Formyl fluoride was prepared according to the method of Olah and Kuhn.[11] *N*-Formylpiperidine, *N,N*-diformylpiperazine, and 1,1′-carbonyldiimidazole were obtained from Aldrich Chemical Co. *N*-Formylimidazole was prepared according to the method of Staab and Polenski.[19]

Protonation of Carboxylic Acid Anhydrides. Protonated anhydrides were prepared by slow addition of an SO_2 solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) to an SO_2 solution of the anhydride at −80°.

Attempted Preparation of the Formyl Cation. (a) An SO_2ClF solution of formyl fluoride was added to an SO_2ClF solution of antimony pentafluoride in a pressure nmr tube at −120°. The nmr tube was then pressurized with carbon monoxide, sealed, and then carefully shaken to allow mixing. (b) Protonation of carbon monoxide was attempted by pressurizing the pressure nmr tube containing an SO_2ClF solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) at −80° with carbon monoxide. (c) Protonated formic acid was prepared by the addition of an SO_2 solution of formic acid to an SO_2 solution of fluorosulfuric acid–antimony pentafluoride (1:1 *M*) at −80°. The solution was transferred to a pressure nmr tube which was sealed under a pressure of carbon monoxide at −80°. The temperature was raised until cleavage occurred. (d) Protonated ethyl formate was prepared and treated as above. (e) Solutions of *N*-formylpiperidine, *N,N*-diformylpiperazine, and *N*-formylimidazole were made up in $FSO_3H–SbF_5–SO_2ClF$ at −80°.

Pressure Nmr Tube. The pressure nmr tubes[13] were prepared by mounting a Fischer–Porter threaded glass needle valve on a 5 mm o.d., 3 mm i.d. thick-walled Pyrex nmr tube. The valve consists of a glass body of 1.25 mm bore and a Teflon stem which is double-sealed by a Viton-A O-ring and a machined Teflon neck. The head of the Teflon stem was machined to a 10/30 male joint and a fine gas bleed was drilled through the Teflon stem to the seal (Figure 2).

Acknowledgment. Support of our work by the National Institutes of Health and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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(19) H. A. Staab and B. Polenski, *Justus Liebigs Ann. Chem.*, **655**, 95 (1962)

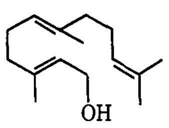
Platinum Hydride Addition to Geranyl and Farnesyl Methyl Ether[1]

Martin A. Schwartz* and T. Jeffrey Dunn[2]

Contribution from the Department of Chemistry, The Florida State University, Tallahassee, Florida 32306. Received October 5, 1971

Abstract: The reaction of geranyl methyl ether with dipotassium tetrachloroplatinate(II) in aqueous ethanol afforded the σ-complex di-μ-chloro-bis(1-methoxy-3,7-dimethyl-2-octene-6σ,2π)diplatinum(II) (**7**) and 2,6-dimethyl-8-methoxy-6-octen-3-one (**9**) as major products. Proof of structure for these compounds and a study of the mechanism of the reaction are given. Similar treatment of farnesyl methyl ether gave a large number of products from which two σ complexes and an analogous ketone were isolated.

In an attempt to carry out a laboratory synthesis based on the proposed[3] enzymic conversion of farnesol (**1**) to medium ring sesquiterpenes such as germacrene B[4,5] (**2**), we were interested in preparing an olefin–transition metal π complex of general structure **3**. It was hoped that the conformational restrictions imposed by the metal on the farnesyl moiety in complex **3** would be sufficient to allow acid-catalyzed ten-membered ring cyclization to take precedence over the usually favored[6] six-membered ring formation.



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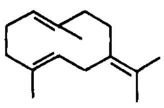
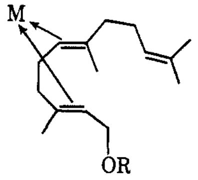


2



3

Consequently an investigation into the formation of such a complex was undertaken.

A number of metals such as silver, platinum, palladium, rhodium, iron, and nickel have been shown to give relatively stable π complexes with various olefinic ligands.[7] The stability of these complexes depends on several factors, including the nature of the metal, the nature of the substituents on the olefinic carbons,[8] the nature of the inorganic ligands,[9] and in the case of some diolefin–metal complexes, on the conformational rigidity of the diolefin.[9] The choice of metal to be used in complex **3** was restricted in that it had to be one that would accept an acyclic 1,5-diene as a bidentate ligand to give a stable complex, but not cause double bond isomerization. The most closely related known complexes were those of 1,5-hexadiene with platinum(II) and rhodium(I); no examples of complexes involving a more highly substituted acyclic diene could be found. The platinum complex, dichloro(1,5-hexadiene)platinum(II)[9,10] (**4**), was chosen as the best analogy on which to base the desired investigation.[11]

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(1) For a preliminary account of portions of this work, see M. A. Schwartz and T. J. Dunn, *J. Amer. Chem. Soc.*, **91**, 4007 (1969). We gratefully acknowledge the Research Corporation for partial support of this work.

(2) Abstracted in part from the Ph.D. Thesis of T. J. Dunn, Florida State University, 1971.

(3) J. B. Hendrickson, *Tetrahedron*, **7**, 82 (1959).

(4) K. Morikawa and Y. Hirose, *Tetrahedron Lett.*, 1799 (1969).

(5) K. Nishimura, N. Shinoda, and Y. Hirose, *ibid.*, 3097 (1969).

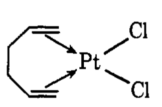
(6) C. D. Gutsche, J. R. Maycock, and C. T. Chang, *Tetrahedron*, **24**, 859 (1968), and references therein.

(7) (a) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962); (b) E. O. Fischer and H. Werner, "Metal π Complexes," Elsevier, Amsterdam, 1966.

(8) R. Cramer, *J. Amer. Chem. Soc.*, **89**, 4621 (1967), and references therein.

(9) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496 (1957).

(10) K. A. Jensen, *Acta Chem. Scand.*, **7**, 866 (1953).



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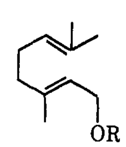
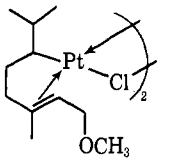
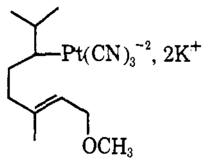


5, R = H
6, R = CH$_3$

Initial complex formation studies were carried out in the geranyl, rather than the farnesyl, series in order to avoid potential complications due to the presence of the third double bond. Geraniol (5) was methylated with sodium hydride and methyl iodide to give the ether 6. Treatment of excess geranyl methyl ether (6) with dipotassium tetrachloroplatinate(II)[9,10] in aqueous ethanol for 4 days resulted in the formation of several complexes[12] as determined by thin layer chromatographic (tlc) analysis.[13] The major complex was insoluble under the reaction conditions and could be obtained after filtration and recrystallization from ether as a white crystalline solid, mp 147–150° (decomposition after melting), in 36% yield.[14] The compound was stable to air, insoluble in water, and soluble in all common organic solvents, including hexane. Rather than being a π complex analogous to the 1,5-hexadiene complex 4, this product could be shown to be the dimeric σ complex, di-μ-chloro-bis(1-methoxy-3,7-dimethyl-2-octene-6σ,2π)diplatinum(II) (7).



7



8

The elemental analysis and osmometric molecular weight of 7 were in accord with the dimeric formulation, and the mass spectrum confirmed that a hydroplatination had occurred (see Table I). Treatment of 7 with aqueous potassium cyanide afforded a water soluble organoplatinum salt, probably 8 on the basis of spectral data (see below), whereas hydrogenation of 7 gave rise to tetrahydrogeranyl methyl ether as the sole organic product. Reaction of 7 with triphenylphosphine in tetrahydrofuran yielded the platinum hydride *cis*-[PtHCl(PPh$_3$)$_2$],[15] and an organic mixture consisting primarily (80%) of geranyl methyl ether (6) along with two other components.

Comparison of the nmr spectrum of 7 with those of the starting material 6 and the cyanide reaction product 8 (see Table II) provided final confirmation of the assigned structure. The spectrum of 7 exhibited a pair of doublets at δ 0.84 and 1.17 (6 H total) indicative of nonequivalent methyls of an isopropyl group; these signals remained intact, although somewhat shifted, in the spectrum of the cyano complex 8. The absorptions due to the methoxy methyl and vinyl methyl of 7 were both shifted downfield with respect to their positions in the spectrum of 6 and the vinyl methyl showed satellites due to ^{195}Pt coupling, all indicating the Δ^2 double bond to be π bonded to platinum;[16] the signals due to these same groups returned to their original positions in the spectrum of 8. Finally, the multiplet centered at δ 2.82 (1 H) in the spectrum of 7 was consistent, both in chemical shift and in magnitude of the ^{195}Pt coupling constant, with a σ-bonded CH–Pt grouping.[17] The fact that geranyl methyl ether (6) was the major product from the treatment of 7 with triphenylphosphine required that the σ bond be located at C-6 of the geranyl moiety, thus completing the structure determination.

Table I. Relative Intensities of Isotope Clusters in Mass Spectrum of 7

m/e	Obsd[b]	(M/2)$^+$ calcd[a] for $C_{11}H_{21}$-OPtCl	*m/e*	Obsd[b]	(M)$^+$ calcd[a] for $(C_{11}H_{21}$-$OPtCl)_2$
398	91	81	796	25	28
399	100	94	797	60	61
400	97	100	798	98	100
401	37	39	799	100	100
402	44	42	800	95	95
403	4	5	801	68	65
404	5	6	802	45	47
			803	19	21
			804	11	13

[a] Relative intensities were calculated for the indicated empirical formula using reported natural abundances of ^{12}C, ^{13}C, ^{35}Cl, ^{36}Cl, ^{194}Pt, ^{195}Pt, ^{196}Pt, and ^{198}Pt: R. C. Weast, Ed., "Handbook of Chemistry and Physics," 47th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1966, p B-4. [b] The observed intensities were normalized with respect to the largest peak in the cluster.

After removal of 7, the original K$_2$PtCl$_4$ reaction mixture was subjected to extraction, fractional crystallization, and preparative tlc to afford two platinum-free products, a yellow solid platinum complex, and a red liquid platinum complex. The least polar (tlc) organic compound was identified as a 60:40 mixture of geranyl methyl ether and neryl methyl ether (*cis*-6) by vapor-phase chromatographic (vpc) comparison with authentic samples. That cis–trans isomerization of the uncomplexed olefin had occurred was not surprising since the reaction mixture had become strongly acidic during the course of the reaction.

The second platinum-free product, isolated in 39% yield,[14] was shown to be a 70:30 mixture of ketone 9 and its geometric isomer (*cis*-9). The structure assignment was made on the basis of ir, nmr (see Table II), and mass spectral data, as well as by comparison with an independently synthesized sample of 9. The latter was prepared by selective oxidation[18] of geranyl methyl ether with *N*-bromosuccinimide in aqueous 1,2-dimethoxyethane, base treatment of the resulting bromohydrin to give the epoxide 10, and finally rearrange-

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(11) For recent work on palladium complexes of terpenes see (a) K. Dunne and F. J. McQuillin, *J. Chem. Soc. C*, 2196 (1970); (b) *ibid.*, 2200 (1970). None of the complexes reported in these papers have structures analogous to 3.

(12) Attempts to prepare complexes of geraniol itself under these conditions resulted in the immediate precipitation of metallic platinum, presumably with concomitant oxidation of geraniol.

(13) The organoplatinum compounds could be readily distinguished from organic compounds during the analysis by virtue of their giving intense black spots upon staining with iodine vapor.

(14) (a) All complexation reactions were carried out in the presence of an excess of the organic substrate; product yields are therefore reported as per cent of starting K$_2$PtCl$_4$. (b) The stoichiometry of the reaction requires that 1 mol of K$_2$PtCl$_4$ give rise to 0.5 mol of dimeric complex 7 and 1 mol of ketone 9; the yields of 7 and 9 were calculated accordingly.

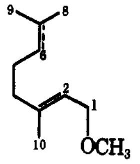
(15) J. C. Bailar, Jr., and H. Itatani, *Inorg. Chem.*, 4, 1618 (1965).

(16) P. D. Kaplan, P. Schmidt, A. Brause, and M. Orchin, *J. Amer. Chem. Soc.*, 91, 85 (1969).

(17) P. D. Kaplan, P. Schmidt, and M. Orchin, *ibid.*, 90, 4175 (1968), and references therein.

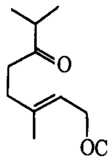
(18) E. E. van Tamelen and T. J. Curphey, *Tetrahedron Lett.*, 121 (1962).

Table II. Nmr Spectra of Geranyl Methyl Ether and Derivatives[a]

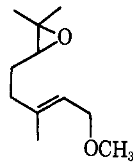


	H-1	H-2	H-6	H-8	H-9	H-10	OCH_3
6[b]	3.88 (d, J = 7)	5.30 (t, J = 7)	5.05 (br)	1.67	1.60	1.67	3.26
7	3.44–4.17 (m)		2.82 (m, sat,[d] J = 78)	0.84 (d, J = 7)	1.17 (d, J = 7)	1.80 (sat, J = 58)	3.39
8[c]	3.90 (d, J = 7)	5.26 (t, J = 7)	2.29 (m)	0.95 (d, J = 5.5)	1.02 (d, J = 5.5)	1.62	3.26
9	3.88 (d, J = 7)	5.30 (t, J = 7)		1.08 (d, J = 6.5)		1.67	3.28
11	3.6–4.4 (m)		*e*	*e*	1.90 (sat, J = 49)	1.80 (sat, J = 36)	3.43

[a] Chemical shifts are reported in ppm δ and coupling constants in Hz; spectra were obtained in $CDCl_3$ unless otherwise noted. [b] In CCl_4. [c] In D_2O. [d] Refers to satellite peaks due to ^{195}Pt–H (natural abundance 34%) coupling. [e] These protons may be accounted for by a multiplet at 2.4–3.1 (1 H), a triplet at 4.78 (J = 8, 1 H), and a triplet at 5.01 (J = 6, 1 H).



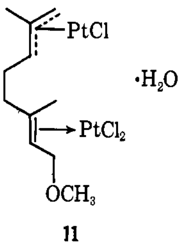
9



10

ment of **10** by heating with lithium perchlorate[19] in benzene. The resulting ketone (**9**) was identical with the major ketone isomer previously isolated.

The yellow solid platinum complex was obtained in widely varying yield (0–26%), although in certain cases it was the only complex that could be isolated. Attempts to correlate this variability of yield with purity of reactants and solvents were unsuccessful. The complex was insoluble in ether, but could be slowly dissolved in refluxing chloroform and recrystallized from the same solvent. Its elemental analysis was consistent with the formula $C_{11}H_{19}OPt_2Cl_3 \cdot H_2O$ but no reproducible osmometric or mass spectral molecular weight data could be obtained. The nmr spectrum (see Table II) showed only two C-methyl groups, both with satellites due to ^{195}Pt coupling, and the infrared spectrum confirmed the presence of a hydroxyl group. These data allowed tentative assignment of the π and π-allyl bonded part structure **11** to this compound. Additional support for this assignment came from the observations that (1) the mass spectrum of **11** exhibited a prominent ion at m/e 166 ($C_{11}H_{18}O$), a peak absent in the mass spectrum of **7** but present in the spectrum of a recently reported[11a] geranyl methyl ether–palladium π-allyl complex; this ion presumably arises by loss of metal hydride from a π-allyl complex; (2) hydrogenation of **11** afforded tetrahydrogeranyl methyl ether as the sole organic product; (3) treatment of **11** with aqueous potassium cyanide gave rise to a 95:5 mixture of geranyl methyl ether (**6**) and an unidentified isomer (not *cis*-**6**). However, a definitive structure could not be ascertained due to the intractable nature of the compound.



11

The final complex, an unstable red oil, was obtained by preparative tlc of the original reaction mixture. The same material was also obtained upon attempted preparative tlc purification of **11**, leading to uncertainty as to whether it was actually a direct product of the K_2PtCl_4 reaction. The nmr spectrum of this compound again exhibited only two C-methyl group absorptions, both with ^{195}Pt satellites, at δ 1.85 (J = 46) and 2.25 (J = 79) suggestive of another π-allyl complex, while the infrared spectrum showed no hydroxyl absorption. Treatment of the complex with hydrogen and with aqueous potassium cyanide gave rise to the same products as were obtained from **11** under the same conditions. Although these results indicated the liquid complex to be related in structure to **11**, the instability of the compound prevented obtention of elemental and mass spectral analyses, thus precluding further identification.

When the reaction of geranyl methyl ether (**6**) with K_2PtCl_4 in aqueous ethanol was allowed to proceed for 15 days, the σ-complex **7** and ketone **9** were obtained in yields of 70 and 67%, respectively.[14] Submission of the π-allyl complex **11** to the original reaction conditions (geranyl methyl ether in aqueous ethanol containing a drop of hydrochloric acid; the latter was added because the original reaction mixture was observed to become acidic with time) also resulted in generation of **7** and **9**.

The σ,π-bonded structure of **7** is precedented in that similar complexes have been prepared by the addition of various nucleophiles to one double bond of π-coordinated diolefins;[20] the resulting alkyl platinum(II)

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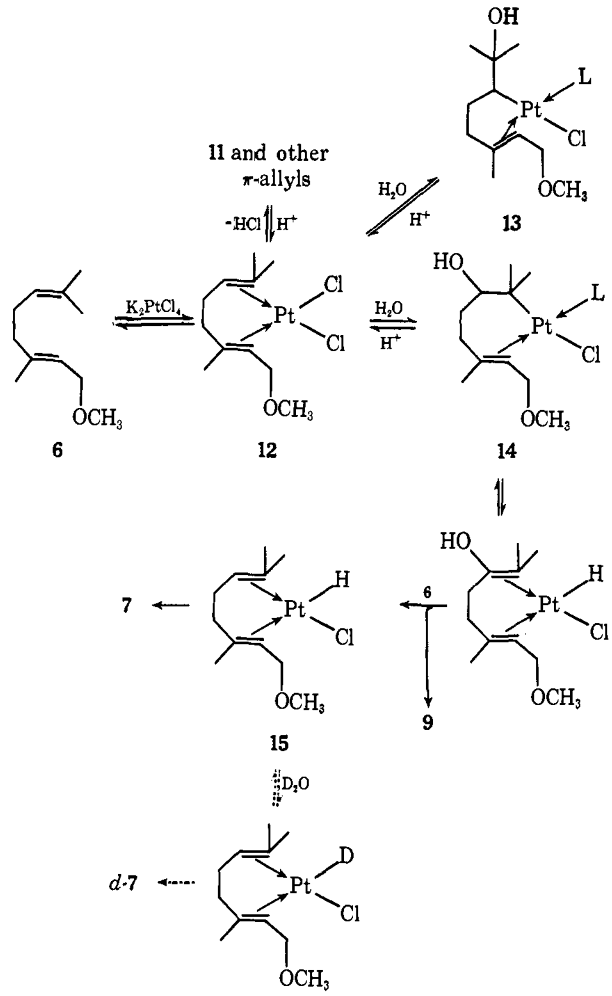
(19) B. Rickborn and R. M. Gerkin, *J. Amer. Chem. Soc.*, **90**, 4193 (1968).

(20) (a) J. K. Stille and R. A. Morgan, *ibid.*, **88**, 5135 (1966), and references therein; (b) J. K. Stille and D. B. Fox, *ibid.*, **92**, 1274 (1970); (c) W. Hewertson and I. C. Taylor, *J. Chem. Soc. D*, **428** (1970).

Scheme I



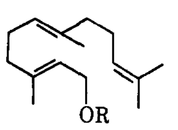
complexes are stabilized by coordination to the second double bond which provides the requisite large crystal field splitting.[20a] The formation of **7** is unusual, however, in that it presumably requires the addition of a platinum hydride to an olefin to give a secondary alkyl platinum derivative. The reversible addition of platinum hydrides to olefins has been proposed as the key step in the platinum-catalyzed isomerization[21] and hydrogenation[22] of olefins, but the reaction has previously given isolable σ-bonded complexes only with 1-olefins, and in these cases only primary alkyl platinum derivatives could be isolated.[23,24] The dependence of the stability of the C–Pt σ bond on the nature of the other platinum ligands is clearly demonstrated in our case by the observations that treatment of **7** with triphenylphosphine resulted in ready elimination of platinum hydride, while treatment of **7** with potassium cyanide gave the water soluble salt **8** in which the σ bond remained intact.

The cooccurrence of σ-complex **7** and ketone **9** in equivalent amounts suggested that the necessary platinum hydride was being formed with concomitant oxidation of geranyl methyl ether. Oxidation of solvent was eliminated as a source of platinum hydride by carrying out the reaction in aqueous *tert*-butyl alcohol; σ-complex **7** was isolated in undiminished yield. The possible intermediacy of a platinum(IV) hydride,[21c] formed by oxidative addition of HCl to platinum(II), was tested by conducting the reaction in EtOD–D_2O and *tert*-BuOD–D_2O; the resulting **7** was shown by nmr analysis to contain only *ca.* 30% deuterium at C-7 in each case, thus eliminating this possibility. The observed results are therefore best explained by the sequence of reactions shown in Scheme I. Hydration of the originally sought π-complex **12** can proceed to give the hydroxyplatinated products **13** and **14**;[25] elimination of platinum hydride from **14** followed by ligand exchange would yield the ketone **9** and the geranyl methyl ether–platinum hydride complex **15**. The deuterium incorporation results can then be accounted for by isotopic exchange of **15** with solvent[26] in competition with its collapse to **7**. The final step was shown to be irreversible under the reaction conditions when treatment of **7** with EtOD–D_2O–DCl for 10 days resulted in no deuterium incorporation at C-7 (nmr).

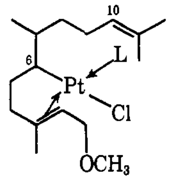
A final attempt was made to prepare the π-complex **12** by the reaction of **6** with $[PtCl_2(C_2H_4)]_2$ (Zeise's dimer) in anhydrous acetone. When the reaction was carried out at −78°, an unstable platinum-containing product was seen to form (tlc[13]) and then rapidly disappear upon warming to room temperature; no tractable products could be isolated. However, addition of water to the cold reaction mixture followed by warming to room temperature gave rise once again to the σ-complex **7** in low yield. When the latter procedure was carried out in acetone-d_6 with addition of D_2O, complex **7** again contained *ca.* 30% deuterium at C-7; ketone **9** could be detected in both cases.

It was apparent from this work that the farnesyl π-complex **3** was no longer a reasonable goal. However, it was felt that a farnesyl σ complex analogous to **7** would still be useful in cyclization studies, since the desired conformational restrictions would still be present and the metal would be removable at a later stage *via* triphenylphosphine-induced elimination.

trans,trans-Farnesyl methyl ether (**16**) was obtained in 95% isomeric purity by methylation of commercial farnesol (**1**) and isolation of the desired isomer by spinning-band distillation. Reaction of excess **16** with dipotassium tetrachloroplatinate(II) in either aqueous ethanol or aqueous *tert*-butyl alcohol for 6–14 days resulted in a complex mixture of platinum-containing products. Two complexes with R_f values similar to



1, R = H
16, R = CH_3



17
L = Cl or Δ^{10} double bond

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(21) (a) J. F. Harrod and A. J. Chalk, *J. Amer. Chem Soc.*, 86, 1776 (1964); (b) *ibid.*, 88, 3491 (1966); (c) R. Cramer and R. V. Lindsey, Jr., *ibid.*, 88, 3534 (1966); (d) H. A. Tayim and J. C. Bailar, Jr., *ibid.*, **89**, 3420 (1967).

(22) M. Giustiniani, G. Dolcetti, R. Pietropaolo, and U. Belluco, *Inorg. Chem.*, **8**, 1048 (1969).

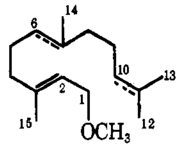
(23) J. Chatt, R. S. Coffey, A. Gough, and D. T. Thompson, *J. Chem. Soc. A*, 190 (1968), and references therein.

(24) Brookes and Nyholm have recently reported the second example of formation of a cyclic *sec*-alkyl platinum derivative *via* platinum hydride addition: P. R. Brookes and R. S. Nyholm, *J. Chem. Soc. D*, 169 (1970).

(25) Both directions of addition have been observed in the reaction of hexadiene complex **4** with ethylamine: R. Palumbo, A. DeRenzi, A. Panunzi, and G. Paiaro, *J. Amer. Chem. Soc.*, **91**, 3874 (1969).

(26) C. D. Falk and J. Halpern, *ibid.*, **87**, 3523 (1965).

Table III. Nmr Spectra of Farnesyl Methyl Ether and Derivatives[a]

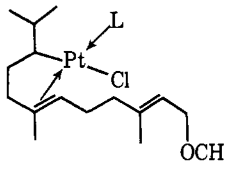


	H-1	H-2	H-6	H-10	H-12	H-13	H-14	H-15	OCH$_3$
16	3.90 (d, J = 7)	5.35 (t, J = 7)	5.10	5.10	1.67	1.60	1.60	1.67	3.30
17	3.50–4.21 (m)		2.89 (m)	5.08	1.66	1.59	0.86 (d, J = 7) 1.16 (d, J = 7)	1.83 (sat, J = 57)	3.41
18	3.91 (d, J = 7)	5.31 (t, J = 7)	*b*	*b*	0.87 (d, J = 7)	1.11 (d, J = 7)	1.78 (sat, *b*)	1.69	3.33
19	3.87 (d, J = 7)	5.29 (t, J = 7)	5.06 (br)		1.04 (d, J = 7)		1.57	1.64	3.26

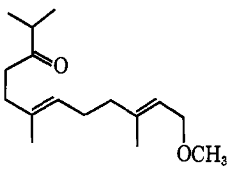
[a] See reference *a* of Table II. [b] Definite assignments could not be made due to impurities in the sample.

that of the geranyl complex **7** could be isolated by preparative tlc; both compounds were thermally unstable colorless oils. The first of these, isolated in 6.4% yield,[14a] could be assigned the 6σ-bonded structure **17** on the basis of the excellent correlation of its nmr spectrum (see Table III) with that of geranyl complex **7**. It could not be determined if **17** existed in the neat state as a chloride-bridged dimer, or as a monomer with the Δ^{10} double bond occupying the fourth coordination site on platinum. The latter was deemed more likely since in contrast to **7**, the highest observable cluster of peaks in the mass spectrum of **17** occurred at *m*/*e* 430–434; osmometric molecular weight data could not be obtained due to the instability of the compound. In any event, it was clear from the nmr spectrum that the Δ^{10} double bond of **17** was not π complexed in $CDCl_3$ solution. The reaction of **17** with triphenylphosphine afforded a 65:35 mixture of *trans,trans*- and *cis*,[27]*trans*-farnesyl methyl ether respectively, along with *ca.* 17% of an identified isomer (vpc).

The second complex, isolated in 23% yield, could not be completely freed of contaminents. Its nmr spectrum (see Table III) was in accord with the 10σ-bonded structure **18**. Interestingly, a neat sample of



18



19

18 stored at 0° for several weeks was observed to partially rearrange to a mixture of **17** and **18** (tlc), but no further work was done with this material. Attempts to separate and identify the other products of the original reaction proved fruitless, except for isolation (22% yield)[14a] of a ketone assigned structure **19** on the basis of spectral data.

When the 6σ-complex **17** was cyclized with stannic chloride in benzene and the metal eliminated by treatment with triphenylphosphine, there was obtained essentially the same mixture of products as was generated by similar treatment of farnesyl methyl ether (**16**) itself. No germacrene B (**2**) could be detected in either case; this approach to sesquiterpene synthesis was therefore terminated.

The occurrence of unusual Wacker-type oxidation and hydroplatination reactions in these systems is almost certainly due to the instability of the initially formed π-complexes **3** and **12**. It has been shown that stabilities of platinum π complexes decrease with structure modifications that increase electron density at the olefinic bond.[28] Therefore, while 1,5-hexadiene forms a stable platinum π complex,[9] other dienes containing tri- and tetraalkyl substituted double bonds are likely to give reactions of the type described here. It might be of some interest to further investigate the scope and limitations of these reactions.

Experimental Section

Melting points were measured on a Kofler microscope hot stage and are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 137 spectrophotometer, Nuclear magnetic resonance spectra were obtained with Varian A-60 (60 MHz) and Bruker HFX-10 (90 MHz) spectrometers; chloroform was used as internal standard for the organoplatinum derivatives and tetramethylsilane for the rest. Mass spectra were determined using Nuclide 12-90G (low resolution) and Associated Electronics Industries MS 902 (high resolution) instruments. Microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich., or by M-H-W Laboratories, Garden City, Mich.

Spinning-band distillations were carried out using a 24-in. Nester-Faust annular Teflon spinning-band column. Baker silica gel 7GF or E. Merck silica gel PF were used for thin layer chromatography. Vapor-phase chromatographic analyses were performed on Varian Aerograph Models 90-P-3 and 1200 instruments; retention times (t_R) are reported in minutes from initial injection. All solvents were purified by distillation; tetrahydrofuran and 1,2-dimethoxyethane were distilled from lithium aluminum hydride immediately prior to use.

***trans*-1-Methoxy-3,7-dimethyl-2,6-octadiene (Geranyl Methyl Ether) (6).** To a solution of 15.4 g (0.100 mol) of geraniol (**5**) (ICN, 95% isomeric purity by vpc analysis on 10% Carbowax 20M, 150°) in 400 ml of anhydrous ether was added 19.7 g of sodium hydride (61% in mineral oil, 0.500 mol). The suspension was stirred at room temperature for 10 min, 28.4 g (0.200 mol) of methyl iodide was added, and the mixture was stirred at room temperature for 48 hr. The reaction mixture was poured onto ice and extracted with ether; the combined ether extracts were washed with saturated aqueous sodium chloride, dried over sodium sulfate, and evaporated. Distillation of the residue gave 11.5 g (0.0684 mol, 68%) of **6**, bp 92–97° (20 mm), in 95% isomeric purity (vpc, Carbowax 20M, 150°); ir (film) 3.45, 6.00, 6.92, 7.28, 8.30, 8.50, 8.90, 9.05, 9.20, 10.45, 10.94, 12.05 μ; nmr (CCl_4), see Table II; mass spec-

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(27) This designation refers to the geometry of the Δ^2 double bond.

(28) R. G. Denning, F. R. Hartley, and L. M. Venanzi, *J. Chem. Soc. A*, 328 (1967).

trum, *m/e* 168, 153, 136, 69 (base peak); molecular ion at *m/e* 168.1514 (calcd for $C_{11}H_{20}O$, 168.1514).

Reaction of Geranyl Methyl Ether with Dipotassium Tetrachloroplatinate(II). To a solution of 1.27 g (3.06 mmol) of K_2PtCl_4 (Engelhard Industries) in 15 ml of distilled water were added 18 ml of ethanol (small amount of pink precipitate) and 1.44 ml of diene **6**. The reaction mixture was stirred at room temperature for 4 days. The resulting suspension was filtered to remove **7**; the acidic filtrate was extracted with chloroform, and the combined extracts were washed with water, dried over sodium sulfate, and concentrated to *ca.* 5 ml. In some instances cooling of this solution resulted in precipitation of the yellow solid complex **11**. The remaining chloroform soluble products were separated by preparative tlc on 2-mm plates (benzene–10% ethanol).

a. **Di-μ-chloro-bis(1-methoxy-3,7-dimethyl-2-octene-$6\sigma,2\pi$)diplatinum(II) (7).** Filtration of the reaction mixture gave 475 mg of off-white solid, mp 141–146° dec. Recrystallization of the material from ether afforded 433 mg (0.541 mmol, 36%) of σ-complex **7** as white crystals, mp 147–150° dec; ir (KBr) 3.41, 6.85, 6.95, 7.0, 7.28, 8.40, 8.85, 9.01, 9.25, 9.42, 9.80, 10.30, 10.40, 10.80, 11.62, 12.50, 13.3 μ; nmr ($CDCl_3$, 90 MHz), see Table II; mass spectrum, see Table I.

Anal. Calcd for $(C_{11}H_{21}OPtCl)_2$: C, 33.04; H, 5.30; Pt, 48.78; Cl, 8.87; molecular weight, 799. Found: C, 33.12; H, 5.26; Pt, 48.69; Cl, 9.09; molecular weight, 783 (osmometric, CCl_4).

A suspension of 59 mg (0.074 mmol) of **7** in 1 ml of decane was stirred with 1 ml of 10% aqueous potassium cyanide for 20 min. Vpc analysis of the organic layer showed no products. The aqueous layer was concentrated under reduced pressure and methanol was added; the resulting precipitate was filtered and dried under high vacuum to give **8** as a hygroscopic white solid; ir (KBr) 4.92 μ; nmr (D_2O, 90 MHz), see Table II.

Hydrogen gas was bubbled through a solution of 20 mg (0.025 mmol) of **7** in 6 ml of absolute ethanol for 1 hr. The resulting black precipitate was filtered; vpc analysis (10% Carbowax 20M, 100°) of the filtrate revealed one product, t_R 5.2. An authentic sample of tetrahydrogeranyl methyl ether, prepared by catalytic hydrogenation (Pd–C) of **6**, showed t_R 5.2 under the same conditions.

To a solution of 100 mg (0.125 mmol) of **7** in 2 ml of tetrahydrofuran was added 131 mg (0.500 mmol) of triphenylphosphine, and the mixture was stirred at room temperature for 2 hr. The resulting suspension was cooled and filtered to yield 140 mg (0.185 mmol, 74%) of *cis*-bis(triphenylphosphine)chlorohydridoplatinum(II) as white needles, mp 215–220° (lit.[15] mp 215–220°); ir (KBr) 4.25 μ. The filtrate was evaporated under reduced pressure and the residue was triturated with ether. Vpc analysis (10% Carbowax 20M, 130°) of the ether solution showed three components, t_R 4.6, 6.4, and 7.7, in a ratio of 12:80:8, respectively; *cis*-**6** and **6** had t_R 5.7 and 6.4 under the same conditions. An nmr spectrum of the mixture confirmed that it contained primarily **6**.

b. **2,6-Dimethyl-8-methoxy-6-octen-3-one (9).** Removal of the preparative tlc band with $R_f \sim 0.8$ resulted in isolation of 219 mg (1.19 mmol, 39%) of ketone **9** as a yellow oil, one spot on tlc (benzene–10% ethanol); ir ($CHCl_3$) 5.87, 5.99 (weak), 6.87, 6.93, 7.28, 7.37, 8.99, 9.19, 10.52, 11.00 μ; nmr ($CDCl_3$), see Table II; mass spectrum *m/e* 184, 152, 98, 71. Vpc analysis (15% Carbowax 20M, 150°) of the product showed it to be a mixture of two components in a 30:70 ratio. The two ketones were separated by preparative vpc (SE-30, 130°); the resulting pure components showed only slight differences in the infrared: major component 5.87, 5.99 (weak) μ; minor component 5.87, 6.09 (weak) μ. The major ketone isomer was identical in all respects with an independently synthesized sample of **9** (see below).

c. **π-Allyl Complex 11.** The yellow solid precipitated from the chloroform extract was recrystallized from chloroform to give material which decomposed at 160–190°; ir (KBr) 2.99, 3.45, 6.11, 6.60, 6.91, 7.00, 7.30, 7.41, 7.65, 8.50, 8.66, 9.02, 9.25, 9.59, 9.85, 10.12, 10.50, 10.65, 10.85, 11.15, 12.75, 14.3 μ; nmr ($CDCl_3$, 90 MHz), see Table II.

Anal. Calcd for $C_{11}H_{19}OPt_2Cl_3 \cdot H_2O$: C, 19.38; H, 3.10; Pt, 57.23; Cl, 15.60. Found: C, 19.41; H, 3.11; Pt, 57.10; Cl, 15.61.

Hydrogen gas was bubbled through a solution of 23 mg of **11** in 6 ml of absolute ethanol for 15 min. The resulting black precipitate was removed by filtration and the filtrate was concentrated to 1 ml; vpc analysis of this solution showed tetrahydrogeranyl methyl ether as the only product.

A slurry of 36 mg of **11** in 1 ml of hexane was stirred vigorously with 1 ml of 10% aqueous potassium cyanide for 10 min. Vpc analysis (3% Carbowax 20M, 130°) of the hexane layer revealed two components, t_R 4.4 and 5.7, in a 5:95 ratio, respectively. Authentic samples of *cis*-**6** and **6** had t_R 4.9 and 5.7 under the same conditions.

A mixture of 20 mg of **11**, 0.09 ml of diene **6**, and 1 drop of concentrated hydrochloric acid in 0.9 ml of water and 1.1 ml of ethanol was stirred at room temperature for 4 days. Filtration of the resulting suspension and recrystallization of the solid from ether gave 6 mg of σ-complex **7**, mp 146–149°. The ketone **9** was detected by tlc (benzene–10% ethanol) examination of the filtrate.

d. **Unidentified Complex.** Removal of the preparative tlc band with $R_f < 0.5$ gave 200 mg of a red oil which showed one major and two minor spots on tlc (benzene–10% ethanol). Repeated preparative tlc purification of the mixture gave 123 mg of a red oil, one spot on tlc; ir ($CHCl_3$) 3.40, 6.89, 6.95, 7.28, 7.50, 7.62, 8.12, 9.02, 9.20, 9.30, 9.75, 10.45 μ; nmr ($CDCl_3$) δ 1.85 (3, satellites, J = 46), 2.25 (3, satellites, J = 79), 2.60 (m, 3), 3.35 (s, 3), 3.4–4.7 (m, 5). The oil turned black upon standing at room temperature for 1 day.

e. **Longer Reaction Time.** To a solution of 425 mg (1.02 mmol) of K_2PtCl_4 in 5 ml of distilled water were added 6 ml of absolute ethanol and 0.48 ml of geranyl methyl ether (**6**). The mixture was stirred at room temperature for 15 days; the resulting white precipitate was filtered to yield 285 mg (0.357 mmol, 70%) of σ-complex **7**, mp 141–146° dec. Treatment of the filtrate in the same manner as before resulted in the isolation of 125 mg (0.680 mmol, 67%) of ketone **9**.

Synthesis of 2,6-Dimethyl-8-methoxy-6-octen-3-one (9). A solution of 1.68 g (10.0 mmol) of geranyl methyl ether (**6**) in 46 ml of 1,2-dimethoxyethane and 14 ml of water was cooled to 5° (ice bath) and 1.75 g (9.85 mmol) of *N*-bromosuccinimide was added.[18] The reaction mixture was stirred at room temperature in the dark for 24 hr, and was then concentrated to *ca.* one-third its original volume by distillation under reduced pressure. The residue was extracted with ether and the organic layer was washed with saturated aqueous sodium chloride, dried over sodium sulfate, and evaporated to leave 2.80 g of yellow oil. The crude product was chromatographed on 84 g of silica gel–15% water; elution with hexane–20% ether afforded 2.01 g (7.58 mmol, 76%) of geranyl methyl ether monobromohydrin, one spot on tlc (benzene–10% ethanol); ir (CCl_4) 2.82, 2.92, 3.40, 6.00, 6.90, 7.30, 7.52, 7.80, 8.05, 9.00, 9.25, 10.50, 11.00, 11.60 μ; nmr ($CDCl_3$) δ 1.28 (s, 6, $(CH_3)_2CO$), 1.63 (s, 3, vinyl CH_3), 1.7–2.3 (m, 4), 2.40 (s, 1, OH), 3.22 (s, 3, OCH_3), 3.82 (m, 3, vinyl CH_2O, and CHBr), 5.27 (t, 1, J = 7, vinyl H).

To a solution of 2.01g (7.58 nmol) of the bromohydrin in 90 ml of methanol was added 4.16 g of anhydrous potassium carbonate and the mixture was stirred at room temperature overnight. The inorganic salts were precipitated by addition of 90 ml of ether and removed by filtration. After evaporation of the filtrate, the residue was dissolved in hexane and dried over sodium sulfate. Evaporation of the hexane afforded 1.12 g (6.09 mmol, 80%) of the epoxide **10** as a light yellow oil, one spot on tlc (benzene–10% ethanol); ir ($CHCl_3$) 3.40, 6.01, 6.92, 7.30, 8.12, 8.94, 9.21, 10.54, 11.02, 11.50 μ; nmr ($CDCl_3$) δ 1.18 and 1.22 (6, $(CH_3)_2CO$), 1.63 (s, 3, vinyl CH_3), 1.7–2.4 (m, 4), 2.60 (t, 1, J = 6, CHO), 3.18 (s, 3, OCH_3), 3.78 (d, 2, J = 7, vinyl CH_2O), 5.24 (t, 1, J = 7, vinyl H).

The monoepoxide **10** (100 mg, 0.544 mmol) was added to a slurry of 64 mg (0.60 mmol) of anhydrous lithium perchlorate in 3 ml of benzene,[19] and the mixture was refluxed for 48 hr. The reaction mixture was diluted with ether, washed with saturated aqueous sodium chloride, dried over sodium sulfate, and evaporated to afford 95 mg of an orange oil. The material was chromatographed on 5 g of silica gel–10% water and eluted with hexane–10% ether to give 50 mg (50%) of the ketone 9 as a pale yellow oil, identical in all respects with the major ketone isomer previously isolated.

Deuteration Experiments. **a.** To a solution of 425 mg (1.02 mmol) of K_2PtCl_4 in 5 ml of deuterium oxide and 6 ml of ethanol-d_1 was added 0.48 ml of geranyl methyl ether (**6**) and the mixture was stirred at room temperature for 5 days. The resulting suspension was filtered to give 158 mg of impure σ-complex **7**. The nmr spectrum ($CDCl_3$) of a recrystallized sample of this material was identical with that of **7** prepared in undeuterated solvent, except for singlet absorptions at 0.84 and 1.17 superimposed upon doublets (J = 7) centered at the same positions; the peak height of the singlet was somewhat less than one-half the sum of the heights of doublet lines (exact measurements were impossible due to partial overlapping of the peaks).

b. The same procedure was followed except that *tert*-butyl alcohol-d_1 was used in place of ethanol-d_1. After stirring at room temperature for 4 days, a yellow precipitate had formed. Removal of a small amount of the solid and analysis of it by ir and tlc indicated it to be a mixture of σ-complex **7** and π-allyl complex **11**. Consequently 4 drops of DCl (20% in D_2O) was added and the mixture was stirred for an additional 2 days. The resulting σ-complex **7** was isolated in the usual manner; its nmr spectrum was essentially the same as described in a above.

c. A slurry of 80 mg of σ-complex **7** in 2.5 ml of deuterium oxide and 3 ml of ethanol-d_1 containing DCl (pH ~2) was stirred at room temperature for 10 days. The complex was recovered by filtration; its nmr ($CDCl_3$) spectrum was identical with that of the starting material.

Reaction of Geranyl Methyl Ether with Zeise's Dimer. a. A solution of 117 mg (0.199 mmol) of tetrachlorobis(ethylene)diplatinum(II)[29] (Zeise's dimer) in 2 ml of anhydrous acetone was cooled to −78° and 0.1 ml of geranyl methyl ether was added. Tlc analysis (benzene–10% ethanol) of the reaction mixture after 45 min indicated the presence of two platinum complexes. Water (0.5 ml) was added to the cold solution and the mixture was warmed to room temperature. After 1 hr at room temperature the initial complexes had disappeared (tlc); after 24 hr, tlc analysis showed the presence of σ-complex **7**, ketone **9**, and products whose tlc polarity was consistent with π-allyl complexes. Preparative tlc separation of the products afforded 5 mg (0.006 mmol, 3%) of **7**, mp 147–150°.

b. The same procedure as above was followed, except for use of acetone-d_6 and deuterium oxide. Nmr analysis, as before, of the isolated σ-complex showed *ca.* 30% deuterium incorporation.

***trans,trans*-1-Methoxy-3,7,11-trimethyl-2,6,10-dodecatriene (*trans,trans*-Farnesyl Methyl Ether) (16).** To a solution of 25.0 g (0.112 mol) of farnesol (Aldrich; 65:35 mixture of trans,trans and cis[27],trans) in 500 ml of 1,2-dimethoxyethane was added 19.7 g of sodium hydride (61% in mineral oil, 0.500 mol). The suspension was stirred at room temperature for 10 min, 28.4 g (0.200 mol) of methyl iodide was added, and the mixture was stirred for 3 days. Methanol was added to destroy the excess hydride and the mixture was poured onto ice and extracted with ether; the ether layer was washed with saturated aqueous sodium chloride, dried over sodium sulfate, and evaporated. Distillation of the residue gave 20.0 g (0.0849 mol, 76%) of the isomeric farnesyl methyl ethers, bp 104–106° (0.1 mm). Spinning-band column distillation of the mixture afforded 5.60 g (0.0238 mol, 21%) of *trans,trans*-farnesyl methyl ether (**16**) in 95% isomeric purity (vpc, 3% SE-30, 130°); ir ($CHCl_3$) 3.42, 6.00, 6.92, 7.28, 8.12, 8.45, 9.00, 9.20, 10.52, 11.00 μ; nmr ($CDCl_3$), see Table III.

Anal. Calcd for $C_{16}H_{28}O$: C, 81.29; H, 11.93. Found: C, 81.02; H, 11.87.

Reaction of Farnesyl Methyl Ether with Dipotassium Tetrachloroplatinate(II). To a solution of 1.27 g (3.06 mmol) of K_2PtCl_4 in 15 ml of distilled water was added 18 ml of *tert*-butyl alcohol and 2.04 ml of *trans,trans*-farnesyl methyl ether. The reaction mixture was stirred at room temperature for 14 days, a yellow solid (95 mg) was removed by filtration, and the filtrate was extracted with chloroform. The chloroform solution was concentrated to *ca.* 10 ml and applied to 2-mm preparative tlc plates which were developed in hexane–15% ethyl acetate.

a. (1-Methoxy-3,7,11-trimethyl-2,10-dodecadiene-6σ,2π)chloroplatinum(II) (17). Removal of the preparative tlc band with R_f 0.7 afforded 92 mg (0.197 mmol, 6.4%) of **17** as a colorless oil, one spot on tlc (hexane–15% ethyl acetate); ir ($CHCl_3$) 3.42, 6.91, 7.00, 7.29, 7.82, 8.10, 8.39, 8.83, 9.11, 9.80, 9.95, 10.15, 10.40, 10.80, 11.15, 12.4 μ; nmr ($CDCl_3$, 90 MHz), see Table III; mass spectrum *m/e* 430–434 (M − HCl), 236 ($C_{16}H_{28}O$); high resolution mass spectrum (M − HCl):

Nominal mass	Exact masses		
	Measured	Calcd	Formula
430	430.1768	430.1767	$C_{16}H_{28}O^{194}Pt$
431	431.1801	431.1787	$C_{16}H_{28}O^{195}Pt$
432	432.1773	432.1789	$C_{16}H_{28}O^{196}Pt$

A solution of 10 mg (0.022 mmol) of the σ-complex **17** in 1 ml of tetrahydrofuran was treated with 11 mg (0.044 mmol) of triphenylphosphine and the mixture was stirred at room temperature for 1 hr. The solvent was removed under reduced pressure and the residue was triturated with hexane. Vpc analysis (10% Carbowax 20M, 60–200°) of the hexane soluble material revealed three components, t_R 14.4, 14.8, and 15.2, in a 17:29:54 ratio, respectively; *cis,trans*- and *trans,trans*-farnesyl methyl ether exhibited t_R 14.8 and 15.2, respectively, under the same conditions.

b. (1-Methoxy-3,7,11-trimethyl-2,6-dodecadiene-10σ,6π)chloroplatinum(II) (18). Removal of the preparative tlc band with R_f ~0.6 afforded 326 mg (0.698 mmol, 23%) of **18** as an oil which showed one elongated spot on tlc (hexane–15% ethyl acetate). Repeated preparative tlc purification of the material did not improve its tlc appearance; ir ($CHCl_3$) 3.46, 6.00, 6.92, 7.30, 7.82, 8.40, 9.12, 9.20, 9.80, 9.97, 10.15, 10.42, 10.80 μ; nmr ($CDCl_3$, 90 MHz), see Table III.

c. 2,6,10-Trimethyl-12-methoxy-6,10-dodecadien-3-one (19). Removal of the preparative tlc band with R_f ~0.55 gave 168 mg (0.668 mmol, 22%) of the ketone **19** as a colorless oil, one spot on tlc; ir ($CHCl_3$) 3.40, 5.85, 6.00, 6.90, 7.26, 8.10, 8.40, 8.99, 9.23, 9.80, 10.50, 10.98; nmr ($CDCl_3$, 90 MHz), see Table III; mass spectrum, *m/e* 252, 237, 220, 71, 43; molecular ion at *m/e* 252.2096 (calcd for $C_{16}H_{28}O_2$, 252.2089). Vpc analysis (10% Carbowax 20M, 200°) of the material revealed two components, t_R 13.5 and 14.8, in a 40:60 ratio, respectively.

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(29) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).