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Thermal Reactions of Platinacyclobutanes: Olefin and Pyridinium Ylide Formation[1]

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Complexes derived from the insertion of Pt(II) into alkyl-substituted cyclopropanes react under mild conditions to produce either olefin or ylide complexes of Pt(II). The course of the reaction is dependent upon the identity of the Lewis base present, since ylide complexes are formed only when pyridine is present, whereas olefin complexes are the sole products in the presence of acetonitrile. The nature of the ring substituents is also important, as platinacyclobutanes substituted on two carbon atoms give only olefin complexes in all solvents. The isolated, thermodynamically more stable, forms of the platinacyclobutanes, PtCCRR′CR″, are not reactive, and the initial step in each case is isomerization to the more sterically constrained PtCCR″CRR′ ring system. Depending upon conditions, this complex reacts to form either the terminal olefins C=CR″CRR′ or the pyridinium ylide complexes $(C_5H_5N)PtCl_2C(H)(C_5H_5N)(CHR''CHRR')$. These results are explained by a mechanism involving β elimination of a ring proton to form an intermediate π-allylplatinum hydride. If steric interactions are severe in this intermediate, immediate reductive elimination to the olefin complex occurs, whereas sterically nondemanding allyls persist long enough to allow attack by pyridine, with subsequent ylide formation.

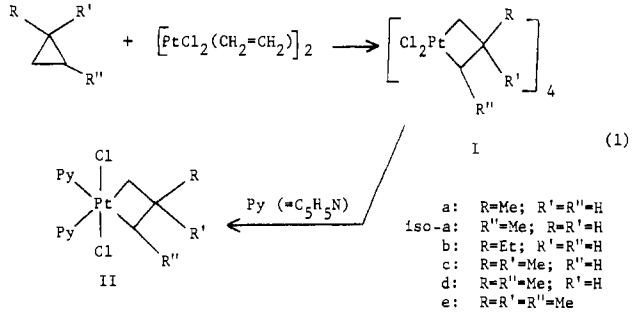
Reactions of organic compounds containing strained (three- or four-membered) rings are frequently promoted by transition-metal complexes.[2] Many of these reactions are believed to involve metallacycloalkanes as intermediates, and in certain cases evidence for such intermediates is compelling. For example, metallacyclobutanes have been implicated not only in the isomerizations of cyclopropanes but also in such diverse reactions as olefin metathesis,[3] carbene elimination from cyclopropanes,[4] the stereospecific polymerization of olefins by Zeigler–Natta catalysts,[5] and in [2 + 2] cycloadditions.[6] In recent years a variety of isolable metallacycloalkanes have been prepared, both by ring closure techniques and, in the case of platinum group metals, by direct insertion into the carbon–carbon bond of a cyclopropane ring. There has been no direct evidence for the transformation of a metallacycloalkane to a metal–olefin complex, although such an isomerization has been implicated in several cases. Certain cyclopropanes react with metal complexes to form olefins and olefin complexes,[7-10] but the intermediacy of metallacyclobutanes has not been demonstrated. Similarly, platinacyclobutanes decompose thermally and photochemically to give mixtures of olefin and cyclopropane,[11-13] but no evidence for metal–olefin complexes as intermediates has been reported. Several other reactions such as the formation of β,γ-unsaturated ketones from cyclopropanes[14], the oxidation of cyclopropanes in the presence of metal complexes,[15,16] and the reactions of metal–neopentylidene complexes with olefins[17] give products which are explicable only if a metallacycle to metal–olefin isomerization step is involved, but again no direct observation of the isomerization has been made.

We have previously reported the synthesis and characterization of several alkyl-substituted platinacyclobutanes,[18] and we have also noted the isomerization of one of these complexes to an olefin complex of platinum(II).[19] Our preliminary results indicated that such an isomerization is a general reaction for alkyl-substituted platinacyclobutanes, and we report herein on the details of this process.

The parent compound of this series, the platinacyclobutane derived from cyclopropane, has been reported to isomerize to a pyridinium ylide complex of platinum(II).[20-22] We have found that, under certain conditions, several alkyl-substituted platinacyclobutanes undergo similar transformations. The structures of the ylide complexes observed here raise some doubt about the validity of the mechanism of formation originally proposed[23] and strongly suggest a common intermediate in the formation of both olefins and ylides from alkylplatinacyclobutanes.

Results

The reactions of methyl-, ethyl-, 1,1-dimethyl-, *trans*-1,2-dimethyl-, and 1,1,2-trimethylcyclopropane with Zeise's dimer in refluxing diethyl ether yield[18] the corresponding platinacyclobutanes Ia–e and iso-Ia as pale yellow powders which are insoluble in solvents with which they do not react (eq 1).



(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) For recent reviews, see: Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461; Sarel, S. *Acc. Chem. Res.* **1978**, *11*, 204; Graziani, M.; Lenarda, M.; Ros, R.; Belluco, U. *Coord. Chem. Rev.* **1975**, *16*, 35.
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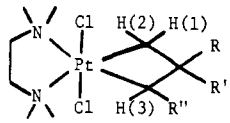
Table I. ^{1}H NMR Spectra ($CDCl_3$) of *N,N,N',N'*-Tetramethylethylenediamine Adducts



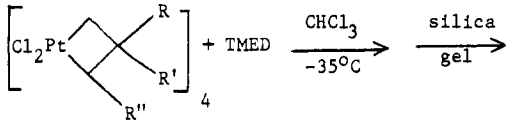
III

complex	substituents R	R'	R''	chemical shift, δ[a] R	R'	R''	H(1)	H(2)	H(3)
IIIa	CH_3	H	H	0.89 (d, 3 H, J(HH) = 6.0, J(PtH) = 4.0)	2.6 (m, 5 H)				
iso-IIIa	H	H	CH_3	2.6 (m, 5 H)		0.62 (d, 3 H, J(HH) = 6.0, J(PtH) = 26.0)			
IIIb	CH_2CH_3	H	H	0.74 (t, 3 H, J(HH) = 7.0), 1.30 (q, 2 H, J(HH) = 7.0)	2.25 (m, 5 H)				
IIIc	CH_3	CH_3	H	1.03 (s, 6 H, J(PtH) = 4.0)		2.40 (s, 4 H, J(PtH) = 84.0)			
IIId	CH_3	CH_3	CH_3	0.93 (s, 3 H, J(PtH) = 4.0)	1.07 (s, 3 H, J(PtH) = 4.0)	0.61 (d, 3 H, J(HH) = 7.0, J(PtH) = 29.0)	[b]	[b]	[b]

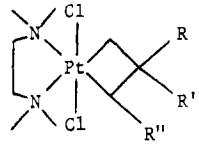
[a] Me_4Si at 0.00 ppm; s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet; all coupling constants are given in hertz. [b] Obscured by TMED resonances.

Although we previously reported very poor yields in the reaction with methylcyclopropane, we now find, in agreement with Puddephatt,[24] that the preparation proceeds smoothly if commercial samples of methylcyclopropane are carefully purified by removal of olefinic impurities.

Dipyridine adducts (IIa–e, iso-IIa) of these insertion products can be prepared by reaction of pyridine with a suspension of the complex in chloroform. Because the complex derived from 1,1,2-trimethylcyclopropane can isomerize to an olefin under these conditions,[19] we have performed all such preparations at low temperatures (ca −40 °C). Although isomerization to olefinic products is negligible under these conditions, the possibility of skeletal isomerization of the platinacyclobutane ring such as has been reported for the complex derived from methylcyclopropane[24-27] cannot be ruled out. This is true because the tetrameric complexes I may be structurally characterized only by dissolution in some coordinating solvent, conditions where isomerization is plausible. In an attempt to circumvent the isomerization problem and in order to confirm the site of initial insertion, we have prepared *N,N,N',N'*-tetramethylethylenediamine (TMED) adducts of several of the insertion products according to eq 2.



I



IIIa-c,e; iso-IIIa

(2)

The isolated products have been characterized by infrared spectroscopy and by ^{1}H NMR spectra with $CDCl_3$ as solvent (Table I). Examination of the spectra in the region δ 0–1.5 shows that isomeric platinacycles are formed only in the products derived from methylcyclopropane (IIIa, iso-IIIa). Skeletal isomerization of the platinacycle does not occur in the presence of TMED,[25] and the low temperatures employed in the synthesis of the TMED adducts should also prevent skeletal isomerization during their formation. In addition, no skeletal isomerizations of the TMED adducts have been observed after $CDCl_3$ solutions were heated to ca. 55 °C for extended periods of time. Thus, the ratio of TMED adducts III/iso-III should be representative of the ratio of the first-formed insertion complexes, suggesting that none of the complexes iso-Ib,c,e were formed in the reaction of the parent cyclopropane with Zeise's dimer. Johnson and Hefty[28] have recently presented inferential evidence that the isomeric complexes iso-Ic and iso-Id are formed in the reaction of Zeise's dimer with 1,1-dimethyl- and *trans*-1,2-dimethylcyclopropane. Olefin distributions following direct injection of THF solutions of product mixtures into a gas chromatograph injection port at 130 °C were consistent with the presence of both isomers. Because of the very different reaction conditions it is not certain that these results are directly relevant to the solution results (for example, Ia and iso-Ia, which have both been shown to be present in solution, gave olefins derived only from iso-Ia in Johnson and Hefty's work). This result does, however, emphasize the need for caution in extrapolating results from one set of conditions to another.

In $CDCl_3$ solution, IIe isomerizes to the olefin complex *trans*-$PyCl_2Pt(CH_2{=}CMeCHMe_2)$.[19] Isomerization is followed by decomposition into the free olefin (2,3-dimethyl-1-butene) and a crystalline yellow solid, identified by its infrared spectrum (ν_{PtCl} = 333 cm^{-1}) and elemental analysis as *trans*-$PtCl_2Py_2$.

An investigation into the scope of this reaction revealed that IId, derived from *trans*-1,2-dimethylcyclopropane, also isomerizes to an olefin complex, *trans*-$PyCl_2Pt(CH_2{=}CMeCH_2Me)$. This product was identified by ^{1}H NMR: δ 4.95 (s, 2 H, J(PtH) = 60 Hz), 1.77 (s, 3 H, J (PtH) = 40 Hz), 1.50 (q, 2 H, J(HH) = 7.0 Hz), 0.97 (t, 3 H, J(HH) = 7.0 Hz). This isomerization is accelerated at elevated temperatures, and is followed by decomposition into uncomplexed 2-methyl-1-butene and *trans*-$PtCl_2Py_2$. In contrast to these results, the complexes derived from methyl-, ethyl-, and 1,1-dimethylcyclopropane, i.e., IIa–c, do not yield olefins or olefin complexes when dissolved in $CDCl_3$ but form pyridinium

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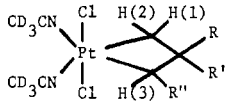
Table II. ^{1}H NMR Spectra (CD_3CN) of Platinacyclobutanes

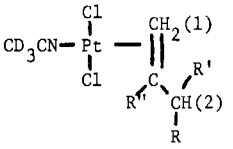


IV

	substituents			chemical shift, δ[a]				
complex	R	R′	R″	R	R′	R″	H(1)	H(3)
IVa	CH_3	H	H	0.87 (d, 3 H, J(HH) = 6.0)	2.40 (m, 5 H)			
iso-IVa	H	H	CH_3	2.40 (m, 5 H)		0.65 (d, 3 H, J(HH) = 6.0, J(PtH) = 36.0)		
IVb	CH_2CH_3	H	H	0.74 (t, 3 H, J(HH) = 6.5), 1.80 (m, 2 H)	b	2.71 (m, 4 H)		
IVc	CH_3	CH_3	H	0.97 (s, 6 H, J(PtH) = 4.0)		2.54 (s, 4 H, J(PtH) = 96.0)		
IVd	CH_3	H	CH_3	0.78 (d, 3 H, J(HH) = 6.0, J(PtH) = 4.0)	b	0.63 (d, 3 H, J(HH) = 6.0, J(PtH) = 36.0)	2.76 (m, 3 H, J(PtH) = 88)	
IVe	CH_3	CH_3	CH_3	0.85 (s, 3 H, J(PtH) = 4.0)	1.00 (s, 3 H, J(PtH) = 4.0)	0.55 (d, 3 H, J(HH) = 7.0, J(PtH) = 35.0)	2.43 (AB pattern)	3.27 (q, J(HH) = 7.0)

[a] Me_4Si at 0.00 ppm; s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet; all coupling constants are given in hertz. [b] Obscured.

Table III. ^{1}H NMR Spectra (CD_3CN) of Olefin Complexes



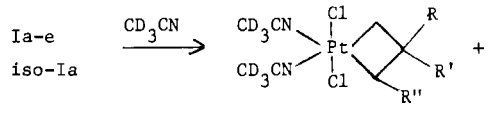
V

	substituents			chemical shift, δ[a]				
complex	R	R′	R″	R	R″	H(1)	R′	H(2)
Va	CH_3	H	H	1.17 (t, 3 H, J(HH) = 7.0)	4.46 (m, 3 H, br)		1.80 (m, 2 H)	
Vb	CH_2CH_3	H	H	0.93 (t, 3 H, J(HH) = 6.0), 1.75 (m, 4 H, br)	4.55 (s, 3 H, J(PtH) = 67.0)		1.75 (m, 4 H, br)	
Vc	CH_3	CH_3	H	1.43 (d, 3 H, J(HH) = 7.0)	4.57 (m, 3 H, br)		1.10 (d, 3 H, J(HH) = 7.0)	2.15 (m, 1 H, br)
Vd	CH_3	H	CH_3	1.27 (t, 3 H, J(HH) = 7.5)	1.80 (s, 3 H, J(PtH) = 42.0)	4.62 (s, 2 H, J(PtH) = 69.0)	b	b
Ve	CH_3	CH_3	CH_3	1.39 (d, 3 H, J(HH) = 7.0, J(PtH) = 4.0)	1.77 (s, 3 H, J(PtH) = 50.0)	4.59 (s, 2 H, J(PtH) = 69.5	1.08 (d, 3 H, J(HH) = 7.0, J(PtH) = 4.0)	2.86 (m, 1 H, J(HH) = 7.0)

[a] Me_4Si at 0.00 ppm; s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; all coupling constants are given in hertz. [b] Obscured by solvent.

ylide complexes of Pt(II) instead (vide infra). Variation of the solvent did not affect these results: IIa–c yielded ylide complexes in $CDCl_3$, C_6D_6, and in CD_3CN, while IId and IIe yielded olefins and *trans*-$PtCl_2Py_2$ in C_6D_6 and in CD_3CN as well as in $CDCl_3$.

Variation of the nitrogeneous base did not have a significant effect on this isomerization process. Dissolution of the complexes Ia–e in CD_3CN results in the initial formation of diacetonitrile adducts (which have not been isolated) according to eq 3. ^{1}H NMR spectra of these solutions show that a



IVa-e

iso-IVa

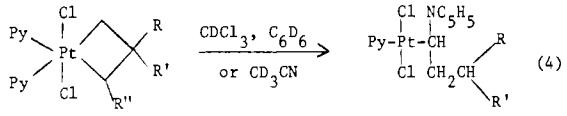
$$(CD_3CN)Cl_2Pt(CH_2{=}CR''CHRR') \quad (3)$$

Va-e

a: R=Me; R′=R″=H
iso-a: R″=Me; R=R′=H
b: R=Et; R′=R″=H
c: R=R′=Me; R″=H
d: R=R″=Me; R′=H
e: R=R′=R″=Me

mixture of the platinacyclobutane (Table II) and olefin complex (Table III) is present in all cases. Also present with the mixture of complexes derived from methyl-, ethyl-, and 1,1-dimethylcyclopropane are some of the parent cyclopropanes. The mixture of platinacycle and olefin complex observed initially in the NMR spectra converts to the olefin complex alone. In each case, the olefin complex formed undergoes slow decomposition into the corresponding free olefin (identified by NMR) and a crystalline precipitate, identified by infrared spectroscopy and elemental analysis as *trans*-$PtCl_2(CD_3CN)_2$ (C–D absorptions at 2325, 2225, and 2200 cm^{-1}; $\nu_{C\equiv N}$ 2100 cm^{-1} and a single strong Pt–Cl absorption at 340 cm^{-1}). The olefins formed from Ia plus iso-Ia, Ib, and Ic in CD_3CN are 1-butene, 1-pentene, and 3-methyl-1-butene, respectively. In all but one case, the NMR spectra were sufficient to unambiguously identify the olefins and to rule out isomeric olefins as products. Confirmation that 1-pentene was the only olefin formed from Ib was provided by gas chromatography.

As mentioned previously, pyridinium ylide complexes form as a result of isomerization of the complexes II derived from methyl-, ethyl-, and 1,1-dimethylcyclopropane according to eq 4. The formation of the ylide complexes is slow at room temperature and somewhat faster at ca. 50 °C and is indicated by a deepening of the yellow color of the solution. The ylide complexes have been identified by elemental analysis and by



IIa-c,f; iso-IIa VIa-c,f

a: R=Me; R'=R"=H
iso-a: R"=Me; R=R'=H
b: R=Et; R'=R"=H
c: R=R'=Me; R"=H
f: R=R'=R"=H

infrared and ^1H NMR spectroscopy (Table IV). Satisfactory elemental analysis of these complexes proved to be difficult to obtain and was impossible to obtain for the complex VIa. As discussed by Gillard and Pilbrow,[23] *trans*-$PtCl_2Py_2$ is formed simultaneously with the ylide complexes, and recrystallization of the ylide complexes was apparently accompanied by some formation of *trans*-$PtCl_2Py_2$ from the ylide complexes themselves.

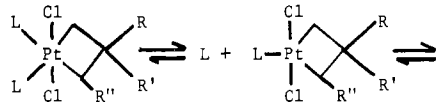
As ylide formation occurs, the NMR spectra exhibit changes in the line shape of the resonances in the region δ 7.0–9.0 arising from the inequivalence of the pyridine ligands in the product. Otherwise, the NMR spectra of the pyridine ylide complexes include a triplet near δ 6.0 (1 H, J(HH) ca. 7.5 Hz), which has ^{195}Pt–^1H spin–spin coupling of ca. 112 Hz, and alkyl resonances corresponding to the remainder of the alkyl chain. These NMR spectra are similar to that of the previously reported ylide complex, VIf, derived from cyclopropane.[20-22] The synthesis of this ylide complex was reproduced here, and its NMR spectrum is nearly identical with that reported in ref 20 (see Table IV). The X-ray crystal structure of this ylide complex has been reported,[21,22] and on the basis of similarities in the ^1H NMR spectra, analogous structures are proposed for the products observed in this work, the only difference being the structure of the alkyl chain.

The infrared spectra of the complexes VIa–c,f are nearly identical, with only slight differences appearing in the region 1000–1200 cm^{-1}. C–H absorptions occur at 3055 (weak) and 2945 cm^{-1} (strong), and a single Pt–Cl stretch (*trans*-dichloro ligands) occurs at 315 cm^{-1}.

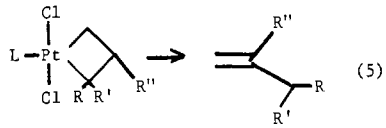
Discussion

The isomerization of a platinacyclobutane to an olefin complex requires a *net* 1,2 hydrogen migration, and isomerization to the pyridinum ylides requires a *net* 1,3 hydrogen migration. As in most hydrogen-transfer reactions involving transition-metal complexes, it is likely that both of these processes include metal hydride intermediates formed by the β-elimination reaction. Full understanding of these reactions, however, requires answers to the following questions. (1) Does β elimination involve the C_2 ring proton or a proton on a C_1 methyl substituent? (2) From which of the isomeric platinacyclobutanes does β-elimination occur? (3) What is the basis for the regiospecificity of these reactions? (4) What are the bases for the effect of ligands and of cyclopropane substituents upon the course of the reactions? (5) Do both reactions involve common intermediates? We believe that our observations may be uniquely accommodated by a mechanism involving β elimination of a C_2 ring proton in the (generally) thermodynamically less stable isomeric platinacycle to form a π-allyl intermediate. Steric interactions within this intermediate then dictate the subsequent steps, toward either olefin or pyridinum ylide, and the stability of the several platinum complexes which form dictates the regiospecificity of both olefin formation and pyridinum ylide complex formation. In the discussion which follows, we detail the arguments which lead to this general mechanism.

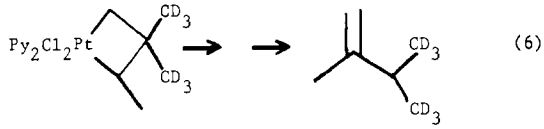
The structure of the product olefins reveals the manner in which hydrogen abstraction occurs. The formation of 2,3-dimethyl-1-butene from complex IIe requires isomerization of the platinacyclobutane structure (to iso-IIe) prior to hydrogen transfer, since the only β-elimination pathway available to IIe involves hydrogen abstraction from the α-methyl substituent. This process would lead to 3,3-dimethyl-1-butene, which is not observed. An alternative process involving α elimination has been ruled out by Johnson and Cheng[29] on the basis of labeling studies. Decomposition of the mixture of IVa and iso-IVa gives only 1-butene, demonstrating that β-hydrogen elimination occurs only from the thermodynamically less stable form iso-IVa. Similarly, the formation of 1-pentene from IVb and 3-methyl-1-butene from IVc requires initial isomerization of the platinacyclobutane as in eq 5. Isomerization of the platinacyclobutane derived from *trans*-1,2-dimethylcyclopropane (IVd) leads to an equivalent platinacyclobutane and, of course, is not reflected in the products. The formation of the linear (or nearly linear) pyridinum ylides from methyl-, ethyl-, and 1,1-dimethylcyclopropane complexes also requires an initial isomerization of this sort, which will be discussed below.



IId,e (L=Pyridine)
IVa-e (L=Acetonitrile)



Several different pathways for the platinacyclobutane isomerization can be conceived. In similar materials, a sequence involving deinsertion of platinum followed by reinsertion into an adjacent bond of the cyclopropane has been ruled out by Casey[30] on the basis of the failure to observe crossover products in the presence of added cyclopropanes. A mechanism involving the intermediacy of a metal–carbene/metal–olefin complex has been ruled out on similar grounds[30] and also because the stereochemical integrity of the organic moiety is maintained.[24,26] As Casey has noted, however, such a mechanism is consistent with the stereochemical results if carbene and alkene rotation is a concerted process. For the complexes derived from 1,1,2-trimethylcyclopropane or methylcyclopropane, the same net isomerization could be produced by a 1,2 methyl shift. In order to examine this possibility, we have prepared 2-methyl-1,1-bis(trideuteriomethyl)cyclopropane and its platinum insertion complex. This complex isomerizes (eq 6) to 2,3-dimethyl-1-butene-d_6 in which

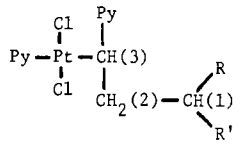


the deuterium labels are in the isopropyl fragment of the molecule, demonstrating that the isomerization does *not* involve a methyl migration. Johnson and Cheng[29] have recently arrived at this same conclusion. The formation of 3-methyl-1-butene starting with the complex derived from 1,1-dimethylcyclopropane is, of course, also incompatible with a methyl migration. Although it is mostly negative, the accumulated evidence supports a concerted isomerization such as has been proposed by Puddephatt[26] and Casey.[30]

In their reactive forms (e.g., iso-Ia–e and various base adducts) all of these complexes contain two distinctly different

(29) Johnson, T. H.; Cheng, S.-S. *J. Am. Chem. Soc.* **1979**, *101*, 5277.
(30) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 4233.

Table IV. ^{1}H NMR Spectra ($CDCl_3$) of Pyridinium Ylide Complexes



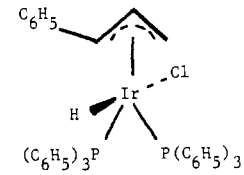
complex	substituents R	substituents R′	chemical shift, δ[a] R	R′	H(1)	H(2)	H(3)
VIa	CH_3	H	0.99 (t, 3 H, J(HH) = 7.0)	1.87 (m, 4 H)			5.88 (t, 1 H, J(HH) = 7.5, J(PtH) = 112.0)
VIb	CH_2CH_3	H	0.97 (t, 3 H, J(HH) = 6.0), 1.49 (m, 6 H, br)	1.49 (m, 6 H, br)			5.95 (t, 1 H, J(HH) = 7.5, J(PtH) = 112.0)
VIc	CH_3	CH_3	1.01 (d, 3 H, J(HH) = 6.0)	1.04 (d, 3 H, J(HH) = 6.0)	2.10 (m, 3 H, br)		6.06 (t, 1 H, J(HH) = 8.0, J(PtH) = 113.0)
VIf[b]	H	H	1.07 (t, 3 H, J(HH) = 7.5)[b]	*b*	*b*	2.43 (m, 1 H),[b] 1.92 (m, 1 H)[b]	5.67 (t, 1 H, J(HH) = 7.5, J(PtH) = 115.0)[b]
VIf[c]	H	H	1.10 (t, 3 H, J(HH) = 7.0)[c]	*c*	*c*	2.25 (m, 2 H, br)[c]	5.83 (t, 1 H, J(HH) = 7.5, J(PtH) = 112.0)[c]

[a] Me_4Si at 0.00 ppm; s = singlet, d = doublet, t = triplet, m = multiplet; all coupling constants are given in hertz. [b] Data reported in ref 20 for ylide complex derived from cyclopropane (220-MHz spectrum). [c] Data observed in this work for ylide complex derived from cyclopropane (60-MHz spectrum).

types of β-hydrogen: those on C_2 of the platinacyclobutane ring and those on methyl or methylene substituents at the C_1 ring carbon. As has been discussed by Whitesides,[31,32] the steric requirements of the platinacyclobutane ring preclude a Pt–C_1–C_2 dihedral angle near 0°. Since β elimination is expected to occur most readily from conformations in which the dihedral angle is 0°, metallacycles are predicted, and found, to undergo β elimination less readily than their acyclic analogues. This suppression of the β elimination of a ring proton should allow other reactions to be observed. Specifically, in these C_1 alkyl substituted platinacyclobutanes, β elimination of an exocyclic hydrogen might be a competitive, or perhaps even dominant, reaction.

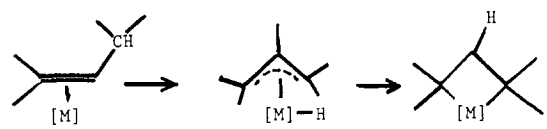
The product observed upon decomposition of IIe does not allow us to distinguish between these two possibilities, since 2,3-dimethyl-1-butene is the predicted product from elimination at either site. On the basis of deuterium-labeling studies, Johnson and Cheng[29] have clearly demonstrated that this reaction does in fact involve β elimination from both sites, although elimination of the C_2 ring hydrogen is preferred. Quantitative data may be complicated somewhat by isotope effects, but it appears that approximately two-thirds of the product arises by hydrogen elimination from C_2. As in the case of the platinacycle derived from 1,1,2-trimethylcyclopropane, the product distribution from the thermal isomerization of the methylcyclopropane complex is ambiguous, since iso-IIa is predicted to give 1-butene by either route. The other metallacycles are expected to give different products from the different elimination processes, yet in each case only a single product—that obtained by elimination of the C_2 ring proton—is observed. Thus, IVb–d give exclusively 1-pentene, 3-methyl-1-butene, and 2-methyl-1-butene, respectively, whereas β elimination from the exocyclic substituent on C_1 is predicted to lead to 2-pentene, 2-methyl-1-butene, and 3-methyl-1-butene, respectively.

We thus propose that the isomerization of platinacyclobutanes to metal–olefin complexes occurs predominantly by β elimination from the ring to form a π-allylplatinum hydride complex. Formation of the π-allyl complex is preceded by reversible loss of the nitrogenous base (acetonitrile or pyridine) and is followed by reductive coupling of the allyl hydride to form a platinum–olefin complex. Although our evidence for a π-allyl metal hydride intermediate comes primarily from product distributions, there is ample precedent for such intermediates. A π-allylmetal hydride intermediate has been invoked in the mechanism of the ring-opening of cyclopropyl fragments to yield isomeric olefins[33] but has never been observed directly. π-Allyl complexes have in fact been isolated from the decomposition of phenyl-substituted platinacyclobutanes, presumably as a consequence of reductive elimination of HCl from an intermediate of the type we propose here.[34] In addition, an attempt to synthesize an iridium metallacyclobutane by reacting phenylcyclopropane with $IrCl(N_2)(P(C_6H_5)_3)_2$ yielded instead the π-allyliridium hydride complex VII.[35] This complex has been characterized by infrared and



VII

^{1}H and ^{31}P NMR spectroscopy and by X-ray crystallography. Furthermore, Green and co-workers[36] have suggested a synthetic sequence for the formation of molybdena- and tungstacyclobutanes (eq 7) which is the reverse of the mechanism proposed here for the isomerization of platinacyclobutanes to olefins.



(7)

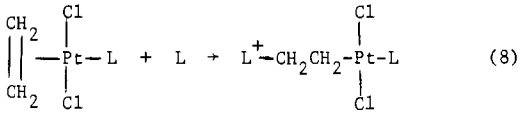
In principle, reductive coupling of the π-allyl/hydride complex could lead to either an internal or terminal olefin. However, the ultimate product observed here is in each case a terminal olefin. This high regioselectivity may be contrasted

(31) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.
(32) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521.
(33) Wiberg, K. B.; Bishop, K. C. *Tetrahedron Lett.* **1973**, 2727.
(34) Irwin, W. J.; McQuillin, F. J. *Tetrahedron Lett.* **1968**, 1937.
(35) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1978**, *100*, 3252; **1979**, *101*, 4201.
(36) Ephritikhine, M.; Green, M. L. H.; Mackenzie, R. E. *J. Chem. Soc., Chem. Commun.* **1976**, 619.

with the results reported[37,38] for the addition of HCl to a series of π-allylic metal complexes. In those cases mixtures of olefins were formed from complexes containing asymmetrical π-allylic groups, some having substitution patterns identical with those in the intermediates proposed here. Our observation that only the least substituted, terminal olefin forms is not surprising since the isomerization takes place within the coordination sphere of the platinum atom *to yield a coordinated olefin.* There is ample precedent for the directive effect of metal–olefin complex formation upon the course of reactions leading to the olefin.[14,39,40] The stability of the Pt–olefin bond is dictated by both steric interactions[41,42] and the electronic perturbation of the platinum-to-olefin π bond by substituents.[41-43] It has been shown that the stabilities of platinum–olefin complexes increase as the electron density at the carbon–carbon double bond is decreased, corresponding to enhanced stability for the smallest degree of alkyl substitution. Since the π-allylplatinum hydride intermediates proposed here lead to relatively stable olefin complexes and since alkylsubstituted terminal olefins from more stable platinum complexes than the isomeric internal olefins, the formation of the more stable olefin complex is to be expected.

The structures of the pyridinium ylide complexes formed upon thermal isomerization of the platinacycles IIa–c are sufficiently unique that most mechanistic pathways for their formation can be eliminated. We believe that pyridinium ylides evolve from the same π-allylplatinum hydride intermediate discussed above, and the evidence which leads to this conclusion is discussed in the following paragraphs.

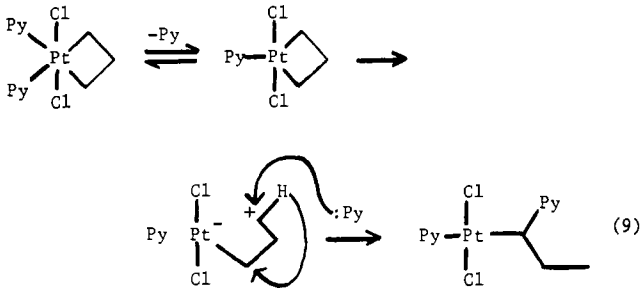
Because the isomerization of platinacyclobutanes to platinum–olefin complexes is firmly established by the data presented above, it is conceivable that pyridinium ylide formation occurs as a result of pyridine attack subsequent to the formation of these metal–olefin complexes. However, the structures of these pyridinium ylide complexes can be contrasted with the products formed in the reaction of free base, L (=pyridine, substituted pyridine, or secondary amine), with olefin complexes of platinum to yield zwitterionic complexes containing Pt–C σ bonds,[44-50] as indicated in eq 8. In such



(8)

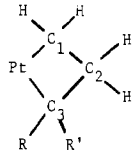
cases the ultimate product is one in which the base is bonded to the β-carbon of the product, e.g., Pt–C–C–N. By contrast, the pyridinium ylide complexes which are formed from platinacyclobutanes all have pyridine bonded in the α-position, e.g., Pt–C–N. This strongly suggests that the pyridinium ylide complexes do not form by attack upon olefin complexes. Recently, Al-Essa and Puddephatt[51] have proposed that the converse is true, e.g., that olefins are formed by decomposition of ylide complexes. However, they propose a reaction sequence involving α elimination in the formation of the ylides, whereas Johnson and Cheng[29] have demonstrated that olefin formation involves β elimination. It is clear that reconciliation of these results will require further investigation.

A study of the kinetics of formation of the ylide complex VIf led Gillard and Pilbrow[23] to propose a mechanism involving initial loss of pyridine followed by cleavage of a Pt–C bond and then attack by pyridine on the resultant ionic intermediate accompanied by a 1,3 hydrogen migration (eq 9). In order



(9)

for this or any other mechanism to explain the products observed in our work, it is necessary to have an initial platinacyclobutane isomerization (eq 5) in order to place the more highly substituted cyclopropyl carbon atom adjacent to platinum. Although the facility of this isomerization has been adequately demonstrated, there is no obvious reason why reaction 9 would be more facile for the isomerized platinacyclobutane. Thus, alternative products might be expected in the Gillard and Pilbrow mechanism, since more highly branched pyridinium ylides would form from the unisomerized platinacyclobutanes. Even if reaction does take place from the isomerized platinacyclobutane, products other than those observed might be expected from the Gillard and Pilbrow mechanism. For a complex with the platinacyclobutane ring VIII, cleavage of either Pt–C_1 or Pt–C_3 could occur. Although



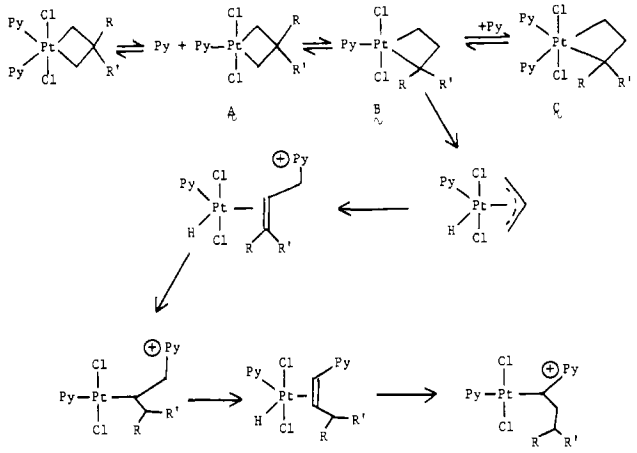
VIII

cleavage of Pt–C_1 would ultimately lead to the proper products, it would require an intermediate primary carbonium ion. By contrast, cleavage of Pt–C_3 would produce a more stable secondary or tertiary carbonium ion (depending on the identities of R and R′). The products of this mode of Pt–C bond fission would be ylide complexes bearing alkyl substituents on the ylidic carbon atom. Consequently, any mechanism involving homolytic fission of a Pt–C bond to yield an ionic intermediate appears unlikely.

As can be seen by comparison of the structures of the ylide complexes VIa–c with those of the olefin complexes Va–c, there is a definite similarity in the structures of the organic moiety in each. This strongly suggests a common intermediate in their formation. As has been discussed, a π-allylmetal hydride complex is the most plausible intermediate in the formation of the olefin complexes Va–e as well as those derived from IId and IIe. We propose that it is this same intermediate

(37) Nixon, J. F.; Wilkins, B. *J. Organomet. Chem.* **1972**, *44*, C25; **1974**, *80*, 129.
(38) Cairns, M. A.; Nixon, J. F. *J. Chem. Soc., Dalton Trans.* **1974**, 2001.
(39) Heinbach, P.; Jolly, P. W.; Wilke, G. *Adv. Organomet. Chem.* **1970**, *8*, 29.
(40) Bogdanovic, B.; Bonnemann, H.; Wilke, G. *Angew Chem.* **1966**, *78*, 591.
(41) Denning, R. G.; Hartley, F. R.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 328.
(42) Hartley, F. R.; Vananzi, L. M. *J. Chem. Soc. A* **1967**, 330.
(43) Denning, R. G.; Hartley, F. R.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 324.
(44) Kaplan, P. D.; Schmidt, P.; Orchin, M. *J. Am. Chem. Soc.* **1968**, *90*, 4175.
(45) Palumbo, R.; DeRenzi, A.; Panunzi, A.; Paiaro, G. *J. Am. Chem. Soc.* **1969**, *91*, 3874. Panunzi, A.; DeRenzi, A.; Palumbo, R.; Paiaro, G. *Ibid.* **1969**, *91*, 3879.
(46) Hollings, D.; Green, M.; Claridge, D. V. *J. Organomet. Chem.* **1973**, *54*, 399.
(47) Pesa, F.; Orchin, M. *J. Organomet. Chem.* **1976**, *108*, 135.
(48) Al-Najjar, I. M.; Green, M. *J. Chem. Soc., Chem. Commun.* **1977**, 212, 926.
(49) Natile, G.; Maresca, L.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1977**, 651.
(50) Natile, G. *J. Chem. Soc., Chem. Commun.* **1978**, 654.
(51) Al-Essa, R. J.; Puddephatt, R. J. *J. Chem. Soc., Chem. Commun.* **1980**, 45.

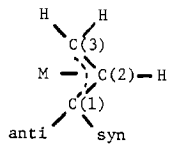
Scheme I



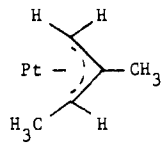
from which the two pathways for olefin and ylide formation diverge. The steps leading to the π-allyl/hydride intermediate are identical in each case. Formation of the π-allylmetal hydride complex is followed by pyridine attack at the unsubstituted terminal carbon atom of the π-allyl ligand. Attack by pyridine will favor the least substituted end of the π-allyl ligand for both steric and electronic reasons. Since pyridine is nucleophilic, the site of lowest electron density in the π-allyl ligand will be the preferred site of attack. This corresponds to the terminal carbon atom with the least alkyl substitution, i.e., the unsubstituted end of the π-allyl ligand. A sequence of olefin insertion, β elimination, and olefin insertion is then proposed to lead to the observed products (Scheme I). This mechanism, which appears most plausible, involves a series of 1,2 hydrogen shifts. Through the use of deuterium labeling, Puddephatt[51] demonstrated that the complex derived from phenylcyclopropane isomerizes via a 1,3 hydrogen shift. Puddephatt proposed a mechanism involving α elimination in order to explain these results. However, as noted above, olefin formation has been shown[29] to involve β elimination. Although it is possible that olefin formation and ylide formation involve totally distinct pathways, the structural similarities which we have noted argue strongly for a common intermediate. It is clear that extensive work is required before the details of these processes can be definitively established.

It should be recalled that ylide formation takes place only for those complexes derived from cyclopropanes which are substituted at only one carbon of the ring. There are two factors which prevent ylide formation and give rise to olefin complexes instead. The first of these is the nature of the ligands on platinum, i.e., pyridine vs. acetonitrile. Acetonitrile is a weaker Lewis base than pyridine and is not capable of forming an ylide complex. The only course open to the π-allyl complex is then reductive elimination to a Pt(II)–olefin complex. This takes place regardless of the substitution pattern on the platinacyclobutane ring when acetonitrile is the ligand. The second factor which promotes olefin formation is the steric hindrance which results from substitution on two of the ring carbon atoms of the starting cyclopropane. Because of steric interactions with the rest of the complex, a terminally monosubstituted π-allylmetal complex preferentially[52] adopts the geometry in which the substituent is in the syn position (IX). However, if the central carbon atom is also substituted, steric interaction between this substituent and that on the terminal carbon atom can favor formation of the anti isomer.

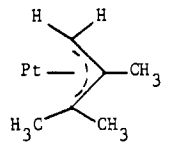
The π-allylplatinum hydride intermediates derived from *trans*-1,2-dimethylcyclopropane and 1,1,2-trimethylcyclopropane are illustrated below as X and XI. In both of these



IX



X



XI

cases, steric factors favor olefin formation. That is, these π-allylmetal hydride complexes are sufficiently destabilized that intramolecular reductive elimination to form olefin complexes becomes fast relative to intermolecular attack by pyridine. When only one carbon atom is substituted, even if it has two substituents as in 1,1-dimethylcyclopropane, the degree of steric compression is insufficient to drive the reaction toward olefin formation, and an ylide complex results.

A required step in these reactions is the skeletal isomerization of the platinacyclobutane to one which has a more highly substituted carbon atom bonded to the platinum atom. In the cases where the platinacycle is derived from a cyclopropane that is gem-disubstituted (i.e., 1,1-dimethyl- and 1,1,2-trimethylcyclopropane) it is easy to see the need for this skeletal isomerization. The formation of a π-allyl moiety is not possible when the β-carbon atom has two alkyl substituents. The necessity for this same type of skeletal isomerization is not as apparent for the monoalkyl-substituted platinacyclobutanes. Since there is a hydrogen atom on the β-carbon atom, the π-allyl complex could form directly. Apparently, the alkyl substituent on the α-carbon atom serves to activate the platinacycle toward π-allyl complex formation through steric interactions with the ancillary ligands on platinum, thus removing this platinacycle (B) from the equilibrium between the isomeric platinacycles (A $\rightleftarrows$ B in Scheme I).

The relative ease with which B is transformed into a π-allylmetal hydride appears to depend largely upon the steric effects of the alkyl substituent(s) in the α-position. When R = Me and R′ = H in B, these steric interactions between the methyl group and the other ligands on Pt are sufficiently small that the dipyridine adduct of B is stable and is observable in the NMR spectrum. In fact, as was discussed for the TMED adduct, the steric compression is small enough so that in the initial insertion step platinum inserts into both the substituted C(1)–C(2) bond and the unsubstituted C(2)–C(3) bond of the methylcyclopropane. Upon increasing the steric bulk of R in going from methylcyclopropane to ethylcyclopropane, B becomes sufficiently destabilized by the steric crowding that its dipyridine adduct C (R = Et, R′ = H) is not observable in the NMR spectrum. Further substitution on this α-carbon atom with two methyl groups increases the steric interactions to such a degree that a noticeable increase in the rate of isomerization is observed when compared to the two cases discussed above. A further increase in the rate is observed when the substitution is extended onto the β-carbon atom, as for the cases derived from *trans*-1,2-dimethylcyclopropane and 1,1,2-trimethylcyclopropane. As has been pointed out, this degree of substitution drives the reaction to olefin formation under all conditions investigated.

Conclusions

The reaction of various methyl- and ethyl-substituted cyclopropanes with Zeise's dimer has been shown to yield alkyl-substituted platinacyclobutanes. Platinum inserts into the least substituted carbon–carbon bond of the starting cyclo-

(52) Clarke, H. L. *J. Organomet. Chem.* **1974**, *80*, 155.

propane, except in the case of methylcyclopropane where a mixture of platinacyclobutanes is formed.

Thermal rearrangement of the complexes L_2Cl_2Pt(alkylcyclopropane) produces olefin complexes or pyridinium ylide complexes of Pt(II), depending on the nature of the ligand L and on the substitution pattern of the ring. When L is acetonitrile, all of the platinacycles investigated yield olefin complexes, but when L is pyridine, pyridinium ylide complexes result from platinacyclobutanes which are substituted at only one carbon atom of the ring.

The structures of both the olefin and the ylide products can only be explained if there is an initial skeletal isomerization of the starting platinacyclobutane in such a manner that platinum becomes bound to the most highly substituted carbon atom. Such an isomeric platinacyclobutane was directly observed only for the complex derived from methylcyclopropane. The similarities in the structures of the ylide and olefin complexes derived from methyl-, ethyl-, and 1,1-dimethylcyclopropane point to a common intermediate in the formation of both types of product. This common intermediate is proposed to be a π-allylplatinum(IV) hydride which is formed by β-hydride elimination from the isomeric platinacyclobutanes.

It is observed that a single olefin is formed from each platinacyclobutane and that in each case the thermodynamically less stable terminal olefin results. However, the fact that the olefin formed is coordinated to platinum indicates that the preferred coordination of a terminal alkene to the metal atom determines the outcome of the hydrogen-transfer process.

The steric bulk of the substituents on the platinacyclobutane ring plays a role at two steps in the isomerization process. First, the preferred formation of olefins and pyridinium ylides from the isomeric platinacyclobutanes which are formed in solution is a result of steric interactions between the alkyl substituent(s) on the carbon adjacent to platinum and the ancillary ligands on the metal atom. This is apparent in the relative rates of isomerization. Second, the exclusive formation of olefins from those platinacyclobutanes which are substituted on two ring carbon atoms is a result of steric interactions between these substituents in the π-allyl/hydride intermediate. These steric effects serve to destabilize the π-allyl/hydride intermediate so that intramolecular reductive coupling to an olefin complex is favored.

Experimental Section

Methylcyclopropane (Columbia Organic Chemicals) was purified to remove olefinic impurities by reaction with aqueous bromine. All other cyclopropanes (Chemical Samples Co. or Columbia Organic Chemicals) were used as received. 1-Pentene (99%) and *trans*-2-pentene were obtained from Pfaultz and Bauer, Inc., 2-methyl-2-butene was purchased from Eastman Kodak Co., and 2-methyl-1-butene (99%), 3-methyl-1-butene (99%) and 2,3-dimethyl-1-butene (99%) were purchased from Chemical Samples Co. All olefins were used as received. Microanalyses were performed by Integral Microanalytical Laboratories, Inc. Infrared spectra in the region 4000–250 cm^{-1} were obtained on a Beckman IR-20-A spectrophotometer. ^1H NMR measurements were recorded on a JEOL C-60HL high-resolution 60-MHz spectrometer and a JEOL JNM-MH-100 100-MHz spectrometer. Gas chromatographic analyses were performed by using a Hewlett-Packard 5700A gas chromatograph with helium carrier gas on a Supelco 10 ft × $^1/_8$ in. column consisting of 10% SP-2100 on 80/100-mesh Supelcoport F-11861.

The tetrameric platinacyclobutanes $[PtCl_2$(alkylcyclopropane)$]_4$ and their dipyridine adducts, $PtCl_2Py_2$(alkylcyclopropane), were prepared as previously described.[18] Complexes derived from methylcyclopropane were prepared in an analogous fashion.

Preparation of $PtCl_2(C_5H_5N)(CH_2{=}CMeCHMe_2)$ from the Olefin. About 0.35 g of Zeise's dimer was dissolved in ca. 15 mL of chloroform in a two-necked, 25-mL, round-bottomed flask. A condenser and drying tube were attached, and 0.5 mL of 2,3-dimethyl-1-butene was added, whereupon an immediate darkening of the orange color of the solution took place. After ca. 1 min, some bubbling took place. Dinitrogen was slowly bubbled through the solution, and it was stirred overnight. Solvent removal yielded a brown liquid which was dissolved in acetone, and 0.2 mL of pyridine was added. A yellow precipitate formed immediately. Water was added to the suspension, increasing the amount of precipitate. After the mixture was cooled at −10 °C for 1 h, filtration yielded a yellow, crystalline solid which was washed with water and dried in vacuo. ^1H NMR spectral analysis of this solid demonstrated that it was $(C_5H_5N)Cl_2Pt(CH_2{=}CMeCHMe_2)$.

Preparation of 1,1-Bis(trideuteriomethyl)-2-methylcyclopropane. (A) Synthesis of Ethyltriphenylphosphonium Bromide.[53] A 50-g sample of triphenylphosphine (Pressure Chemical Co.) and 25 g of ethyl bromide (Fisher Scientific Co.) were refluxed in 500 mL of toluene for 20 h (eq 10). The white product was filtered: yield 46.85 g; mp

$$(C_6H_5)_3P + C_2H_5Br \rightarrow (C_6H_5)_3P(C_2H_5)Br \qquad (10)$$

(uncor) 195.5–199.5 °C (lit. mp 203–204 °C). The mother liquor was retained and recharged with 50 g of triphenylphosphine and 25 g of ethyl bromide for further batches which produced larger yields.

(B) Synthesis of $(CD_3)_2C{=}CHCH_3$.[54] A 6.30-g sample of sodium hydride (57% oil dispersion, Alfa Inorganics) was added to a 1-L, three-necked, round-bottomed flask and washed three times with 50 mL of anhydrous diethyl ether. An N_2 inlet, an addition funnel, and a water condenser were attached to the flask. A dry ice/acetone condenser was placed on top of the water condenser, and the outlet was attached to a dry ice/acetone trap. The system was flushed with dinitrogen, 66 mL of dimethyl sulfoxide (Fisher Scientific Co., certified ACS) was added, and the mixture was heated to ca. 70 °C for ca. 1.5 h until hydrogen evolution ceased and all the sodium hydride was dissolved (eq 11). The resultant blue-green solution of methyl sulfinyl

$$NaH + Me_2SO \rightarrow Na^+{}^-CH_2S(O)Me + N_2 \qquad (11)$$

$$Na^+{}^-CH_2S(O)Me + (C_6H_5)_3P(C_2H_5)Br \rightarrow (C_6H_5)_3P{=}CHCH_3 + NaBr + Me_2SO \qquad (12)$$

$$(C_6H_5)_3P{=}CHCH_3 + (CD_3)_2C{=}O \rightarrow (CD_3)_2C{=}CCH_3 + (C_6H_5)_3P{=}O \qquad (13)$$

carbanion was cooled in an ice/water bath (2–4 °C), and a warm solution of 50 g of ethyltriphenylphosphonium bromide in 126 mL of dimethyl sulfoxide was added slowly over a period of ca. 30 min (eq 12). A red color formed immediately and became more intense as more phosphonium salt was added and as more ethylidenetriphenylphosphorane was formed. Acetone-d_6 (8.50 g) was added to the cold reaction mixture, which was then allowed to warm to room temperature and stirred for 3 h (eq 13). During this time, the color of the solution became brown. The reaction mixture was subsequently heated to 60–70 °C until gas evolution stopped (less than 30 min) and cooled in an ice/water bath, and 600 mL of distilled water was added slowly to control gas evolution. Water addition was accompanied by the formation of triphenylphosphine oxide as a white precipitate. The resulting mixture was then distilled until an aqueous layer began to form in the bottom of the receiving flask (below 95 °C). The distillate was redistilled, with the distillate below 38 °C being collected and stored at −10 °C over anhydrous magnesium sulfate. GC analysis indicated that ca. 84% of the solution was the desired olefin, with diethyl ether and dimethyl sulfoxide being the contaminants.

(C) Synthesis of 1,1-Bis(trideuteriomethyl)-2-methylcyclopropane.[55] A 8.5-g (0.13 mol) sample of zinc powder (Alfa Inorganics), 13 g (0.13 mol) of cuprous chloride (Alfa Inorganics), and 40 mL anhydrous diethyl ether were placed in a 250-mL, three-necked, round-bottomed flask. An N_2 inlet, an addition funnel, and a reflux condenser were attached. The outlet of the reflux condenser was connected to a dry ice/acetone bath. The system was flushed with dinitrogen and then refluxed for 30 min with stirring. Heating was discontinued, and 16.1 g (0.06 mol) of diiodomethane (99%, Aldrich Chemical Co.) was slowly added, resulting in refluxing during addition (see eq 14). The reaction

$$(CD_3)_2C{=}CHCH_3 + Zn + CuCl + Et_2O + CH_2I_2 \longrightarrow \underset{H_2C}{\overset{C(CD_3)_2}{\diagup\diagdown}}CHCH_3 \qquad (14)$$

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mixture was refluxed for 30 min, the heating was discontinued, and ca. 2.25 g (0.03 mol) of $(CD_3)_2C{=}CCH_3$ was added to the reaction mixture, during which refluxing occurred. The reaction mixture was further refluxed for 24 h, and the color changed from grey to purple. The products were distilled into the cold trap by increasing the dinitrogen flow and draining the cooling water from the reflux condenser. This product was distilled, with the distillate below 75 °C being collected. The deuterated trimethylcyclopropane was analyzed by using gas chromatography, and the fraction having a retention time identical with that of a commercial sample of 1,1,2-trimethylcyclopropane was collected. Further characterization was provided by ^1H NMR analysis.

$[PtCl_2$(1,1-bis(trideuteriomethyl)-2-methylcyclopropane)$]_4$. Anhydrous diethyl ether (10 mL), 0.2494 g of Zeise's dimer, and an excess of the hexadeuterated cyclopropane (0.1–0.12 mL) were refluxed in a 10-mL, round-bottomed flask. After 5.5 h, a pale yellow powder was filtered, washed with chloroform and with ether, and dried in vacuo; yield 0.0856 g (28%).

$(C_5H_5N)_2Cl_2Pt$(1,1-bis(trideuteriomethyl)-2-methylcyclopropane). $[PtCl_2$(1,1-bis(trideuteriomethyl)-2-methylcyclopropane$)]_4$ (0.085 g) was suspended in ca. 3 mL of chloroform and cooled in a dry ice/acetone bath. Pyridine (0.04 mL) was added and the mixture allowed to warm slowly. Dissolution took place below −5 °C. The yellow solution was eluted through a short silica gel column by using chloroform as solvent. The effluent was evaporated to dryness and dried in vacuo; yield 0.090 g (73%).

***N,N,N′,N′*-Tetramethylethylenediamine)$PtCl_2$(methylcyclopropane).** IIa (0.057 g) was suspended in 1–2 mL of chloroform and cooled in a dry ice/acetone bath. *N,N,N′,N′*-Tetramethylethylenediamine (0.03 mL, Aldrich Chemical Co.) was added and the mixture allowed to warm slowly. Dissolution took place between −40 and −30 °C. The yellow solution was eluted through a short silica gel column, and the solvent was removed from the yellow effluent. The yellow solid was then dried in vacuo; yield 0.0513 g (66%). *N,N,N′,N′*-Tetramethylethylenediamine adducts of the ethylcyclopropane (72% yield), 1,1-dimethylcyclopropane (55% yield), and 1,1,2-trimethylcyclopropane (97% yield) insertion complexes were prepared in an analogous fashion.

$(C_5H_5N)Cl_2Pt[C(H)(C_5H_5N)(CH_2CHMe_2)]$. IIc (ca. 50 mg) was dissolved in 4 mL of benzene-d_6. The solution was heated in a 50 °C water bath and the formation of the ylide complex monitored by using ^1H NMR. After several days, no platinacyclobutane was detectable in the NMR spectrum, and a yellow precipitate had formed. The yellow solution was filtered and allowed to evaporate to dryness under vacuum (H_2O aspirator), yielding 18 mg (ca. 36%) of VIc. VIb and VIf were prepared in a similar manner.

Registry No. Ia, 77629-62-0; iso-Ia, 77629-63-1; Ib, 68472-65-1; Ic, 68472-64-0; Id, 68508-44-1; Ie, 67235-51-2; I, R = R′ = CD_3, R″ = Me, 77629-64-2; IIa, 68111-87-5; iso-IIa, 68111-86-4; IIb, 68487-93-4; IIc, 68472-68-4; IId, 68111-91-1; IIe, 67605-97-4; IIf, 36569-03-6; II, R = R′ = CD_3, R″ = Me, 77647-93-9; IIIa, 77629-65-3; iso-IIIa, 77629-66-4; IIIb, 77629-67-5; IIIc, 77629-68-6; IIIe, 77629-69-7; IVa, 68111-89-7; iso-IVa, 68111-88-6; IVb, 77629-70-0; IVc, 77629-71-1; IVd, 75597-46-5; IVe, 77629-72-2; Va, 77629-73-3; Vb, 77629-74-4; Vc, 77629-75-5; Vd, 77629-76-6; Ve, 77661-60-0; VIa, 77629-77-7; VIb, 77629-78-8; VIc, 77629-79-9; VIf, 35327-31-2; $PtCl_2(C_5H_5N)(CH_2{=}CMeCHMe_2)$, 67235-52-3; Zeise's dimer, 12073-36-8; 1,1-bis(trideuteriomethyl)-2-methylcyclopropane, 72195-38-1; $(CD_3)_2C{=}CHCH_3$, 1787-45-7; $(C_6H_5)_3P(C_2H_5)Br$, 1530-32-1; $(CD_3)_2C{=}O$, 666-52-4; *trans*-$PyCl_2Pt(CH_2{=}CMeCH_2Me)$, 77629-80-2.

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Novel Reactions of Metal–Metal Bonds. Reactions of $Pd_2\{(C_6H_5)_2PCH_2P(C_6H_5)_2\}_2Cl_2$ with Acetylenes, Olefins, and Isothiocyanates

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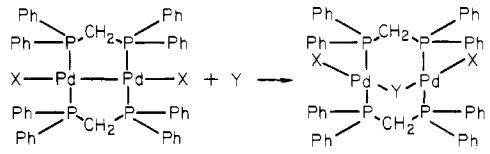
Acetylenes with electron-withdrawing substituents react with $Pd_2(dpm)_2X_2$ (dpm = $(C_6H_5)_2PCH_2P(C_6H_5)_2$; X = Cl, Br, I) to form $Pd_2(dpm)_2(\mu$-acetylene$)X_2$ (acetylene = $C_2(CF_3)_2$, $C_2(CO_2CH_3)_2$, $C_2(CO_2C_2H_5)_2$, HC_2CO_2H, $HC_2CO_2CH_3$) which have been characterized by infrared and $^{31}P\{^1H\}$ and ^1H NMR spectroscopy. These acetylene adducts are resistant to acetylene exchange and to protonation. Reaction with methyl isocyanide yields $[Pd_2(dpm)_2(\mu\text{-}C_2\{CO_2CH_3\}_2)(CNCH_3)_2][PF_6]_2$ which is also formed by reaction of $[Pd_2(dpm)_2(\mu\text{-}CNCH_3)(CNCH_3)_2][PF_6]_2$ with dimethyl acetylenedicarboxylate. $Pd_2(dpm)_2Cl_2$ is a catalyst for the cyclotrimerization of dimethyl acetylenedicarboxylate and $Pd_2(dpm)_2(\mu\text{-}C_2\{CO_2CH_3\}_2)Cl_2$ is formed during the reaction. The reaction of $Pd_2(dpm)_2I_2$ with maleic anhydride results in the formation of $Pd(dpm)I_2$ and two other incompletely characterized products which can also be obtained through the addition of maleic anhydride to $Pd_2(dpm)_3$. Ethylene, norbornadiene, and chlorotrifluoroethene are unreactive toward $Pd_2(dpm)_2Cl_2$. Phenyl and methyl isothiocyanate react with $Pd_2(dpm)_2Cl_2$ to yield $Pd_2(dpm)_2(\mu$-CNR$)Cl_2$ in 50% isolated yield; some $Pd_2(dpm)_2(\mu$-S$)Cl_2$ is formed in the process.

Introduction

Continuing studies in this laboratory have focused on the interaction of $Pd_2(dpm)_2X_2$ (**1**) (dpm = bis(diphenylphosphino)methane, X = halide ion) and $Pd_2(dam)_2X_2$ (dam = bis(diphenylarsino)methane) with small molecules. These dimeric Pd(I) complexes undergo facile and sometimes reversible insertion of a variety of substances, including carbon monoxide,[1,2] sulfur dioxide,[3] atomic sulfur (from cyclooctasulfur or an episulfide),[3] and diazonium ions,[4] into the metal–metal bond. The products are complexes which have become known as molecular A frames.[5] This is shown in eq 1.



(1)

1 **2**

Y = CO, CNR, NNPh, SO_2, S

Tin(II) chloride, however, inserts into the Pd–Cl bonds to form $Pd_2(dpm)_2(SnCl_3)Cl$ and $Pd_2(dpm)_2(SnCl_3)_2$.[6]

We have recently reported that acetylenes also add to **1**.[7] Acetylenes can bind two metal centers in two distinct ways.[7–9]

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