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Metal Hydride Induced Ring-Opening Reactions of Methylenecyclopropane Derivatives. Formation of Butenylplatinum(II) Complexes[1]

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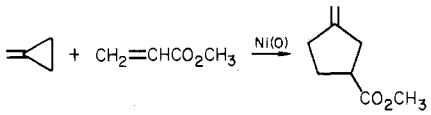
The platinum(II) hydrides *trans*-PtH(solvent)$(PEt_3)_2PF_6$ and *trans*-$PtHX(PEt_3)_2$, X = Cl or NO_3, react with the *trans*- and *cis*-dimethyl esters of Feist's acid stereospecifically with cleavage of the 1,2 bond of the cyclopropane ring to afford the but-3-enylplatinum(II) complexes $\{Pt[CH(COOCH_3)CH(COOCH_3)(CH{=}CH_2)](PEt_3)_2\}X$ and, in some cases, the but-2-enyl complexes $\{Pt[CH(COOCH_3)C(COOCH_3){=}CHCH_3](PEt_3)_2\}X$. Retention of configuration at carbon during ring opening is tentatively assigned on the basis of NMR data. The initial product in all of the reactions is the but-3-enyl isomer which then rearranges to the but-2-enyl isomer. Only the diastereomers formed in the reactions of the trans diester were found to undergo this isomerization to the but-2-enyl complex. The but-2-enyl complex when X = Cl has a solvent-dependent structure. In methanol the chloride is anionic and an ester carbonyl occupies the fourth coordination site on platinum. In chloroform or dichloromethane the chloride displaces the coordinated carbonyl to give the η^1-allylic complex *trans*-$Pt[CH(COOCH_3)C(COOCH_3){=}CHCH_3]Cl(PEt_3)_2$. The corresponding reaction of the cis diester gives the but-3-enyl complex *cis*-$Pt[CH(COOCH_3)CH(COOCH_3)(CH{=}CH_2)]Cl(PEt_3)_2$ rather than the but-2-enyl isomer. When X = NO_3, a mixture of the but-3-enyl and but-2-enyl isomers is isolated. Upon standing in solution, this mixture isomerizes to the but-2-enyl complex.

Introduction

The reactions of methylenecyclopropane derivatives and the complexes of the platinum-group metals have received a great deal of attention recently. The major impetus for such studies arises from the ability of transition metals (1) to catalyze the rearrangement of highly strained hydrocarbons and (2) to catalyze [2 + 2] cycloaddition reactions of methylenecyclopropanes. Paquette et al.[2] have demonstrated the utility of Ag(I)-catalyzed ring-opening reactions of strained hydrocarbons. Nickel(0) complexes have been reported to act as catalysts in oligomerization and codimerization reactions of methylenecyclopropanes.[3,4] In some reactions the cyclopropane ring is opened, while in others the ring remains intact.



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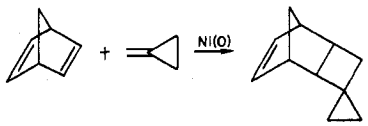

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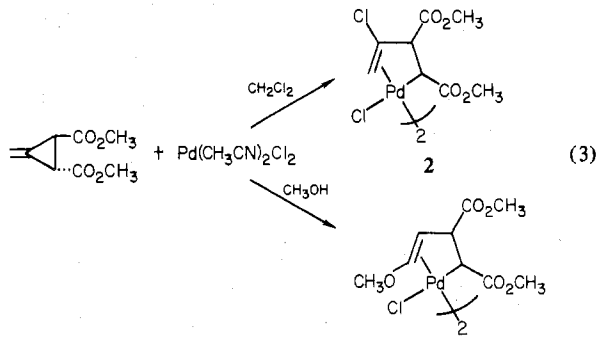
A variety of organometallic complexes have been isolated from the reactions of methylenecyclopropane derivatives and zerovalent and divalent complexes of palladium and platinum. η^3-Allylpalladium complexes have been isolated from the reactions of methylenecyclopropane and 2,2-diphenylmethylenecyclopropane and $Pd(PhCN)_2Cl_2$.[5] The palladium(II) salt cleaves the 1,2 bond of methylenecyclopropane and the 2,3 bond of the diphenyl derivative to give these allylic complexes. In contrast to these results, a similar reaction of *trans*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate (the dimethyl ester of Feist's acid), *trans*-**1**, and $Pd(CH_3CN)_2Cl_2$ affords the but-3-enylpalladium(II) derivatives, **2** and **3**, in dichloromethane and methanol, respectively.[6,7] A communication describing the formation of η^3-allylplatinum(II) complexes from the reaction of methylenecyclopropane and *trans*-$PtH(NO_3)(PPh_3)_2$ appeared during the course of this work.[8] The syntheses of a number of η^2-methylenecyclopropane derivatives of Ir(I), Rh(I), Pt(0), and Pt(II) have been reported by Green et al.[9] X-ray crystallographic studies confirm the η^2 nature of the bonding of the methylenecyclopropane ligand and show that no ring opening or formal oxidative insertion of the metal has occurred in these reactions.



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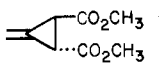
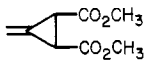
In view of the facile opening of the cyclopropane ring in these reactions with Pd(II) salts, it was felt that the reactions of platinum(II) hydrides and methylenecyclopropane derivatives would lead to ring-opened products rather than methylcyclopropyl- or cyclopropylplatinum(II) products formed by 1,2 addition of the Pt–H bond across the exocyclic double bond of the methylenecyclopropane. Herein are described the results of studies of the reactions of *trans*-$PtHCl(PEt_3)_2$ and several of its derivatives with *trans*- and *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate, *trans*-**1** and *cis*-**1**. A preliminary communication of this work has already been published.[10]



trans-**1**



cis-**1**

Results and Discussion

Both cationic and neutral bis(triethylphosphine)platinum(II) hydrides react with *trans*-**1** and *cis*-**1** to afford alkylplatinum(II) complexes that contain either a but-3-enyl or a but-2-enyl group. The reactivity of these hydrides can be correlated to the leaving-group ability of the ligand trans to the hydride. Thus, for the cationic hydrides and for neutral hydrides having good leaving groups such as nitrate, the reactions are essentially complete upon mixing. However, when the trans ligand is a poor leaving group such as chloride, much longer reaction times (ca. 8 days) are required. The products are isolated as white crystalline solids or colorless oils. All attempts to induce crystallization of these oils failed. They were, therefore, treated with $NaBPh_4$ and characterized as the crystalline BPh_4 salts. The physical properties and spectral data are given in Tables I–III.

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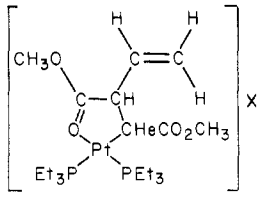
Table I. Analytical Data, Melting Points, and Infrared Spectra of Some But-3-enyl and But-2-enylplatinum(II) Complexes

complex	mp, °C	% C		% H		IR spectra,[e] cm^{-1}	
		calcd	found	calcd	found	ν(CO)[b]	ν(C=C)
4	116-117	32.13	32.70	5.53	5.83	1675 s, 1599 s	1635 sh
5	139-140	32.13	32.53	5.53	5.31	1678 s, 1600 s	1632 sh
8	124-125	57.33	57.48	6.67	6.65	1687 s, 1591 s	1644 w
10	oil	*a*	*a*	*a*	*a*	1700 s, 1572 s[c]	
11	oil	*a*	*a*	*a*	*a*	1720-1700 s (br)[d]	
12	140-144	37.65	37.61	6.48	6.37	1731 s, 1701 s	1631 w
14	101-102	57.33	57.65	6.67	6.44	1678 s, 1599 s	

[a] Compound not analyzed. [b] Nujol mull. [c] CH_3OH solution. [d] CH_2Cl_2 solution. [e] Abbreviations: s, strong; w, weak; sh, shoulder; br, broad.

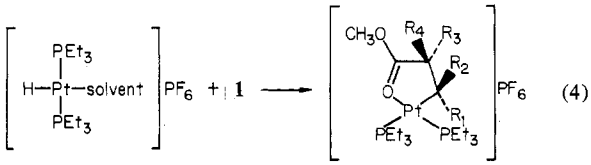
Table II. ^{1}H NMR Spectra[a] of Some But-3-enylplatinum(II) Complexes



complex	X	H_a	H_b	H_c	H_d	H_e	OCH_3	PCH_2	PCH_2CH_3
4[b]	PF_6	5.92 m J(ac) = 18 J(ab) = 10 J(ad) = 7.2	5.19 dt J(ab) = 10 J(bc) = 1.3 J(bd) = 1.3	5.19 dt J(ac) = 18 J(bc) = 1.3 J(cd) = 1.3	3.80 m J(de) = 5.2	2.79 m J(de) = 5.2 $J(P_c$-e) = 3 $J(P_t$-e) = 9.5	4.16 s, 3.69 s	2.0 bm	1.38 t 1.11 t J(HH) =7.5
5[b]	PF_6	5.79 m J(ac) = 17 J(ab) = 9.2 J(ad) = 7	5.18 d J(ab) = 9.2	5.16 d J(ac) = 17	3.71 m J(de) < 1	2.46 m J(de) < 1 $J(P_c$-e) = 3 $J(P_t$-e) = 10	3.93 s, 3.50 s	1.81 bm	1.14 t 0.92 t J(HH) = 7.5
13[b]	NO_3	5.87 m J(ac) = 17 J(ab) = 9 J(ad) = 7	5.20 d J(ab) = 9	5.16 d J(ac) = 17	*d*	2.47 m J(de) < 1 $J(P_c$-e) = 3 $J(P_t$-e) = 10	3.97 s, 3.48 s	1.85 bm	1.18 t 0.90 t J(HH) = 7.5
15[c]	NO_3	5.95 m J(ac) = 17 J(ab) = 10 J(ad) = 7.2	5.15 d J(ab) = 10	5.18 d J(ac) = 17	*d*	2.86 m J(de) = 6 $J(P_c$-e) = 3 $J(P_t$-e) = 12	4.07 s, 3.59 s	1.9 bm	1.28 t 1.06 t J(HH) = 7.5
14[b,e]	BPh_4	5.77 m J(ac) = 17 J(ab) = 10 J(ad) = 7.2	5.22 d J(ab) = 10	5.18 d J(ac) = 17	3.89 m J(ad) = 7.2 $J(P_t$-d) = 3.4 $J(P_t$-d) = 40	2.42 m J(de) < 1 $J(P_c$-e) = 2 $J(P_t$-e) = 9.6	3.65 s, 3.52 s	1.5 bm	1.04 t 0.83 t J(HH) = 7.5
7[b,f]	Cl	5.62 m J(ac) = 17 J(ab) = 10 J(ad) = 7	4.92 dd J(ab) = 10 J(bc) = 1.8	5.02 dd J(ac) = 17 J(bc) = 1.8	*d*	*g*	3.54 s, 3.43 t J(PtH) = 4.8	1.95 bm	1.09 t 1.04 t J(HH) = 8

[a] Chemical shifts are in ppm relative to Me_4Si. J are in hertz. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; dd, doublet of doublets; dt, doublet of triplets; qd, quartet of doublets; m, multiplet; bm, broad multiplet. [b] In $CDCl_3$ solution. [c] In CD_3OD solution. [d] Signal lies under CH_3O resonance. [e] BPh_4, 7.4-6.9 m. [f] See text for structure. Numbering system based upon chelated structure given above. [g] Signal lies under PEt_3 resonance.

Reactions of Feist's Esters with Cationic Platinum(II) Hydrides. Addition of 1 equiv of either *trans*-**1** or *cis*-**1** to a methanol solution of *trans*-$PtH(CH_3OH)(PEt_3)_2PF_6$ or to an acetone solution of *trans*-$PtH((CH_3)_2CO)(PEt_3)_2PF_6$ gave after concentration of the solution and recrystallization from methanol white crystals of the but-3-enylplatinum(II) salts **4** and **5**. The structures of **4** and **5** are assigned on the basis



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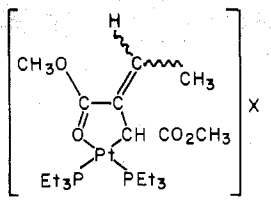
4, **5**

	product	R_1	R_2	R_3	R_4
for *trans*-**1**	**4**	CO_2CH_3	H	$CH{=}CH_2$	H
for *cis*-**1**	**5**	CO_2CH_3	H	H	$CH{=}CH_2$

of infrared and NMR data, as well as elemental analyses. A ν(CO) in the infrared spectra between 1675 and 1680 cm^{-1} is assigned to the uncoordinated ester carbonyl on C-1 of the but-3-enyl ligand. A second ν(CO) which is shifted to considerably lower wavenumbers at approximately 1590–1600 cm^{-1} is assigned to the coordinated ester carbonyl on C-2. This large shift to lower wavenumbers is indicative of the reduced C–O bond order resulting from coordination of the carbonyl to the platinum. In addition to the two strong ν(CO) absorptions, a weak absorption between 1630 and 1645 cm^{-1} is assigned to the ν(C=C) of the but-3-enyl ligand.

The ^{1}H NMR spectra of **4** and **5** are consistent with a structure in which the carbonyl rather than the C=C bond is coordinated to the platinum. An ABC pattern of relative intensity 3 between 5.1 and 6.0 ppm is assigned to the three vinylic protons of the but-3-enyl group. The C=C bond is not coordinated to the platinum since these resonances appear in the normal olefinic region of the NMR spectrum. A large

Table III. ^{1}H NMR Spectra[a] of Some But-2-enylplatinum(II) Complexes



complex	X	H_a	H_e	OCH_3	PCH_2	PCH_2CH_3	comments
8[b]	BPh_4	6.50 q J(a-CH_3) = 7	3.24 dd $J(P_c\text{-}e)$ = 4 $J(P_t\text{-}e)$ = 9.5	3.63 s, 3.51 s	1.6 bm	1.06 t 0.85 t J(HH) = 8	BPh_4, 7.5-6.9 m CH_3 lies under PEt_3
10[c]	Cl	6.52 q J(a-CH_3) = 7	3.20 dd $J(P_c\text{-}e)$ = 3 $J(P_t\text{-}e)$ = 9	3.91 s, 3.44 s	1.8 bm	1.17 t 0.88 t J(HH) = 7.5	CH_3 lies under PEt_3
11[b,d]	Cl	6.66 qd J(a-CH_3) = 7.3 J(ae) = 2.5	4.13 m	3.68 s, 3.52 t J(PtH) = 4.5	1.95 bm	1.10 qu J(HH) = 8	CH_3 lies under PEt_3
16[c]	NO_3	6.73 q J(a-CH_3) = 7	3.38 dd $J(P_c\text{-}e)$ = 2.2 $J(P_t\text{-}e)$ = 9.3	4.10 s, 3.60 s	1.9 bm	1.28 t 1.06 t J(HH) = 7.5	CH_3 lies under PEt_3

[a] Chemical shifts are in ppm relative to Me_4Si. J are in hertz. Abbreviations given in Table II. [b] In $CDCl_3$ solution. [c] In CD_3OD solution. [d] See text for structure. Numbering system based upon chelated structure given above.

upfield shift would be expected upon coordination of the C=C bond to the platinum. The cis stereochemistry of the two PEt_3 ligands was assigned from the pair of triplets for the methyl groups of the PEt_3 ligands. A pair of triplets is expected when the two phosphines have a cis stereochemistry, while a 1:4:6:4:1 quintet is expected when the phosphines have a trans geometry.[11,12]

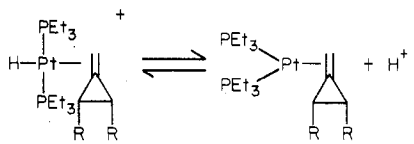
Stereochemistry. Complexes **4** and **5** are diastereomers due to the presence of the two chiral carbons of the but-3-enyl ligand. Since **4** and **5** have different NMR spectra, the stereospecificity of these reactions can easily be monitored by NMR spectroscopy. Both reactions occur with 100% stereospecificity since **5** was not detected in the reactions of *trans*-**1**, and **4** was not detected in the reactions of *cis*-**1**. By using molecular models it can be shown that the dihedral angle between the two vicinal protons on C-1 and C-2 is approximately 20° for one diastereomer and approximately 90° for the other. When the dihedral angle between vicinal hydrogens is between 80 and 90°, the coupling constant between these protons is approximately zero. The coupling constant increases from 0 to about 8 Hz as the dihedral angle decreases from 90 to 0°.[13] The structure of the but-3-enyl complex formed by the ring opening of *cis*-**1** has been assigned to **5**, in which the dihedral angle is approximately 80–90° since J(HH) < 1 Hz. Similarly, **4** has been assigned to the diastereomer with a dihedral angle between these two hydrogens of approximately 20° since J(HH) = 5.2 Hz. Stereochemically, if these assignments are correct, the ring opening of *trans*-**1** and *cis*-**1** by platinum(II) hydrides occurs with retention of configuration at the α carbon. Such assignments are consistent with the X-ray crystallographic studies of Green which show unequivocally that the ring opening of *trans*-**1** by $Pd(CH_3CN)_2Cl_2$ to give but-3-enylpalladium(II) complexes occurs with retention of configuration at the α carbon.[14] Unequivocal proof of the stereochemical changes in the reactions described above must be provided by the X-ray crystallographic structure determination of either **4** or **5**.

The reaction of the corresponding deuteride, *trans*-$PtD(CH_3OH)(PEt_3)_2PF_6$, and *trans*-**1** afforded $\{Pt[CH(COOCH_3)CH(COOCH_3)(CD{=}CH_2)](PEt_3)_2\}PF_6$, **4**-*d*. The NMR spectrum of **4**-*d* clearly showed that the deuterium is located exclusively on C-3 of the but-3-enyl group. Thus the overall result of the ring-opening reaction is cleavage of the 1,2 bond of the cyclopropane ring with the platinum adding to C-2 and the hydride adding to C-1 of the cyclopropane ring.

Interestingly, this same isomer, **4**-*d*, is isolated with approximately 55–60% deuterium incorporation at C-3 from the reaction of *trans*-$PtH(CH_3OH)(PEt_3)_2PF_6$ and *trans*-**1** in methanol-d_1. Since the hydride starting material is stable to H–D exchange under the reaction conditions, exchange between a hydride ligand and the deuterated methanol must occur with a hydride intermediate formed during the reaction. Presumably the hydride ligand is released into solution as a proton, the proton exchanges with the deuterated solvent, and then D^+ subsequently attacks the resulting platinum(0) complex. H–D-exchange reactions with deuterated methanol have been previously observed in the addition reactions of platinum(II) hydrides and acetylenes.[15] The equilibrium

$$[HPt(RC{\equiv}CR)L_2]^+ \rightleftharpoons L_2Pt(RC{\equiv}CR) + H^+ \quad (5)$$

was postulated to account for such behavior. This equilibrium is favored to the right for acetylenes with electron-withdrawing substituents and the vinylic addition products are isolated with one deuterium in the vinyl group. When the equilibrium is favored to the left, no incorporation of deuterium in the products is observed. Equilibria such as eq 5 may be present in all insertion reactions of platinum(II) hydrides with olefins and acetylenes. The lability of the hydride is dependent upon the substituents of the unsaturated hydrocarbon and the stabilizing ligands on the platinum. That an equilibrium such as eq 6 may exist is supported by our success in isolating the



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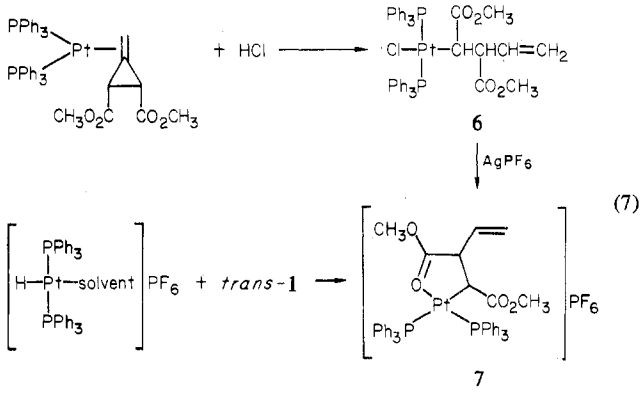
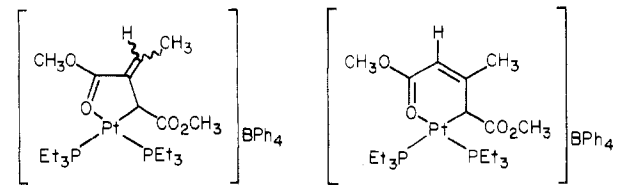
platinum(0) olefin complex (*cis*-1-methylenecyclopropane-2,3-dicarboxylic anhydride)bis(triphenylphosphine)platinum(0) from the reaction of *trans*-$PtH(CH_3OH)(PPh_3)_2PF_6$ and the cis anhydride of Feist's acid.[10] Furthermore, the addition of anhydrous HCl to a solution of $Pt(PPh_3)_2$(*trans*-**1**) gives in high yield the but-3-enyl complex *trans*-$Pt[CH(CO_2CH_3)CH(CO_2CH_3)(CH{=}CH_2)]Cl(PPh_3)_2$, **6**.[16] Removal of the chloride ligand with $AgPF_6$ in methanol affords white crystals

of **7**. Complex **7** is also isolated from the reactions of *trans*-**1** and *trans*-$PtH(CH_3OH)(PPh_3)_2PF_6$.[10]

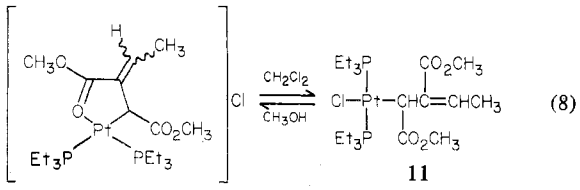


Reaction of Feist's Esters with Neutral Platinum(II) Hydrides. The 1,2-cyclopropane ring of Feist's esters is cleaved by neutral platinum hydrides to give both but-3-enyl and but-2-enyl complexes. The reaction of *trans*-**1** and *trans*-$PtHCl(PEt_3)_2$ affords a colorless oil after chromatography on Florisil. All attempts to induce crystallization failed; therefore, methanolic $NaBPh_4$ was added and the white crystals of the BPh_4 salt precipitated. On the basis of the infrared and NMR data, two possible structures can be suggested for the structure of this BPh_4 salt, **8** and **9**. Both are consistent with the



infrared spectrum which has two carbonyl absorptions at 1687 and 1571 cm^{-1}, assigned to the uncoordinated and the coordinated carbonyls, respectively. Structures **8** and **9** are differentiated on the basis of the coupling constant between the olefinic proton and the methyl group on the C=C bond in the NMR spectrum. The broad quartet (J = 7 Hz) of relative intensity 1 is assigned to this olefinic proton. The coupling constant of 7 Hz is the expected value for a *geminal* coupling constant between the olefinic proton and the methyl group in structure **8**. A coupling constant of 0–3 Hz would be expected for the coupling constant in structure **9**. That **8** is the correct structure is supported by the observations that, in some cases, but-3-enyl complexes will isomerize to these but-2-enyl complexes. Structure **9** would result from cleavage of the 2,3-cyclopropane bond rather than the 1,2 bond of the cyclopropane ring. The methyl group of the but-2-enyl ligand lies under the large resonance of the methylene protons of the PEt_3 ligands. The stereochemistry of the substituents on the C=C bond of the but-2-enyl group cannot be definitively assigned. The side of the double bond that contains the uncoordinated ester carbonyl does appear to be less sterically hindered than the side that contains the coordinated carbonyl in molecular models.

The structure of the initial product isolated from the reaction of *trans*-**1** and *trans*-$PtHCl(PEt_3)_2$ is solvent dependent. In methanol both the infrared and the NMR spectra are consistent with the ionic structure **10**, analogous to **8**. The infrared spectrum indicates the presence of both a coordinated and an uncoordinated carbonyl, while the NMR spectrum is essentially identical with that of **8**. The pair of triplets for the methyl groups of the PEt_3 ligands are indicative of the cis stereochemistry at platinum. In dichloromethane or chloroform the structure of the complex is **11** with the chloride



coordinated to platinum. The infrared spectrum in dichloromethane has two broad, poorly resolved ν(CO) absorptions between 1720 and 1690 cm^{-1} consistent with the presence of two uncoordinated carbonyls rather than one coordinated and one uncoordinated carbonyl. The NMR spectrum in $CDCl_3$ has a well-resolved doublet of quartets of relative intensity 1 which is assigned to the olefinic proton. The triplet (J(PtH) = 4.5 Hz) at 3.52 ppm in chloroform and the singlet at 3.44 ppm in methanol are assigned to the methyl ester on the α carbon. The chemical shift of this group shows little dependence upon solvent or structure. The methyl ester on the β carbon does, however, exhibit a large chemical shift difference which is dependent upon structure. The singlets at 3.68 and at 3.91 ppm are assigned to this methyl group in chloroform and methanol, respectively. The methyl groups of the PEt_3 ligands appear as a 1:4:6:4:1 quintet indicative of a trans geometry of the PEt_3 ligands on platinum. These observations are best explained in terms of the equilibrium between the ionic complex **10** and the neutral complex **11**. Dissociation of the chloride ligand and subsequent coordination of a carbonyl is favored in protic solvents such as methanol.

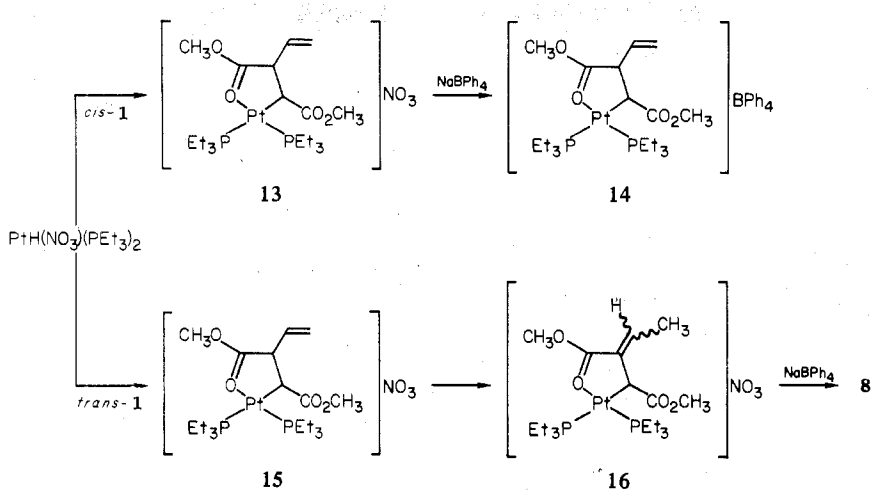
Allylplatinum(II) chloride complexes have previously been shown to have dynamic structures in solution.[17,18] An equilibrium between a neutral η^1-allyl species and a cationic η^3-allyl species has been suggested to account for this behavior and has been supported recently by the isolation and crystallographic determination of single crystals of the η^1-allyl complex *trans*-$Pt(CH_2CH{=}CH_2)Cl(PPh_3)_2$, isolated from bulk solutions of the η^3-allylic species.[19] In the equilibrium described above, the chelated ionic structure **10** which is trapped by coordination of a carbonyl predominates in methanol solutions rather than a η^3-allylic structure, while the η^1-allylic structure **11** predominates in chloroform solutions.

Complex **11** is also isolated by addition of CsCl to a methanolic solution of the corresponding nitrate **16**, which is readily prepared in high yield from the reaction of *trans*-**1** and *trans*-$PtH(NO_3)(PEt_3)_2$. This metathetical reaction is the preferred method for the preparation of **11** because long reaction times are required to obtain **11** from the reactions of *trans*-**1** and *trans*-$PtHCl(PEt_3)_2$.

The reaction of *cis*-**1** and *trans*-$PtHCl(PEt_3)_2$ afforded the but-3-enyl complex *cis*-$Pt[CH(COOCH_3)CH(COOCH_3)(CH{=}CH_2)]Cl(PEt_3)_2$, **12**, rather than a but-2-enyl complex isomeric with **10**. The two ν(CO) absorptions at 1731 and 1701 cm^{-1} are consistent with two uncoordinated carbonyls. The C=C bond is uncoordinated since the vinylic protons appear as an ABC multiplet of relative intensity 3 between 4.9 and 5.7 ppm. The cis geometry of the PEt_3 ligands gives rise to a pair of triplets for the methyl groups of the PEt_3 ligands. Presumably the presence of the chloride ligand does not require coordination of a carbonyl in order that the platinum obtain a four-coordinate, square-planar geometry. Thus, the reactions of *trans*-$PtHCl(PEt_3)_2$ and *trans*-**1** afford but-2-enyl complexes, while the corresponding reactions with *cis*-**1** give neutral but-3-enyl complexes. This difference in reactivity of *cis*-**1** and *trans*-**1** in these reactions will be discussed in a subsequent paper.

The reactions of *trans*-$PtH(NO_3)(PEt_3)_2$ and *trans*-**1** and *cis*-**1**, unlike the corresponding reactions of *trans*-$PtHCl(PE_3)_2$, are rapid. This difference in reactivity is, of course, related

Scheme I



to the coordinating ability of the trans ligand in methanol. The reaction of *cis*-**1** afforded the but-3-enyl complex **13** (Scheme I) as a colorless oil which was subsequently treated with $NaBPh_4$ and characterized as the BPh_4 salt, **14**. The reaction of *trans*-**1** gives, after concentration of the reaction mixture, a mixture of both the but-3-enyl complex **15** and the but-2-enyl complex **16**. Upon standing, this mixture isomerizes to the but-2-enyl complex which is subsequently isolated as the BPh_4 salt, **8**. Complexes **13** and **15**, like **5** and **4**, are the diastereomers formed in the reactions of *cis*-**1** and *trans*-**1**, respectively.

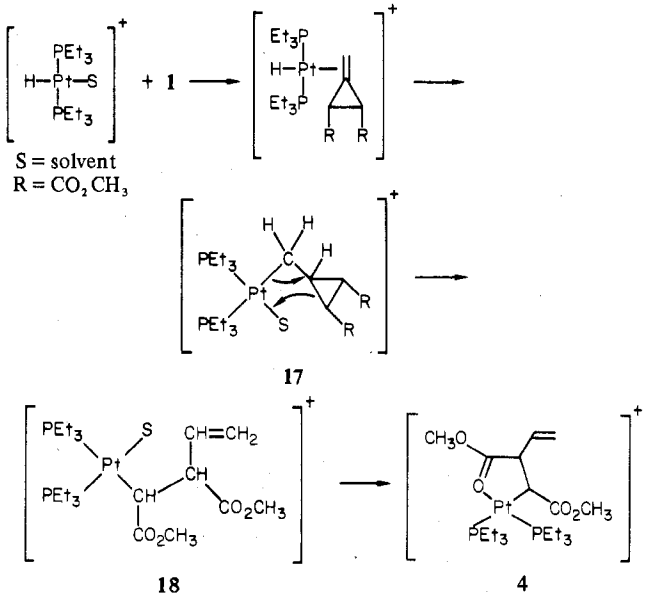
Both but-3-enyl and but-2-enyl complexes are isolated from these reactions of methylenecyclopropane derivatives with platinum(II) hydrides. In some cases, the but-3-enyl complexes initially formed isomerize to the but-2-enyl complexes. This is supported by the observations that a mixture of but-3-enyl and but-2-enyl species isolated from these reactions will upon standing isomerize to the but-2-enyl complex. The but-3-enyl ligand results from cleavage of the 1,2 bond of the cyclopropane ring. A suggested mechanism for this ring-opening reaction is depicted in Scheme II. Addition of the Pt–H bond across the exocyclic double bond of the methylenecyclopropane gives the methylcyclopropyl species **17**. Facile ring opening of this cyclopropyl species gives the but-3-enyl complex **18**. The four-coordinate geometry of the platinum is subsequently satisfied by coordination of the ester carbonyl group on the β carbon.

While both palladium(II) salts and platinum(II) hydrides appear to cleave the cyclopropane ring in a similar fashion to give but-3-enyl products, the mode of chelation of the but-3-enyl group to give the square-planar products is different. The fourth coordination site is occupied by the C=C bond of but-3-enyl ligand with palladium, while the ester carbonyl on the β carbon occupies this site in the platinum complexes. Since the sizes of platinum and palladium are approximately the same, this difference is not related to the size of the chelate ring. Therefore, these differences presumably are due to differences in the electronic and steric requirements of the ancillary ligands. The steric requirement of the larger PEt_3 ligands may not permit the coordination of the C=C bond to the platinum. Such arguments are supported by the observation that addition of 2 mol of pyridine to the palladium complex **2** causes dissociation of the C=C bond and gives the η^1 but-3-enyl complex $Pd[CH(COOCH_3)CH(COOCH_3)(CCl{=}CH_2)]Cl(py)_2$.[14] Addition of pyridine to **4**, on the other hand, results in the isomerization of **4** to a but-2-enyl complex analogous to **16**.[16]

Experimental Section

The following compounds were prepared by literature methods:

Scheme II



trans-1-methylenecyclopropane-2,3-dicarboxylic acid,[20] *trans*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate,[21] *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate,[22] *trans*-$PtHCl(PEt_3)_2$,[23] *trans*-$PtH(NO_3)(PEt_3)_2$,[24] *trans*-$PtDCl(PEt_3)_2$.[25]

Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer as Nujol mulls or in dichloromethane or methanol solutions and were calibrated with a polystyrene film. Proton NMR spectra were obtained on a Varian T-60 spectrometer at 60 MHz or on a Varian CFT-20 spectrometer at 80 MHz with Me_4Si as an internal standard. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Ind.

Preparation of $\{Pt[CH(COOCH_3)CH(COOCH_3)(CH{=}CH_2)](PEt_3)_2\}PF_6$, 4 and 5. To a rapidly stirred solution of 280 mg (0.60 mmol) of *trans*-$PtHCl(PEt_3)_2$ in 10 mL of methanol was added 161 mg (0.57 mmol) of $AgPF_6$ in 5 mL of methanol. After removal of the AgCl by centrifugation, the resulting solution was treated with 100 mg (0.59 mmol) of *trans*-**1**. The solution was stirred for 1 h and then concentrated, and upon cooling of the mixture, white crystals of **4** precipitated. Recrystallization from methanol gave 320 mg (75%) of **4**. Similarly, **5** was isolated in 72% yield from the reaction of *trans*-$PtH(CH_3OH)(PEt_3)_2PF_6$ and *cis*-**1**.

Preparation of $\{Pt[CH(COOCH_3)CH(COOCH_3)(CD{=}CH_2)](PEt_3)_2\}PF_6$, 4-*d*. **4**-*d* was isolated from the reaction of *trans*-**1** and *trans*-$PtD(CH_3OH)(PEt_3)_2PF_6$. **4**-*d* was also isolated with 55–60% D from the reaction of *trans*-$PtH(CH_3OD)(PEt_3)_2PF_6$ and *trans*-**1** in CH_3OD. The percentage of deuterium in **4**-*d* was determined by integration of the vinyl protons between 5.1 and 6.0 ppm in the NMR spectrum.

Preparation of *trans*-Pt[CH(COOCH$_3$)C(COOCH$_3$)=CHCH$_3$]Cl(PEt$_3$)$_2$. Method A. A solution of 280 mg (0.60 mmol) of *trans*-PtHCl(PEt$_3$)$_2$ and 100 mg (0.57 mmol) of *trans*-**1** in 0.5 mL of methanol was placed in an NMR tube, and the reaction was followed by NMR spectroscopy. After 8 days, the solvent was removed and the residue chromatographed on Florisil with dichloromethane. Removal of the solvent gave the title compound as a colorless oil.

Method B. The addition of 1 equiv of CsCl dissolved in methanol to a concentrated solution of **16** in methanol gave immediate precipitation of $CsNO_3$. The volume of the solution was reduced by half, the $CsNO_3$ was filtered off, and the resulting solution was evaporated to dryness to give the product as a colorless oil.

Preparation of *cis*-Pt[CH(COOCH$_3$)CH(COOCH$_3$)(CH=CH$_2$)]Cl(PEt$_3$)$_2$, 12. A solution of 280 mg (0.60 mmol) of *trans*-PtHCl(PEt$_3$)$_2$ and 100 mg (0.57 mmol) of *cis*-**1** in 0.5 mL of methanol was placed in an NMR sample tube and the reaction monitored by NMR spectroscopy. After 8 days, the solvent was removed and the residue was chromatographed on Florisil with dichloromethane. Addition of hexane gave 294 mg (81%) of **12** as white crystals.

Preparation of {Pt[CH(COOCH$_3$)CH(COOCH$_3$)(CH=CH$_2$)](PEt$_3$)$_2$}X (X = NO$_3$, BPh$_4$), 13 and 14. Method A. To a methanol solution of *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ was added 1 equiv of *cis*-**1**. The solution was stirred for 10 min and the solvent was evaporated. The residue was chromatographed on Florisil with dichloromethane and the resulting solution evaporated to dryness to give **13** as a colorless oil. A methanol solution of **13** was treated dropwise with 1 equiv of $NaBPh_4$ in methanol, and **14** immediately precipitated. Recrystallization from dichloromethane–methanol gave white crystals of **14** in 81% yield. Complex **14** was also isolated in 75–80% yield by each of the following methods.

Method B. White crystals of **14** precipitate from a methanol solution of *trans*-PtHX(PEt$_3$)$_2$ (X = Cl, NO$_3$), $NaBPh_4$, and *cis*-**1**.

Method C. The complex was also obtained from the metathetical reaction of **12** and $NaBPh_4$ in methanol.

Preparation of {Pt[CH(COOCH$_3$)CH(COOCH$_3$)(CH=CH$_2$)](PEt$_3$)$_2$}NO$_3$, 15. To a methanol solution of 200 mg (0.40 mmol) of *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ was added 69 mg (0.40 mmol) of *trans*-**1**. The solution was stirred 10 min and the solvent was evaporated to give a colorless oil. The NMR spectrum of this oil showed the presence of **15** and a small amount of **16**. All attempts to isolate **15** as a crystalline solid failed. The structure of **15** was assigned on the basis of its NMR spectrum.

Preparation of {Pt[CH(COOCH$_3$)C(COOCH$_3$)=CHCH$_3$](PEt$_3$)$_2$}NO$_3$, 16. Complex **15** slowly isomerizes in either methanol or dichloromethane. All attempts to isolate **16** as a solid failed. The structure of **16** is based upon its NMR spectrum and was further characterized as the BPh_4 salt, **8**.

Preparation of {Pt[CH(COOCH$_3$)C(COOCH$_3$)=CHCH$_3$](PEt$_3$)$_2$}BPh$_4$, 8. Method A. To a solution of 200 mg (0.43 mmol) of *trans*-PtHCl(PEt$_3$)$_2$ and 146 mg (0.43 mmol) of $NaBPh_4$ in 5 mL of methanol was added 73 mg (0.43 mmol) of *trans*-**1**. After 4 days, the resulting crystals were filtered and recrystallized from dichloromethane–methanol to give 396 mg (78%) of **8**.

Method B. White crystals of **8** immediately precipitated in 81% yield upon addition of 1 equiv of *trans*-**1** to a methanol solution of *trans*-PtH(NO$_3$)(PEt$_3$)$_2$ and $NaBPh_4$.

Method C. Complex **8** was isolated in 75% yield upon addition of methanolic $NaBPh_4$ to a solution of **10**.

Method D. Addition of 1 equiv of $NaBPh_4$ to a methanol solution of **16** gave crystals of **8** in 85% yield.

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Registry No. **4**, 65914-82-1; **4**-*d*, 67584-13-8; **5**, 65914-82-1; **7**, 65942-32-7; **8**, 67584-15-0; **10**, 67584-16-1; **11**, 67584-17-2; **12**, 65912-99-4; **13**, 67650-24-2; **14**, 67650-25-3; **15**, 67651-13-2; **16**, 67598-74-7; *trans*-PtHCl(PEt$_3$)$_2$, 16842-17-4; *trans*-PtH(CH$_3$OH)(PEt$_3$)$_2$PF$_6$, 64459-44-5; *trans*-**1**, 14750-79-9; *cis*-**1**, 51019-97-7; *trans*-PtD(CH$_3$OH)(PEt$_3$)$_2$PF$_6$, 67584-19-4; *trans*-PtH(NO$_3$)(PEt$_3$)$_2$, 19582-28-6.

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