scheme I



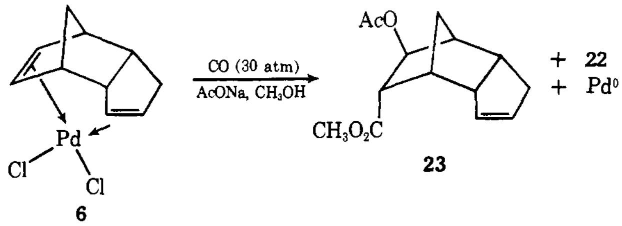
Conditions for the conversion of 1,5-cyclooctadiene, **21**, to the carbonylation product, **11**, by employing a catalytic amount of palladium chloride were investigated. In this process, cupric chloride was used to reoxidize the zerovalent palladium formed in the carbonylation reaction to palladium(II), thereby making the reaction catalytic with respect to palladium chloride. A mixture of 1,5-cyclooctadiene, **21**, palladium chloride, cupric chloride, lithium chloride, and sodium acetate in methanol at 100° was allowed to react with carbon monoxide to afford a 75% yield (based on cupric chloride) of **11**.[15] In this reaction 2.6 mmol of palladium gave 18.7 mmol of ester for a catalytic turnover of 7.2 times.



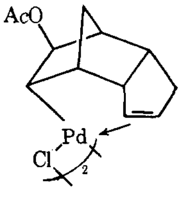
The carbonylation of the *endo*-dicyclopentadiene methoxy complex **3** in methanol in the presence of sodium acetate provided an 83% yield of the ester, **22**.[16]



Under similar conditions the diene complex **6** afforded a mixture of **22** (65%), the acetate derivative **23** (29%), and two minor components which were not identified.



Compound **23** probably results from the attack of acetate ion on **6**, to afford adduct **24**, in competition



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(13) Other workers have reported that the reaction of complex **2** with carbon monoxide in benzene solvent gave a mixture of the diene complex **5**, 1,5-cyclooctadiene, and methyl 8-methoxy-4-cyclooctenecarboxylate of undetermined stereochemistry.[3]

(14) A. C. Cope and G. L. Woo, *J. Amer. Chem. Soc.*, **85**, 3601 (1963).

(15) The synthetic scope and utility of this reaction with respect to other olefins are currently being investigated.

(16) The carbonylation of either **3** or **6** in methanol in the absence of sodium acetate afforded an ester product which has not been identified.

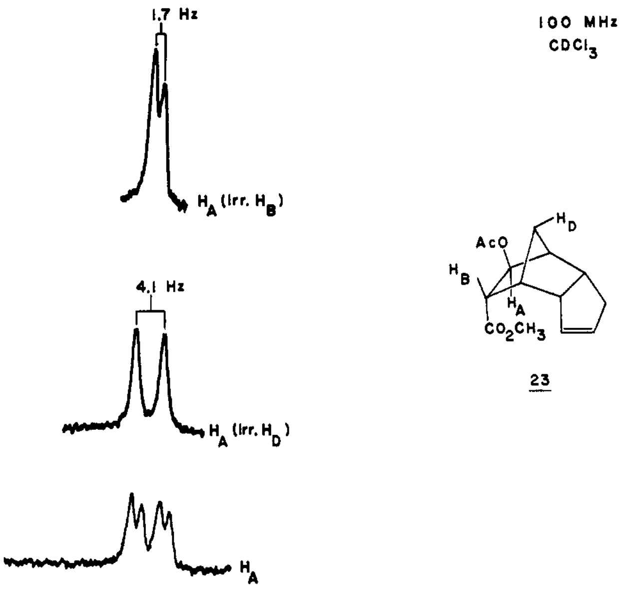


Figure 1.

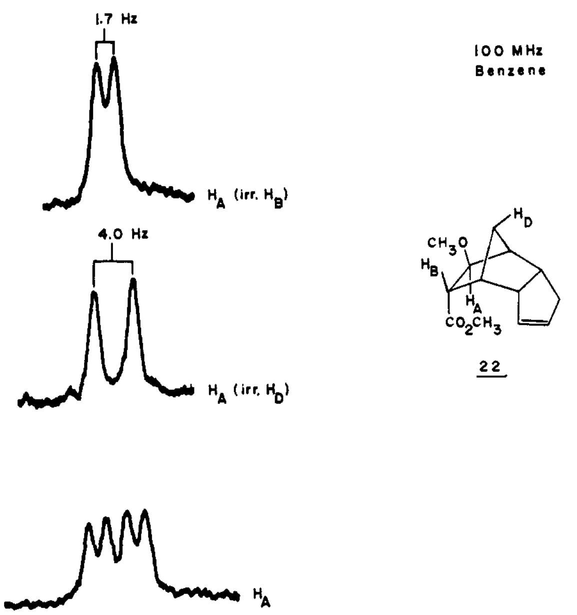


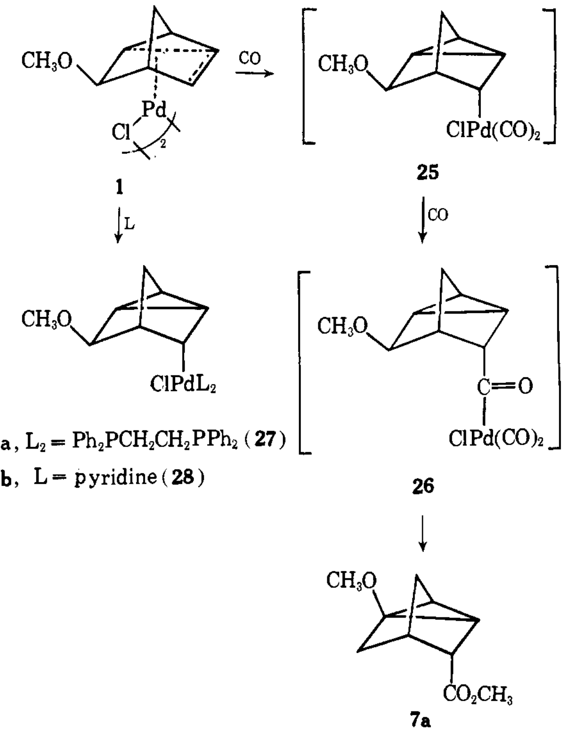
Figure 2.

with the formation of 3.[17] The stereochemical assignments of **22** and **23** are based on nmr coupling constant data obtained by double irradiation techniques. In the 100-MHz nmr spectrum of **23** a doublet of doublets centered at δ 5.10 was assigned to proton H_A (Figure 1) and a tentative assignment of a broadened doublet (J = ~4 Hz) centered at δ 2.63 was made for H_B. Two broadened doublets (J = 10 Hz) centered at δ 1.70 and 1.45 were assigned to the C-8 bridge protons. Irradiation of the resonance assigned to H_A removed the 4 Hz splitting in the resonance assigned to H_B and caused a noticeable loss of fine structure in the doublet centered at δ 1.45. Irradiation of the doublet at δ 1.45 converted the H_A signal into a doublet (J = 4.1 Hz). Irradiation of H_B also converted the H_A signal into a doublet (J = 1.7 Hz). The value of 4.1 Hz for J_{AB} is in agreement with trans endo–exo coupling constants observed for systems of similar structure.[18] The 1.7-Hz splitting of H_A is consistent with the commonly observed "W-letter" coupling between an endo proton (H_A) and the anti-8 proton, H_D, in systems of this type. Application of the same irradiation techniques on protons H_A, H_B, and H_D in the spectrum of **22** gave the coupling constants J_{AB} = 4.0 Hz and J_{AD} = 1.7 Hz (Figure 2).

Conclusion

In all of these carbonylation reactions, the ester products were obtained from breaking a carbon–palladium σ bond and replacement by the carbonyl function with retention at carbon. A stepwise mechanism for the carbonylation of **1**, assuming the occurrence of an alkyl–acyl rearrangement, is outlined in Scheme II. The first step involves attack on palladium by carbon monoxide to form intermediate **25**. Closure of **1** to the tricyclic structure **25** in this step is reasonable in light of the fact that other coordinating ligands effect this transformation. It has been shown that **1** reacts with bis(diphenylphosphino)ethane **27** or pyridine **28**, for example to afford **29a** and **29b**, respectively.[10,19] The intermediate **25** then undergoes an alkyl–acyl rearrangement to **26** which subsequently decomposes to the observed products: **7a**, palladium metal, and hydrogen chloride. Similar pathways involving an alkyl–acyl rearrangement may be used to account for the conversion of **2** and **3** to the esters **11** and **22**.

Scheme II



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[17] Reaction of dichloro(4-vinylcyclohexene)palladium(II) with sodium acetate in methanol gave exclusively acetate adduct: G. Paiaro, A. De Renzi, and R. Palumbo, *Chem. Commun.*, 1150 (1967).

[18] (a) J. Meinwald and Y. C. Meinwald, *J. Amer. Chem. Soc.*, **85**, 2514 (1963); (b) J. C. Davis and T. V. Van Auken, *ibid.*, **87**, 3900 (1965).

[19] E. Vedejs and M. F. Salomon, *J. Amer. Chem. Soc.*, **92**, 6965 (1970).

Experimental Section

Carbonylation of Di-μ-chloro-bis(6-methoxybicyclo[2.2.1]hept-2-ene-*endo*-5σ,2π)dipalladium(II) (1) in methanol. Formation of 3-*endo*-Carbomethoxy-5-*exo*-methoxynortricyclene (7a). A mixture of 5.4 g (10.2 mmol) of **1** and 150 ml of absolute methanol was placed in a 500-ml, glass-lined autoclave, which was pressurized with 45 atm of carbon monoxide and stirred at room temperature for 72 hr. After the reaction, the precipitated palladium was removed by gravity filtration and was washed with methanol. The combined methanol filtrates were concentrated and the remaining residue was extracted with pentane. The pentane was removed and 2.7 g (73%) of the product, 3-*endo*-carbomethoxy-5-*exo*-methoxynortricylene, **7a**, was obtained. Final purification of **7a** was achieved by short-path distillation: bp 60° (0.3 mm); ir (neat) 1745 (C=O), 1100 (CO), and 810 cm^{-} (nortricyclene ring system); nmr ($\mathrm{CDCl_3}$), δ 3.75 (s, 4, $\mathrm{CO_2C}H_3$ and $H\mathrm{COCH_3}$), 3.31 (s, 3, $\mathrm{OC}H_3$), 2.50 (m, 1, $H\mathrm{CCO_2CH_3}$), 2.30 (m, 1), 2.00 (br d, 1, J = 10 Hz), and 1.6–1.3 ppm (4); mass spectrum (70 eV) *m/e* 182 ($\mathrm{M^+}$).

Anal. Calcd for $\mathrm{C_{10}H_{14}O_3}$: C, 65.93; H, 7.69. Found: C, 66.23; H, 7.76.

Epimerization of 3-*endo*-Carbomethoxy-5-*exo*-methoxynortricyclene (7a) with Sodium Methoxide. A mixture of 2.7 g (15 mmol) of **7a** and 1.8 g (33 mmol) of sodium methoxide in 45 ml of dry methanol was stirred at the reflux temperature for 45 hr, after which time the reaction mixture was cooled and neutralized with dilute hydrochloric acid. The resulting solution was concentrated and extracted with methylene chloride, and the combined extracts were dried ($\mathrm{CaCl_2}$). Removal of the solvent afforded 1.6 g of liquid product. Vpc analysis using a 20 ft × 0.375 in. 15% SE-30/Chromsorb W column showed two components which were separated by preparative vpc employing the same column. The major component (62% of peak area) was identified as **7a**. The minor component (38% of peak area) was identified as 3-*exo*-carbomethoxy-5-*exo*-methoxynortricyclene (**7b**): nmr ($\mathrm{CDCl_3}$) δ 3.68 (s, 3, $\mathrm{CO_2C}H_3$), 3.43 (m, 1, $H\mathrm{COCH_3}$), 3.30 (s, 3, $\mathrm{OC}H_3$), 2.46 (m, 1, $H\mathrm{CCO_2CH_3}$ 2.37 (m, 1), 1.80 (br d, 1, J = 10 Hz), and 1.6–1.2 ppm (4).

Anal. Calcd for $\mathrm{C_{10}H_{14}O_3}$: C, 65.93; H, 7.69. Found: C, 65.72; H, 7.58.

Carbonylation of Dichloro(norbornadiene)palladium(II) (4) in Methanol.[9a] Formation of 3-*endo*-Carbomethoxy-5-*exo*-methoxynortricyclene (7a). A mixture of 6.09 g (22.6 mmol) of **4** and 150 ml of methanol was allowed to react with carbon monoxide (55 atm) in the usual manner for 48 hr at room temperature. Work-up provided 1.66 g (9.1 mmol, 40%) of **7a**. In a similar manner **4** was reacted with carbon monoxide (33 atm) in methanol saturated with dry hydrogen chloride for 125 hr at room temperature to afford a 56% yield of **7a**.

Carbonylation of Dichloro(norbornadiene)palladium(II) (4) in Ethanol. Formation of 3-*endo*-Carboethoxy-5-*exo*-ethoxynortricyclene (9a). A mixture of 6.0 g (22.3 mmol) of **4** and 150 ml of absolute ethanol was allowed to react with carbon monoxide (53 atm) for 72 hr at room temperature. Normal work-up afforded 1.8 g (8.6 mmol, 39%) of **9a**: bp 75° (0.6 mm); ir (neat) 1740 (C=O), 1100 (CO), and 810 cm^{-} (nortricyclene ring system); nmr ($\mathrm{CDCl_3}$) δ 4.15 (q, 2, J = 7 Hz, $\mathrm{CO_2C}H_2\mathrm{CH_3}$), 3.80 (m, 1, $H\mathrm{COC_2H_5}$), 3.48 (q, 2, J = 7 Hz, $\mathrm{OC}H_2\mathrm{CH_3}$), 2.48 (m, 1, $H\mathrm{C\text{-}CO_2C_2H_5}$), 2.27 (m, 1), 1.98 (br d, 1, J = 10 Hz), 1.28 (t, 3, J = 7 Hz, $\mathrm{CO_2CH_2C}H_3$), 1.19 (t, 3, J = 7 Hz, $\mathrm{OCH_2C}H_3$), and 1.5–1.2 ppm (4); mass spectrum (70 eV) *m/e* 210 ($\mathrm{M^+}$).

Anal. Calcd for $\mathrm{C_{12}H_{18}O_3}$: C, 68.57; H, 8.57. Found: C, 67.89; H, 8.49.

Carbonylation of Di-μ-chloro-bis(6-methoxybicyclo[2.2.1]hept-2-ene-*endo*-5σ,2π)dipalladium(II) (1) in Ethanol. Formation of 3-*endo*-Carboethoxy-5-*exo*-ethoxynortricyclene (9a) and 3-*endo*-Carbethoxy-5-*exo*-methoxytricyclene (8). A mixture of 5.0 g (9.4 mmol) of **1** and 125 ml of absolute ethanol was allowed to react with carbon monoxide (33 atm) for 43 hr at room temperature. After the usual work-up, 3.2 g (86%) of product was obtained. Vpc analysis showed the presence of two components. These two components were incompletely separated by preparative vpc using a 20 ft × 0.375 in. 15% SE-30 column. The minor component (7% of peak area) was identified as **9a**. The major component (93% of peak area) was identified as **8**: nmr ($\mathrm{CDCl_3}$) δ 4.16 (q, 2, J = 7 Hz, $\mathrm{CO_2C}H_2\mathrm{CH_3}$, 3.71 (m, 1, $H\mathrm{COCH_3}$), 3.31 (s, 3, $\mathrm{OC}H_3$), 2.48 (m, 1, $H\mathrm{CCO_2C_2H_5}$), 2.25 (m, 1), 1.95 (br d, 1, J = 10 Hz), 1.5–1.2 (4), and 1.27 ppm (t, 3, J = 7 Hz, $\mathrm{CO_2CH_2C}H_3$).

Carbonylation of Dichloro(norbornadiene)palladium(II) (4) in Benzene. A mixture of 5.0 g (18.5 mmol) of **4** and 135 ml of dry benzene was placed in a 500-ml, glass-lined autoclave. The autoclave was sealed and pressurized with 33 atm of carbon monoxide, and the contents of the autoclave were stirred at 90° for 83 hr. After the reaction, the solid residue was removed by gravity filtration. The filtrate was combined with 50 ml of methanol and the resulting mixture was heated at the reflux temperature for 1 hr. The solution was concentrated and the residue was extracted with pentane. After removal of the pentane by distillation 1.3 g of residual liquid was obtained. Vpc analysis using a 5 ft × 0.25 in. 3% SE-30/Chromsorb W column showed the presence of two components. The major component (>90%) was obtained pure by preparative vpc using a 20 ft × 0.375 in. 15% SE-30/Chromsorb W column. This material was identified as 3-*endo*-carbomethoxy-5-*exo*-chloronortricyclene (**9b**)[12] by nmr analysis. The 60-MHz nmr spectrum ($\mathrm{CDCl_3}$) was interpreted as follows: δ 4.23 (m, 1, $H\mathrm{CCl}$), 3.68 (s, 3, $\mathrm{CO_2C}H_3$), 2.58 (m, 1, $H\mathrm{CCO_2CH_3}$), 2.32 (m, 1), 2.18 (br d, 1, J = 10 Hz), 1.8–1.3 (4).

Carbonylation of Di-μ-chloro-bis(1-methoxycyclooct-4-ene-8σ,4π)-dipalladium(II) (2)[8,9] in Methanol in the Presence of Sodium Acetate. Formation of *trans*-Methyl 8-Methoxy-4-cyclooctenecarboxylate (11).[3b] A mixture of 7.6 g (13.5 mmol) of **2** and 3.33 g (40.6 mmol) of anhydrous sodium acetate in 150 ml of methanol was allowed to react with carbon monoxide (40 atm) at room temperature for 85 hr. The usual work-up provided 4.1 g (20.7 mmol, 77%) of **11**:[3b] nmr ($\mathrm{CDCl_3}$) δ 5.57 (m, 2, vinyl), 3.57 (s, 3 $\mathrm{CO_2C}H_3$), 3.5 (m, 1, $H\mathrm{COCH_3}$), 3.28 (s, 3, $\mathrm{OC}H_3$), 2.8 (m, 1, $H\mathrm{CCO_2CH_3}$), and 2.5–1.5 ppm (8); mass spectrum (70 eV) *m/e* 198 ($\mathrm{M^+}$).

When the sodium acetate was omitted from the reaction mixture an 50% conversion to dichloro(1,5-cyclooctadiene)palladium(II) **5** occurred accompanied by formation of some metallic palladium and a minor amount of organic product. Vpc analysis of the organic material showed the presence of at least six components. This material was not investigated.

Carbonylation of 1,5-Cyclooctadiene (21) in Methanol. Formation of *trans*-Methyl 8-Methoxy-4-cyclooctenecarboxylate (11). A mixture of 15 ml of **21**, 0.452 g (2.6 mmol) of palladium chloride, 6.73 g (50 mmol) of cupric chloride, 4.28 g (100 mmol) of lithium chloride, and 8.21 g (100 mmol) of sodium acetate in 150 ml of methanol was allowed to react with carbon monoxide (33 atm) for 42 hr at 100°. After the reaction, the solid residues were removed by gravity filtration and washed with methanol. The combined filtrates were concentrated by distillation at atmospheric pressure and the remaining residue was extracted with pentane. Removal of the pentane afforded 3.7 g (18.7 mmol, 75% based on cupric chloride) of **11**.

Reaction of *trans*-Methyl 8-Methoxy-4-cyclooctenecarboxylate (11) with Sodium Methoxide. A mixture of 1.0 g (5.1 mmol) of **11** and 0.7 g (13 mmol) of sodium methoxide in 45 ml of methanol was heated at the reflux temperature for 48 hr. After the reaction, the mixture was concentrated by distillation at atmospheric pressure and the residue was neutralized with dilute hydrochloric acid. The resulting solution was extracted with methylene chloride and the combined extracts were dried ($\mathrm{MgSO_4}$). The methylene chloride was removed by distillation to afford 0.8 g of liquid product. Vpc analysis showed the presence of three components having relative peak areas of 70%, 15%, and 15% in order of increasing retention time. The three components were separated with difficulty by preparative vpc using a 20 ft 15% SE-30 column. One of the minor components was identified as the starting material, **11**, while the other minor component was identified as the epimeric *cis*-methyl 8-methoxycyclooctanecarboxylate, **13**: ir (neat) 1740 (C=O) and 1100 cm^{-} (CO); nmr ($\mathrm{CDCl_3}$) δ 5.65 (m, 2, vinyl), 3.9 (m, 1, $H\mathrm{COCH_3}$), 3.67 (s, 3, $\mathrm{CO_2C}H_3$), 3.37 (s, 3, $\mathrm{OC}H_3$), and 3.01–1.5 ppm (9); mass spectrum (70 eV) *m/e* 198 (M+).

Anal. Calcd for $\mathrm{C_{11}H_{18}O_3}$: C, 66.39; H, 9.03. Found: C, 66.20; H, 9.26.

The major component was identified as **12**: nmr ($\mathrm{CDCl_3}$), δ 7.06 (m, 1, $H\mathrm{C{=}CCO_2CH_3}$), 5.60 (m, 2, vinyl), 3.76 (s, 3, $\mathrm{CO_2C}H_3$), 2.82 (m, 2), and 2.7–2.3 ppm (6).

Anal. Calcd for $\mathrm{C_{10}H_{14}O_2}$: C, 72.29: H, 8.43. Found: C, 71.98; H, 8.10.

Hydrogenation of *trans*-Methyl 8-Methoxy-4-cyclooctenecarboxylate (11). Formation of *trans*-Methyl 2-Methoxycyclooctanecarboxylate (14). A mixture of 1.75 g (8.8 mmol) of **11** and 0.1 g of platinum oxide in 80 ml of dry ether was shaken in a Paar hydrogenation apparatus at 3 atm until hydrogen absorption ceased. Work-up provided 1.53 g (7.7 mmol, 87%) of the product **14**: bp 84° (2 mm); nmr ($\mathrm{CDCl_3}$), δ 3.7 (m, 1, $H\mathrm{COCH_3}$), 3.69 (s, 3,

CO_2CH_3), 3.28 (s, 3, OCH_3), 2.6 (m, 1, $HCCO_2CH_3$), and 2.1–1.2 ppm (12).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 66.00; H, 10.00. Found: C, 66.31; H, 9.69.

Reduction of *trans*-Methyl 2-Methoxycyclooctanecarboxylate (14) with Lithium Aluminum Hydride. Formation of *trans*-2-Methoxycyclooctanemethanol (15). A solution of 1.53 g (7.65 mmol) of **14** in 15 ml of dry ether was added dropwise to a suspension of 0.40 g (10.5 mmol) of lithium aluminum hydride and 15 ml of dry ether. The resulting mixture was stirred at room temperature for 24 hr. After the reaction, 0.5 ml of water was added followed by 0.5 ml of 15% sodium hydroxide and 1.5 ml of water. The precipitated salts were removed by gravity filtration and washed with ether. The ether filtrates were then combined and dried ($MgSO_4$). Removal of the ether by distillation at atmospheric pressure afforded 1.23 g (7.15 mmol, 93%) of **15**: bp 83° (1.5 mm); ir (neat) 3600 (OH) and 1100 cm^{-}(CO); nmr ($CDCl_3$) δ 3.6 (m, 2, CH_2OH), 3.3 (m, 2, OH and $HCOCH_3$), 3.32 (s, 3, OCH_3), and 2.1–1.2 ppm (13).

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.77; H, 11.63. Found: C, 69.87; H, 11.63.

Conversion of *trans*-2-Methoxycyclooctanemethanol (15) to *trans*-1-Methyl-2-methoxycyclooctane (17). A solution of 1.76 g (10.2 mmol) of **15** in 25 ml of dry pyridine was cooled to 0° and treated with 3.0 g (15 mmol) of *p*-toluenesulfonyl chloride. The reaction mixture was allowed to stand for 48 hr at 0° at the end of which time 0.5 ml of water was added to the cold mixture. The reaction mixture was then poured onto 100 g of ice water and the resulting solution was extracted with methylene chloride. The combined extracts were washed with dilute hydrochloric acid and dried ($MgSO_4$). Removal of the methylene chloride under diminished pressure afforded 2.10 g (6.4 mmol, 63%) of the tosylate **16**: nmr ($CDCl_3$) δ 7.78, 7.32 (m, 4, aromatic), 4.09 (d, 2, J = 5 Hz, CH_2OTS), 3.13 (s, 3, OCH_3), 3.1 (m, 1, $HCOCH_3$), 2.43 (s, 3, CH_3), and 2.1–1.2 ppm (13).

A solution of 2.10 g (6.4 mmol) of the tosylate in 20 ml of dry ether was added dropwise to a suspension of 0.76 g (19 mmol) of lithium aluminum hydride in 15 ml of dry ether. The resulting mixture was heated at the reflux temperature for 72 hr. After the reaction, the mixture was cooled to room temperature and 1 ml of water was added followed by the addition of 1 ml of 15% sodium hydroxide and 3 ml of water. The precipitated salts were removed by gravity filtration and washed with ether, and the combined ether filtrates were dried ($MgSO_4$). The ether was removed by distillation and the remaining liquid distilled under diminished pressure using a short-path system to afford 0.3 g (1.9 mmol, 30%) of **17**: bp 70° (16 mm); ir (neat) ~1100 m (CO); nmr ($CDCl_3$) δ 3.29 (s, 3, OCH_3), 2.85 (m, 1, $HCOCH_3$), 1.9–1.1 (13), and 1.01 ppm (d, 3, J = 6.3 Hz, CH_3); mass spectrum (70 eV) m/e 156 (M^+). This sample of **17** was identical with an authentic sample prepared as described below.

Anal. Calcd for $C_{10}H_{20}O$: C, 76.92; H, 12.82. Found: C, 76.60; H, 12.87.

Preparation of *trans*-1-Methyl-2-methoxycyclooctane (17). A solution of 1.5 g (10.6 mmol) of **18**[14] in 10 ml of dry ether was added dropwise to a suspension of 1.0 g (42 mmol) of sodium hydride (from 50% dispersion in oil; prewashed with benzene) in 30 ml of dry ether and the mixture was heated at the reflux temperature for 3 hr. The reaction mixture was cooled to room temperature and was treated with 4 g (29.1 mmol) of methyl iodide in 10 ml of dimethyl sulfoxide. The resulting mixture was heated at the reflux temperature for 8 hr. After the reaction, 25 ml of water was added dropwise to the cooled mixture followed by 15 ml of pentane. The organic layer was separated and was washed with five 20-ml portions of water and one 20-ml portion of saturated sodium chloride solution and was dried ($MgSO_4$). The reaction solvents were removed by distillation to provide 1.0 g of liquid product. Vpc analysis indicated the presence of a single major component contaminated by a minor amount of impurities. The major component was purified by preparative vpc using a 20 ft × 0.375 in. 15% SE-30 column. The purified material gave only a single peak upon vpc analysis using a number of different columns. The nmr spectrum of the product was identical with **17** but also showed absorptions which could be attributed to ~10% of **20** as impurity.

Preparation of *cis*-1-Methyl-2-methoxycyclooctane (20). A mixture of 1.0 g (7.1 mmol) of **19**,[14] 0.65 g (27.0 mmol) of sodium hydride in 20 ml of dry ether, and 3 g (21.1 mmol) of methyl iodide was allowed to react in the same manner as described above. Work-up provided 0.8 g of crude product which was purified by preparative vpc. The product purified in this manner showed a single peak upon vpc analysis using a number of columns. Nmr analysis, however, showed the presence of ~5% **17** as impurity. The product was identified as **20**: nmr ($CDCl_3$), δ 3.30 (s, 3, OCH_3), 3.3 (m, 1, $HCOCH_3$), 2.1–1.2 (13), and 0.91 ppm (d, 3, J = 7.7 Hz, CH_3).

Anal. Calcd for $C_{10}H_{20}O$: C, 76.92; H, 12.82. Found: C, 77.06; H, 12.41.

Carbonylation of Di-μ-chloro-bis(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) (3)[9a] in Methanol in the Presence of Sodium Acetate. Formation of *endo*-5-Carbomethoxy-*exo*-6-methoxy-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-4,7-methanoindene (22). A mixture of 2.0 g (3.3 mmol) of **3** and 0.82 g (10.1 mmol) of anhydrous sodium acetate in 125 ml of methanol was allowed to react with carbon monoxide (43 atm) for 72 hr at room temperature. After the reaction, the precipitated palladium was removed by gravity filtration and was washed with methanol. The methanol filtrates were concentrated under diminished pressure and the residue was extracted with pentane. The pentane extracts were combined and the solvent was removed by distillation to provide 1.2 g (5.5 mmol, 83%) of **22**. Final purification of **22** was effected by short-path distillation under diminished pressure: bp 100–101° (1.2 mm); ir 1740 (C=O) and ~1100 cm (CO); nmr ($CDCl_3$) δ 5.47 (m, 2, vinyl), 3.65 (m, 1, $HCOCH_3$), 3.63 (s, 3, CO_2CH_3), 3.30 (s, 3, OCH_3), 3.1–2.1 (7), 1.71 (br d, 1, J = 10 Hz), and 1.38 ppm (br d, 1, J = 10 Hz); mass spectrum (70 eV) m/e 222 (M^+).

Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.27; H, 8.11. Found: C, 70.42; H, 8.19.

Carbonylation of Dichloro(*endo*-dicyclopentadiene)palladium(II)[9a] (6) in Methanol in the Presence of Sodium Acetate. Formation of 22 and *endo*-5-Carbomethoxy-*exo*-6-acetoxy-3a,4,5,6,7,7a-hexahydro-*endo*-4,7-methanoindene (23). A mixture of 2.2 g (7.1 mmol) of **6** and 2.35 g (29.0 mmol) of anhydrous sodium acetate in 75 ml of methanol was stirred at room temperature for 30 min. The mixture was then allowed to react with carbon monoxide (36 atm) for 72 hr at room temperature. The usual work-up provided 1.0 g of product. Vpc analysis showed the presence of four components. The peak areas, in order of increasing retention time on an SE-30 column, were 3.0%, 65.3%, 28.5%, and 3.2%. The two major components were separated by preparative vpc using the 20 ft × 0.375 in. 15% SE-30/Chromosorb W column. The 65.3% component was identified as **22** by nmr analysis. The 28.5% component was identified as **23**; mp 72–73°; nmr δ 5.50 (m, 2, vinyl), 5.10 (m, 1, $HCOAc$), 3.63 (s, 3, CO_2CH_3), 3.3–2.2 (7), 2.00 (s, 3, OAc), 1.70 (br d, 1, J = 10 Hz, and 1.45 ppm (br d, 1, J = 10 Hz); mass spectrum (70 eV) m/e 250 (M^+), 190 (M^+ − HOAc).

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.20; H, 7.20. Found: C, 66.65; H, 7.19.

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