stancy of i_d^{total} suggests that D for the two discharging species is very similar, and since Vreugdenhil[6f] reports $MgBr_2$ to be almost completely monomeric in ether at such low concentrations, the form of the Schlenk equilibrium used for the calculations seems warranted. Calculations of K from the above data using i_d values and $MgBr_2$ working curves gives for R: i-C_3H_7, 3.3 ± 0.3; C_6H_5, 6.1 ± 0.3; C_2H_5, 2.2 ± 0.3. It is the authors' opinion that the figures are more precise than accurate. Problems posed by accurate measurements of diffusion currents in systems where drop characteristics are affected greatly by small amounts of surface active agents, where the rates of k_f and k_r are only bracketed and may vary from R to R′, and where the effects of the inhomogeneous potential field near the drop surface are unknown, make it seem wise to conclude that the method merely indicates that in highly polar, basic media simple Grignard reagents exhibit an equilibrium with approximately a statistical distribution of groups about Mg. It is unfortunate that an extrapolation of this method to solutions lacking a supporting electrolyte are, of course, impossible. It would provide the long-needed physical probe. However, the unsurprising conclusion from a comparison of the data of Mosher,[6c] Ashby,[6a] and Smith and Becker[6e] with the present data is that K is very solvent dependent.

A comparison of the present work with Evans' data indicates that the only major conflict is on the nature of the process at the cathode where he suggested $2MgX^+ \rightarrow 2MgX \rightarrow MgX_2 + Mg$. The loss of alkyl moiety in the experiments described by eq 10a and b precludes this.[5] It seems highly likely that actually his conditions (two-electrode cell, several hundred volts potential) led to $RMg + e \rightarrow R{:}^- + Mg$ processes, which could be followed by alkylation, $R{:}^- + RMgX \rightarrow R_2Mg + X{:}^-$. A comparison of the potentials for the RHgX, RMgX series seems to support such a concept which places the reduction of the postulated RMg to $R{:}^-$ beyond −3.7 v,[2] the limit set by the present supporting electrolyte, which was, of course, absent in Evans' work.

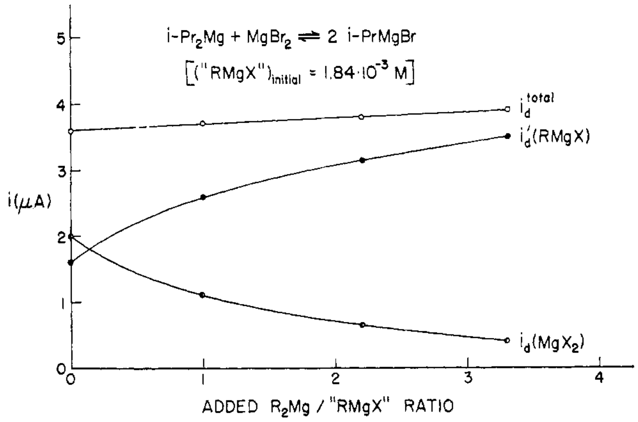

Figure 1.

Acknowledgments. The authors wish to thank the National Science Foundation for its support in the form of Grant GP 1984. R. E. D. wishes to thank the A. P. Sloan Foundation for its encouragement and support during the time when the equipment for this work was being constructed.

Oxyplatination and Oxypalladation Reactions of Diolefins[1]

John K. Stille and Richard A. Morgan[2]

Contribution from the Department of Chemistry, University of Iowa,
Iowa City, Iowa 52240. *Received May 19, 1966*

Abstract: The structures of the methoxy platinum(II) and palladium(II) complexes formed from the reaction of the corresponding diolefin complexes with methanol and base have been determined. Oxyplatination of *endo*-dicyclopentadiene, dipentene, 1,5-cyclooctadiene, and norbornadiene and oxypalladation of *endo*-dicyclopentadiene and norbornadiene were investigated. Structural assignment was made by reduction of the complexes to known or independently synthesized ethers and by nmr studies on the complexes. Several reactions of the methoxy complexes were studied.

Some unusual complexes of platinum(II) and palladium(II) have been reported from the reaction of alcohols with the corresponding diolefin complex.[3] The products were assigned the general dimeric structure involving chloride bridges and both a metal–carbon σ bond and a π-coordinate bond from the remaining olefin ligand to the metal.[3] Alkyl platinum(II) and palladium(II) complexes are generally stable only when some other ligand is present which affords large crystal field splitting.[4] The olefins which form these products have the geometry necessary to accomplish this stabilization.

The first preparation of this type of complex was realized from the reaction of dicyclopentadiene with potassium chloroplatinite in aqueous alcohol,[5] al-

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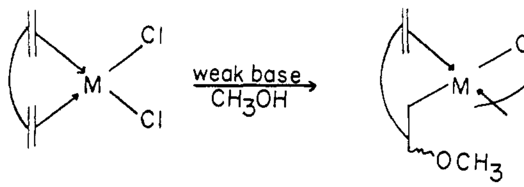
[1] A portion of this work appears in a preliminary communication: J. K. Stille, R. A. Morgan, D. D. Whitehurst, and J. R. Doyle, *J. Am. Chem. Soc.*, **87**, 3282 (1965).

[2] Abstracted in part from the Ph.D. thesis of R. A. Morgan, University of Iowa, Iowa City, Iowa, June 1966.

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

[4] (a) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959); (b) G. Calvin and G. E. Coates, *ibid.*, 2008 (1960); (c) J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *J. Am. Chem. Soc.*, **83**, 2768 (1961); (d) C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, **2**, 1255 (1963).

[5] K. A. Hoffman and J. V. Narbutt, *Ber.*, **41**, 1625 (1908).

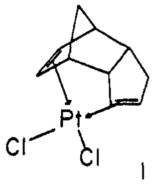


though an incorrect structure was assigned. The preferred method of preparation is the reaction of the diolefin complex with alcohol in the presence of a weak base. In this way the methoxy platinum(II) complexes derived from dicyclopentadiene, 1,5-cyclooctadiene, and dipentene have been prepared;[3a] the analogous methoxy palladium(II) complexes derived from dicyclopentadiene and 1,5-cyclooctadiene have been reported.[3b]

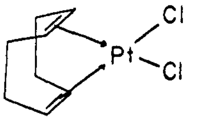
Although the type of metal-ligand linkage has been described,[1] the stereoisomerism associated with the organic moiety has not been established and little information on the details of the reaction is available. A variety of structures are possible. Some of the many structural problems present in the complexes derived from dicyclopentadiene have been recognized, although not investigated.[6] The many structures possible for the complexes derived from dicyclopentadiene made them appear the most desirable for our investigation. In addition, these complexes appeared to have the least tendency to decompose in solution and were the most easily obtained.

Results and Discussion

The platinum(II)-diolefin complexes of *endo*-dicyclopentadiene (**1**),[3a] 1,5-cyclooctadiene (**2**),[3a] dipentene (**3**),[7] and norbornadiene (**4**)[8,9] and the palladium(II)-diolefin complexes of *endo*-dicyclopentadiene (**5**)[3b] and norbornadiene (**6**)[8,9] are well known and characterized. Crystal structure determinations have been made on dichloro(dipentene)platinum(II) (**3**),[10] dichloro(*endo*-dicyclopentadiene)platinum(II) (**1**),[11] and dichloro(norbornadiene)palladium(II) (**6**).[11]



1



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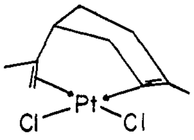

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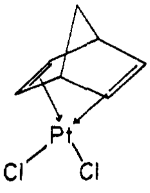

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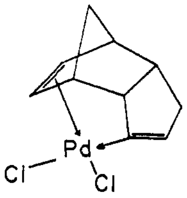

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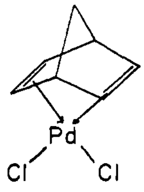


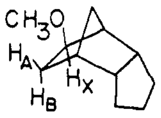
6

The methoxylations of the diolefin complexes were carried out using the published procedures.[3a,b]

Methoxy(*endo*-dicyclopentadiene)platinum(II) and -palladium(II) Complexes. The two unequivalent double bonds in dicyclopentadiene present two different sites for the methoxy metalation. Moreover, the addition may occur *cis*, with the addends either *endo* or *exo*, or the reaction may proceed by a *trans* addition with the metal either *exo* or *endo*. The relation of the remaining double bond to the addends (*i.e.*, whether the remaining double bond is positioned closer to the metal or methoxy addend) doubles the number of possible isomers. Finally, rearrangement often occurs in ionic additions to *endo*-dicyclopentadiene to provide products containing the *exo*-dicyclopentadiene skeleton.[12] The 5,6 double bond (norbornene double bond) is known to be much more reactive than the 2,3 double bond with respect to ionic additions.

This addition is somewhat analogous to the oxymercuration reaction of dicyclopentadiene in which *cis–exo* addition takes place at the 5,6 double bond without rearrangement.[13] Complexation with an *exo*-platinum or -palladium, however, would not be expected since intramolecular coordination with the remaining double bond would be impossible.

The fact that oxymetalation of the double bond does take place was established by the reduction of the methoxy complex of either platinum(II) or palladium(II) with hydrogen or sodium borohydride to give a methyl ether. The ether was identified as octahydro-*exo*-5-methoxy-4,7-*endo*-methanoindene (**7**) by comparison with an authentic sample.[13b] The nmr spectrum of this compound (**7**) shows a very characteristic pair of quartets (J = 6.8, 2.6, 1.35 cps) for the H_X proton (the proton on the methoxyl-bearing carbon).



7

The identification of **7** established the position and *exo* arrangement of the methoxyl group in the complex. No rearrangement of the carbon skeleton had taken place. These results provide no information, however, as to the direction of the carbon-metal bond, *exo* or *endo*.

The complexes were of poor solubility in suitable solvents and good nmr spectra could not be obtained. The palladium(II) complex was of greater solubility and it was possible to pick out the H_X doublet (J = 2 cps; width at half-height, 3.5 cps). The H_X peak in the spectrum of the platinum(II) complex could only be resolved to a singlet (width at half-height, 3.5 cps). The spectrum of H_X is as expected for being split only by a proton at a 120° angle[14] and is consistent with the coupling, J_{AX}, exhibited by the saturated ether **7**. The coupling constant J_{BX} for **7** is 6.8 cps.[13b] Therefore, the metal-carbon bond must be directed *endo* and the structures of the methoxy dicyclopentadiene complexes must be **8**[15] and **9**.

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(6) R. B. King, *Inorg. Chem.*, **2**, 528 (1963).

(7) J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 2622 (1952).

(8) E. W. Abel, M. A. Bennett, and G. Wilkinson, *ibid.*, 3178 (1959).

(9) R. J. Alexander, N. C. Baenziger, C. Carpenter, and J. R. Doyle, *J. Am. Chem. Soc.*, **82**, 535 (1960).

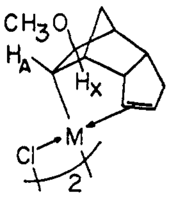
(10) N. C. Baenziger, R. C. Medrud, and J. R. Doyle, *Acta Cryst.*, **18**, 237 (1965).

(11) N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961.

(12) See, for example, S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963), and references therein.

(13) (a) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, **85**, 2746 (1963); (b) J. K. Stille and S. C. Stinson, *Tetrahedron*, **20**, 1387 (1964).

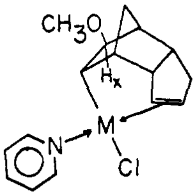
(14) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).



8 M = Pt
9 M = Pd

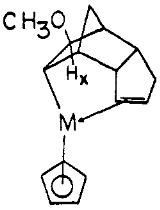
The position of the remaining double bond in relation to the methoxy or metal point of attachment could not be determined by this sequence, but models show a double bond on the metal side of the molecule affords the best angle and distance for efficacious coordination. The complexes, **8** and **9**, have, therefore, been pictured as such.

Reaction of the complexes **8** and **9** with pyridine provided respectively, **10** and **11**, whose structures were assigned by analogy to the reaction of these complexes with *p*-toluidine.[3] Chloro-bridged dimers such as **8** or **9** are readily split by amines, without alteration of the remainder of the complex, to give derivatives of this type.[3] The pyridine derivatives, **10** and **11**, were more soluble than the original dimers, **8** and **9**, and clearer nmr spectra were obtained for these complexes. The spectra showed H_X as a doublet (J = 2 cps, width at half-height, 3.5 cps) in both **10** and **11**.



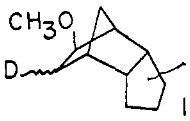
10 M = Pt
11 M = Pd

Reaction of the dimer, **8** or **9**, with thallium cyclopentadienide gave, respectively, **12** and **13**. The palladium(II) complex **13** has been reported from the reaction of **9** with sodium cyclopentadienide,[6] but few other examples of platinum(II)[16] and palladium(II)[17] cyclopentadienyls have been described. The nmr spectra of these derivatives were very similar to those of the amino derivatives. The H_X proton again appeared as a doublet (J = 2 cps).



12 M = Pt
13 M = Pd

The reaction of **8** or **9** with deuterium replaced the carbon–metal bond nonstereospecifically to give **14** as indicated by its nmr spectrum. However, when the reduction was carried out with sodium borodeuteride, the saturated stereospecifically deuterated methyl ether **15** was obtained. The *endo* configuration of the deuterium was established by the H_X doublet, J_{AX} = 2.6 cps.



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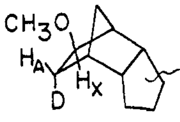
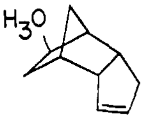


15

Sodium borohydride or deuteride alone would not be expected to reduce the double bond in the complexes. The double bond is probably reduced by the platinum or palladium hydrides formed *in situ*. It has been reported that reduction of noble metal salts with sodium borohydride gives a highly active catalyst for hydrogenation of olefins.[18] Reduction of **9** with half the required amount of sodium borohydride gave the unsaturated methyl ether **16**[13b] and **17**[19] and **18**[19] in addition to **7**. A possible explanation for the formation of **17** and **18** is that the hydrogen chloride which is liberated during the reduction will deoxymetalate other molecules of the complex to give *endo*-dicyclopentadiene which is then hydrogenated to **17** and **18**.



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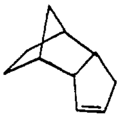

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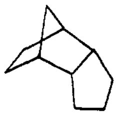
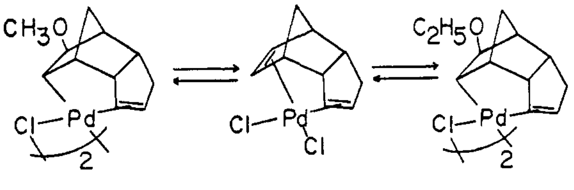
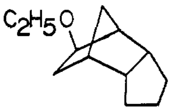


18

Although our work shows that the corresponding platinum(II) and palladium(II) complexes have the same formal structure, the chemistry of the two complexes is somewhat different. The treatment of the palladium(II) complex **9** with concentrated hydrochloric acid readily converts it into the diene complex **5** at room temperature in 15 min,[3b] and the analogous reaction of the platinum complex **8** to give **1** occurs only on boiling the methoxy complex in concentrated hydrochloric acid for 3–4 hr.[3a] We found that there was enough acid in commercial chloroform to cause this reverse reaction for the palladium complex. Treatment of the methoxy complex **9** in chloroform with an excess of ethanol gave quantitative conversion to the corresponding ethoxy complex **19**. Evidently, the trace of acid acts to set up an equilibrium in which the excess of ethanol favors the ethoxy complex. The same ethoxy complex **19** was prepared directly from the diolefin complex **5**. Hydrogenation of the complex prepared by either method gave the same ethyl ether **20**. The ethoxy group was assigned an *exo* configuration by analogy with the corresponding methyl ether **7**.



9 5 19



20

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(15) After this paper was submitted for publication, W. A. Whitla, H. M. Powell, and L. M. Venanzi, *Chem. Commun.*, 310 (1966), confirmed this structure, which we had reported earlier.[1]

(16) (a) B. L. Shaw and N. Sheppard, *Chem. Ind.* (London), 517 (1961); (b) H. P. Fritz and C. G. Kreiter, *Ber.*, **96**, 2008 (1963).

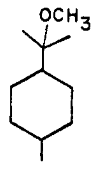
(17) (a) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); (b) *ibid.*, 5002 (1964); (c) B. L. Shaw, *Proc. Chem. Soc.*, 247 (1960).

(18) H. C. Brown and C. A. Brown, *J. Am. Chem. Soc.*, **84**, 1493, 1494, 1495 (1962).

(19) R. W. Alder and M. C. Whiting, *J. Chem. Soc.*, 4595 (1963).

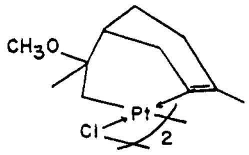
Methoxy(dipentene)platinum(II) Complex. Dipentene also has two nonequivalent double bonds presenting two different sites for the methoxy metalation. While there is still a possibility of *cis* or *trans* addition, the *endo* and *exo* relationships present in the additions to dicyclopentadiene are meaningless in this case.

When the hydrogenation was carried out, a 55:45 ratio of two methyl ethers which were separated by preparative gas–liquid partition chromatography was obtained. The nmr spectrum of each indicated that they were *cis–trans* isomers. Both isomers showed singlets in their nmr spectra for the methoxyl peak at τ 6.92 but no other peaks downfield. An authentic sample of 8-methoxy-*p*-menthane (**21**) was prepared by the acid-catalyzed addition of methanol to dipentene[20,21] followed by hydrogenation. Comparison of physical constants and nmr and infrared spectra of the authentic **21** with the complex hydrogenation product indicated they were the same. Thus the methoxy platination occurred at the 8,9 double bond.



21

The nmr spectrum of the complex could not be obtained, perhaps because of the instability of the complex in solution. This was the least stable of all the methoxy platinum complexes prepared. However, the question of *cis* or *trans* addition could not have been answered by the nmr spectrum. The complex, di-μ-chlorobis(8-methoxy-*p*-menth-1-ene-9σ,2π)diplatinum(II) (**22**), probably has *trans*-related methoxyl and metal functions by analogy to the methoxy(dicyclopentadiene) complexes **8** and **9**.

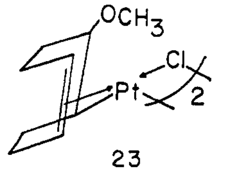


22

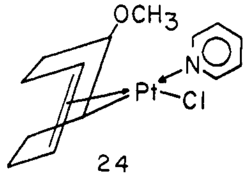
Methoxy(1,5-cyclooctadiene)platinum(II) Complex. The two double bonds of 1,5-cyclooctadiene are equivalent and, unless a transannular rearrangement[22] occurs in the methoxy platination, the number of possible structures is limited.

Hydrogenation of the methoxy(1,5-cyclooctadiene)platinum(II) complex gave methyl cyclooctyl ether as identified by comparison with a sample prepared from the reaction of methyl iodide with sodium cyclooctoxide.

It was hoped that the nmr spectrum of the methoxy complex would afford some information on the structure, but the complex was too insoluble to obtain an nmr spectrum directly. Reaction of the methoxy complex with pyridine and thallium cyclopentadienide again gave the respective derivatives, **24** and **25**, which were soluble enough to obtain nmr spectra. Unfortunately, there was a great deal of peak overlap, and assignments, other than for the methoxyl and cyclopentadienyl protons, were of dubious value. By analogy to the methoxy dicyclopentadiene complexes **8** and **9**, complex **23** probably has *trans*-related methoxyl and metal functions.



23



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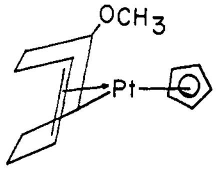
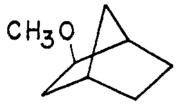


25

The corresponding methoxy(1,5-cyclooctadiene)palladium(II) complex was not investigated. The nmr spectrum of this complex has been reported.[23]

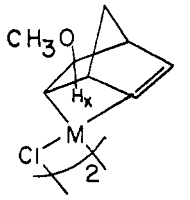
Methoxy(norbornadiene)platinum(II) and -palladium(II) Complexes. The series of diolefin–platinum(II) and –palladium(II) complexes known to undergo methoxy metalation was extended to **4** and **6**.

The hydrogenation of either the platinum(II) or palladium(II) methoxy complex gave *exo*-2-methoxynorbornane (**26**) as established by comparison with an independently synthesized sample from the acid-catalyzed addition of methanol to norbornene. The acid-catalyzed addition of methanol to norbornene has been reported to afford the *exo*-methoxy compound **26**.[24] The identification of **26** elucidated the stereochemistry of the methoxyl group in the complex and established that no rearrangement had taken place. The acid-catalyzed addition of methanol to norbornadiene leads to 67% of the rearranged tricyclene and 33% of the unrearranged product, *exo*-5-methoxy-2-norbornene.[25]



26

The nmr spectrum of both the methoxy complexes showed a doublet (J = 2.5 cps) which may be assigned to the single proton (H_X) on the methoxyl-bearing carbon. This coupling constant correlates with the calculated value[14] (2.2 cps) between H_X and a proton at a 120° angle. This indicates that the metal–carbon bond is directed *trans* to the methoxyl group and the assigned structures are **27** and **28**.



27 M = Pt
28 M = Pd

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[20] E. E. Royals, *J. Am. Chem. Soc.*, **71**, 2568 (1949).

[21] K. Suga and S. Watanabe, *Nippon Kagaku Zasshi*, **81**, 1139 (1960); *Chem. Abstr.*, **56**, 507*b* (1962).

[22] R. Dowbenko, *J. Am. Chem. Soc.*, **86**, 946 (1964), and references therein.

[23] S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 5002 (1964).

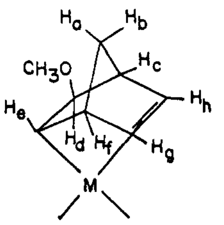
[24] T. G. Traylor, *Tetrahedron Letters*, No. **19**, 14 (1959).

[25] S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, *J. Am. Chem. Soc.*, **84**, 3918 (1962).

Theoretically,[4] these complexes should have poor stability due to the fact that, according to models, the remaining double bond cannot be perfectly perpendicularly coordinated. On standing at room temperature the compounds slowly darkened.

Nuclear Magnetic Resonance Spectra of Methoxy Complexes. The nmr spectra of the platinum(II) cyclopentadienyl complexes **12** and **25** gave a triplet (17:66:17) for the cyclopentadienyl protons indicating they were coupled to the magnetically active ^{195}Pt isotope (33.7% abundant).[16] Integration of the nmr spectra obtained of the platinum(II) complexes indicated that the olefinic protons were also coupled to ^{195}Pt but the satellites of the major peaks could not be resolved. Olefin–^{195}Pt coupling has been reported in other olefin complexes.[4d,26] The hydrogens on the carbons σ bonded to platinum, which also should be split by ^{195}Pt,[4d] could not be distinguished in any of the spectra.

The vinyl proton peaks in the nmr spectra of the methoxy norbornadiene complexes appear as a triplet (1:2:1) and a sextet (1:1:2:2:1:1). Since there are not two equivalent protons in one organic moiety of the complex, the appearance of a triplet must be due to overlap of two separate couplings.



H_h may be coupled to both H_g and either H_c or H_a ($J_{H_h} + J_{H_c}$ (or J_{H_a}) = 8 cps). This would give rise to the observed triplet. The other vinyl proton appears as a triplet split again by 1.8 cps. This additional coupling may be due to long-range coupling of H_e with H_g. The observed coupling constants are larger than those usually observed[27] but this may be due to the additional strain in the molecule due to the metal atom. Table I gives pertinent data for all nmr spectra.

Structure and Mechanism. It appears that the general mechanism for this reaction is the attack of methanol assisted by base on the coordinated olefin. In the reactions of *endo*-dicyclopentadiene and norbornadiene, it was possible to show that this attack occurred *trans* to the metal. The mechanism is very similar to that proposed for the oxymercuration reaction.[28] The elimination of chloride ion, the attachment of the methoxyl group, and the formation of the metal–carbon bond possibly occur simultaneously.

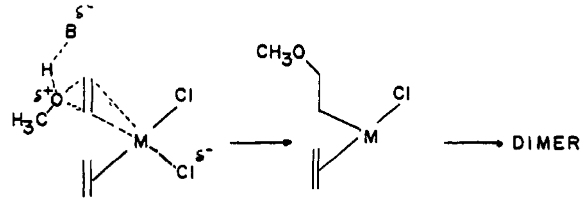


Table I. Nuclear Magnetic Resonance Data

Compound	τ_{OCH_3}	τ_{vinyl}	$\tau_{C_6H_5}$	H_X Band center, τ	H_X Band width, cps	H_X J, cps
8	6.75	*b*	...	6.49	3.5	*b*
9	6.73	3.50 4.07	...	6.44	3.5	2.0
7	6.77	...	...	6.58	11.2	6.8 2.6 1.35
15	6.77	...	...	6.57	4.2	2.6
10	6.57	5.02 5.47	...	6.38	3.0	2.0
11	6.65	3.32 3.86	...	6.28	3.5	2.0
12	6.82	5.31 5.51	4.42[a]	6.52	3.0	2.0
13	6.73	6.41 6.89	4.37	6.42	*b*	*b*
23	6.72	*b*	...	*b*	*b*	*b*
24	6.72	5.00	...	*b*	*b*	*b*
25	6.75	*b*	4.34[a]	*b*	*b*	*b*
26	6.82	...	...	6.86	*b*	*b*
27	6.72	4.52[c] 5.09[d]	...	5.88	4.5	2.5
28	6.72	3.88[c] 4.04[d]	...	5.80	4.0	2.5

[a] $J_{^{195}Pt-CH}$ = 13.5 cps. [b] Unresolvable or unassignable due to overlap with other peaks. [c] Triplet, 1:2:1. [d] Sextet, 1:1:2:2:1:1.

It was of interest that some similarities may be seen between these complexes and a postulated intermediate[29] in the Wacker oxidation of olefins to carbonyl compounds.[29-31] This process uses a palladium–copper catalyst in water for the oxidation. In the case of ethylene, the postulated intermediate[28] is a palladium σ-bonded complex which undergoes hydride transfer and elimination of palladium to give acetaldehyde. This intermediate has a very similar structure to the methoxy complexes discussed herein. The stability of these methoxy palladium complexes **9** and **28** compared to the Wacker-type intermediate can be ascribed to several factors. First, the equilibrium between the palladium–diolefin complexes and the corresponding oxymetalated complexes is more favorable in the case of the bicyclic olefins, since strain in the norbornene moiety is relieved in the transition from sp^2 to sp^3 bonding at carbons 2 and 3. The greater reactivity of the norbornene bond is generally attributed to this factor. Second, the stabilizing olefin ligand in **9** and **28** is not volatile and subject to loss at ordinary pressures. Third, these methoxy derivatives, **9** and **28**, are subject to a chelate effect, in that the olefin ligand is rigidly held in position without freedom of motion. Any elimination reaction that occurs at the 2 and 3 positions of the norbornene skeleton (palladium- and methoxy-bearing carbons) is readily reversed since the palladium continues to be held at the reaction site by the olefin ligand.

Experimental Section

The nmr spectra were obtained on a Varian A-60 spectrometer. The spectra of the complexes were obtained in deuteriochloroform, and the spectra of the hydrocarbons were obtained in carbon tetra-

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(26) D. P. Powell and N. Sheppard, *J. Chem. Soc.*, 2519 (1960).

(27) P. Laszlo and P. von R. Schleyer, *J. Am. Chem. Soc.*, **86**, 1171 (1964), and references therein.

(28) H. Lucas, F. Hepner, and S. Winstein, *ibid.*, **61**, 3102 (1939).

(29) I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, *Dokl. Akad. Nauk SSSR*, **133**, 377 (1960); *ibid.*, **153**, 140 (1963).

(30) J. Smidt, W. Hofner, R. Jira, J. Sedmeier, R. Sieber, R. Ruttinger, and H. Kojer, *Angew. Chem.*, **71**, 176 (1959).

(31) J. Smidt, *Chem. Ind.* (London), 54 (1962).

chloride. Gas–liquid partition chromatography (glpc) was carried out on a F & M Model 500 gas chromatograph using 12-ft columns packed with 10% Apiezon-L, 10% diisodecyl phthalate, or 10% GE XF-1150 (cyanoethylsilicone) on Chromosorb P.

Preparation of Diolefin Complexes. Dichloro(*endo*-dicyclopentadiene)platinum(II) (**1**), dichloro(1,5-cyclooctadiene)platinum (II) (**2**), and dichloro(norbornadiene)platinum(II) (**4**) were obtained by the general procedure of a displacement reaction on Zeise's acid.[32] A 2–5 mole excess of the diolefin was added to the Zeise's acid solution in ethanol, and the mixture was heated at the reflux temperature until ethylene evolution ceased (6–8 hr). Recrystallization of the precipitate from methylene chloride gave **1** (46.0%), mp 210–220° dec (lit.[3a] mp 200–220° dec), or **2** (72.4%), mp 250–280° dec (lit.[3a] mp 220–278° dec), or **4** (72.0%), mp 230–280° dec (lit.[8] mp 230–280° dec).

Dichloro(dipentene)platinum(II) (**3**) was prepared using an adaptation of the published procedure.[7] To 7.6 g (12.9 mmoles) of tetrachlorobis(ethylene)diplatinum(II)[33] in 140 ml of absolute ethanol was added 3.53 g (25.9 mmoles) of dipentene and 1 ml of concentrated hydrochloric acid. The solution was allowed to stand at room temperature with occasional stirring for 48 hr. The evolution of ethylene had ceased after 48 hr, and a cream-colored precipitate had formed. The precipitate was collected on a filter and washed with ethanol and anhydrous ether. After air drying, the compound was recrystallized from a 2:1 ethanol–acetone solvent mixture to yield 6.89 g of cream-colored **3**. Evaporation of the original filtrate and analogous purification of the residue afforded an additional 0.3 g of product. The total yield of **3** was 7.19 g (92.3%), mp 171–172° dec (lit.[3a] mp 171–172° dec). The decomposition of **3** with an aqueous potassium cyanide solution gave dipentene as the only organic product.

Dichloro(*endo*-dicyclopentadiene)palladium(II) (**5**) and dichloro-(norbornadiene)palladium(II) (**6**) were prepared by a displacement reaction of the diene on dichlorobis(benzonitrile)palladium(II).[34] Recrystallization of the product from methylene chloride or chloroform[35] gave pure orange **5** (91.4%), mp 167–170° dec (lit.[3b] mp 165–170° dec), or yellow **6** (90.4%), mp 190–200° dec (lit.[3b] mp 190–200° dec).

Methoxylation Reactions. The known methoxy metalations were all carried out using the published procedures.[1] In this manner, di-μ-chlorobis(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)diplatinum(II) (**8**) (94.2%), mp 210–220° dec (lit.[3a] mp 210–220° dec), di-μ-chlorobis(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) (**9**) (88.6%), mp 165–170° dec (lit.[3b] mp 165–170° dec), di-μ-chlorobis(3a,4,7,7a-tetrahydro-*exo*-6-ethoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) (**19**) (60.0%), mp 155–160° dec (lit.[3a] mp 150–160° dec), di-μ-chlorobis(8-methoxy-*p*-menth-1-ene-9σ,1π)diplatinum(II) (**22**) (2.7%), mp 130–140° dec (lit.[3a] mp 135–140° dec), and di-μ-chlorobis(1-methoxycyclooct-4-ene-8σ,4π)diplatinum(II) (**23**) (60.8%), mp 150–170° dec (lit.[3a] mp 150–170° dec), were obtained.

Di-μ-chlorobis(*exo*-6-methoxy-2-norbornene-*endo*-5σ,2π)diplatinum(II) (**27**) was prepared by heating a solution of 0.86 g (0.0025 mole) of dichloro(norbornadiene)platinum(II) (**4**) and 0.26 g (0.0025 mole) of sodium carbonate in 40 ml of methanol at the reflux temperature for 30 min. The solution was filtered hot and evaporated to dryness. Recrystallization of the residue from methylene chloride gave 0.42 g (59%) of **27**, mp 134–137°. *Anal.* Calcd for $C_{16}H_{22}O_2Cl_2Pt_2$: C, 27.16; H, 3.14. Found: C, 27.45; H, 2.87.

Di-μ-chlorobis(*exo*-6-methoxy-2-norbornene-*endo*-5σ,2π)dipalladium(II) (**28**) was prepared by stirring a solution of 4.0 g (0.015 mole) of dichloro(norbornadiene)palladium(II) (**6**) and 1.58 g (0.015 mole) of sodium carbonate in 200 ml of methanol for 40 min at room temperature. The gray-brown residue which formed was collected on a filter, washed with 20 ml of ether, and air dried. The residue was dissolved in methylene chloride, treated with charcoal, and filtered. The pale yellow precipitate which formed was collected on a filter, washed with ether, and dried under reduced pressure to afford 3.2 g (80.0%) of **28**, mp 108–111° dec. *Anal.* Calcd for $C_{16}H_{22}O_2Cl_2Pd_2$: C, 36.25; H, 4.19. Found: C, 36.24; H, 3.95.

General Procedure for Hydrogenation of Methoxy Complexes. A suspension of 3–5 g of the complex and a 2-equiv excess of sodium acetate in 50–75 ml of the reduction solvent (usually methanol or tetrahydrofuran) was shaken in a Paar hydrogenation apparatus at 25 psi until hydrogen absorption ceased. The hydrogenation was complete in every case within 30 min. The solution was filtered, and the hydrogenation bottle and the filter were washed with two 25-ml portions of pentane. The combined filtrate and pentane washings were fractionally distilled to isolate the product (see Table II). Preparative glpc (12-ft 10% diisodecyl phthalate or 10% GE XF-1150 on Chromosorb P) was used when necessary to isolate >99% pure product. Identificaton of products was made by comparison with authentic samples.

Table II. Reduction of Methoxy Complexes

Complex	Method of reduction	Product	Yield, %	Bp, °C (mm)	$n^{20}\text{D}$
8	H_2	**7**	68.0	108 (20)[a]	1.4921[a]
	$NaBH_4$	**7**	66.5	110 (21)	1.4919
	D_2	**14**	82.5	92 (9)	1.4923
	$NaBD_4$	**15**	58.0	56 (1.5)	1.4922
9	H_2	**7**	78.5	108 (20)[a]	1.4921[a]
	$NaBH_4$	**7**	72.3	95 (10)	1.4920
	D_2	**14**	76.8	78–79 (4)	1.4923
	$NaBD_4$	**15**	32.9	60–61 (2)	1.4922
19	H_2	**20**	81.9	72–73 (4)	1.4864
22	H_2	**23**	47.4	68–69 (4)	1.4494
23	H_2	**26**	37.1	84 (20)	1.4606
27	H_2	**30**	48.0	65–66 (30)	1.4570
28	H_2	**30**	55.1	92–93 (100)	1.4568

[a] Lit.[13b] bp 84–86° (6 mm); $n^{19.5}\text{D}$ 1.4923.

General Procedure for Deuteration of Methoxy Complexes. The procedure was similar to that used for the hydrogenations except that a Paar apparatus was not used. Deuterium from a tank was collected over a column of silicone oil. The reduction flask was evacuated and deuterium was allowed to fill the system, with pressure supplied by the column of silicone oil. The work-up procedure was identical with that given above. Methanol, ethyl acetate, and tetrahydrofuran were used as reduction solvents. Nuclear magnetic resonance spectra were used to indicate the stereospecificity of the reductions.

General Procedure of Sodium Borohydride or Deuteride Reduction of Methoxy Complexes. To a suspension of sodium borohydride (or deuteride) in 50–75 ml of dry monoglyme was added the complex over a period of 30 min with stirring (molar ratio of 2:1, hydride to complex). The solution was then stirred at room temperature for an additional hour. An equal volume of water (deuterium oxide was not needed for the sodium borodeuteride reduction) was then added and the solution was heated on a steam bath for 1 hr. After the reaction mixture had cooled, the black metal precipitate which had formed was collected on a filter. The flask and collected precipitate were washed thoroughly with three 75-ml portions of pentane and these washings were then used to extract the aqueous monoglyme filtrate. The combined extracts were dried over sodium carbonate for 12 hr and then fractionally distilled to afford the product (see Table II). Preparative glpc was used (12-ft 10% diisodecyl phthalate or 10% GE XF-1150 on Chromosorb P colums) when necessary to isolate >99% pure product. Products were identified by comparison with authentic samples. The stereospecificity of the deuteride reductions was indicated by the nmr spectra of the products.

When a 1.5:1 mole ratio of hydride to complex was employed in the reduction of **34**, the product consisted of four compounds. These compounds were separated by preparative glpc and identified by comparison with authentic samples as **7**[13b] (34%), **16**[13b] (31%), **17**[19] (19%), and **18**[19] (16%).

Preparation of 8-Methoxy-*p*-menthane (21). Employing the reported method,[20] 50.0 g (0.37 mole) of dipentene, 10 g of concentrated sulfuric acid, and 90 ml of absolute methanol gave 20.2 g (33.2%) of 8-methoxy-*p*-menth-1-ene, bp 98–101° (15 mm), $n^{20}\text{D}$ 1.4658 (lit.[20] bp 106–107.5° (20 mm); $n^{25}\text{D}$ 1.4642).

Hydrogenation of 10.0 g (0.060 mole) of 8-methoxy-*p*-menth-1-ene in a Paar apparatus (0.2 g of platinum oxide catalyst) at 35 psi

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[32] W. Zeise, *Chem. Zentr.*, 2, 677 (1831).

[33] J. S. Anderson, *J. Chem. Soc.*, 972 (1934).

[34] M. S. Kharasch, R. C. Seyler, and F. R. Mayo, *J. Am. Chem. Soc.*, **60**, 882 (1938).

[35] Chloroform-containing ethanol as a stabilizer should not be used, as the ethoxy complex will be formed.

afforded 7.2 g (71.3%) of 8-methoxy-*p*-menthane (**21**), bp 78–80° (9 mm), $n^{19.5}$D 1.4498. These constants and nmr and infrared spectra were in agreement with those of the hydrogenation product of the methoxy(dipentene) complex **22**.

Methyl Cyclooctyl Ether. To 5.20 g (0.04 mole) of cyclooctanol in 50 ml of benzene was added 2.00 g (0.08 mole) of sodium hydride in 10 ml of benzene. The resulting suspension was heated at the reflux temperature for 10 hr. The flask was then cooled to room temperature, and 45 ml of iodomethane was added. The flask was again heated at the reflux temperature for 20 hr and then cooled and extracted with three 100-ml portions of water. The benzene solution was dried over potassium carbonate for 12 hr and fractionally distilled to afford 4.63 g (80.3%), bp 76–77° (18 mm), n^{19}D 1.4609. Physical constants and spectra were identical with the hydrogenation product of complex **23**. *Anal.* Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.90; H, 12.88.

Preparation of *exo*-2-Methoxynorbornane (26). To a solution of 61.3 g (0.666 mole) of norbornene in 155 ml of absolute methanol was added 15 g of concentrated sulfuric acid. The mixture was stirred at 55–60° for 3 hr and then cooled to room temperature. The solution was washed with three 100-ml portions of water, two 100-ml portions of a saturated sodium bicarbonate solution, and one additional 100-ml portion of water. The red oily product was dried over sodium sulfate for 10 hr. Fractional distillation gave 21.5 g (25.5%) of **30**, bp 154–155°; n^{20}D 1.4573. These physical constants and the infrared and nmr spectra of this product were identical with that obtained for the hydrogenation products of **27** and **28**.

Chloro(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)(pyridine)platinum(II) (10). The method previously described[3a] for the preparation of the corresponding *p*-toluidine complex was used to prepare **10**. From 1.60 g (0.002 mole) of the dimer **8** and 0.32 g (0.004 mole) of pyridine in 50 ml of methylene chloride was obtained 1.53 g (81.0%) of the pure white crystalline **10**, mp 165–170° dec. *Anal.* Calcd for $C_{16}H_{20}ONClPt$: C, 40.64; H, 4.26; N, 2.96. Found: C, 40.36; H, 3.97; N, 2.96.

Chloro(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)(pyridine)palladium(II) (11). Following the published directions for the preparation of the *p*-toluidine analog,[3b] the reaction of 1.2 g (0.0020 mole) of the dimer **9** with 2.0 g (0.025 mole) of pyridine yielded 0.85 g (56.3%) of cream-colored **11**, mp 145–155° dec. *Anal.* Calcd for $C_{16}H_{20}ONClPt$: C, 50.02; H, 5.25; N, 3.64. Found: C, 50.21; H, 5.31; N, 3.49.

Cyclopentadienyl(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)platinum(II) (12).[36] To a suspension of 1.20 g (0.0015 mole) of the dimer **8** in 50 ml of benzene was added 0.675 g (0.0025 mole) of thallium cyclopentadienide in 10 ml of benzene. The mixture was heated at the reflux temperature for 4 hr during which time the solution became yellow-brown in color and a gray precipitate appeared. The solution was allowed to cool to room temperature and was filtered. The filtrate was evaporated to dryness under reduced pressure leaving a yellow residue. The residue was extracted with three 100-ml portions of pentane. The combined pentane extracts were decolorized with charcoal, filtered, and evaporated to a total volume of 50 ml. When the flask was placed in an ice bath, a yellow crystalline precipitate formed. The precipitate was collected on a filter, washed with 10 ml of ether, and dried under reduced pressure to afford 0.30 g (23%) of pure yellow-orange product, **12**, mp 88–89°. There was a tendency for this compound to form an oil. *Anal.* Calcd for $C_{16}H_{20}OPt$: C, 45.39; H, 4.77. Found: C, 45.57; H, 4.88.

Cyclopentadienyl(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)palladium(II) (13). The preparation of **13** was effected according to the procedure followed for the preparation of **12**. From 1.0 g (0.0016 mole) of the dimer **9** and 0.90 g (0.0033 mole) of thallium cyclopentadienide was obtained 0.71 g (64.9%) of the pure orange-red **13**, mp 79–80°. *Anal.* Calcd for $C_{16}H_{20}OPd$: C, 57.41; H, 6.03. Found: C, 57.52; H, 6.18.

Exchange of Alkoxyl Groups in Di-μ-chlorobis(3a,4,7,7a-tetrahydro-*exo*-6-methoxy-*endo*-4,7-methanoindene-*endo*-5σ,2π)dipalladium(II) (9). To 2.50 g (0.0041 mole) of **9** in 150 ml of chloroform was added 11.1 g (0.241 mole) of absolute ethanol. The solution was stirred at room temperature for 3 hr and filtered. The filtrate was evaporated to a total volume of 50 ml and poured into 100 ml of pentane. The pale yellow compound which precipitated was collected on a filter and air dried. Recrystallization from methylene chloride afforded 2.36 g (90.2%) of the ethoxy complex, **19**, mp 155–160° dec (lit.[3b] mp 155–160° dec). The infrared spectrum of this complex was identical with that of the ethoxy complex prepared by the direct reaction of ethanol with dichloro(*endo*-dicyclopentadiene)palladium(II) (**5**). Hydrogenation of the complex prepared in either way gave the same ethyl ether **20**.

Chloro(1-methoxy-cyclooct-4-ene-8σ,4π)(pyridine)platinum(II) (24). The technique followed was similar to that given for the preparation of **10**. The reaction of 9.0 g (0.024 mole) of the dimer **23** and 0.22 g (0.0028 mole) of pyridine yielded 1.02 g (84.0%) of pure white crystalline **24**, mp 130–135° dec. *Anal.* Calcd for $C_{14}H_{20}ONClPt$: C, 37.47; H, 4.46; N, 3.12. Found: C, 37.49; H, 4.52; N, 3.03.

Cyclopentadienyl(1-methoxy-cyclooct-4-ene-8σ,4π)platinum(II) (25). This reaction was effected as described for the preparation of **12**. From the reaction of 1.0 g (0.0014 mole) of the dimer **23** and 0.728 g (0.0028 mole) of thallium cyclopentadienide was obtained 0.66 g (61.5%) of **25**, mp 74–76° dec. *Anal.* Calcd for $C_{14}H_{20}OPt$: C, 42.10; H, 5.05. Found: C, 42.37; H, 5.34.

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[36] This method of preparation involving the use of thallium cyclopentadienide was communicated to us by J. R. Doyle, University of Iowa, Iowa City, Iowa, prior to its publication.