Oxidative Addition and Reductive Elimination Reactions Involving Platinum Metallacycles[1]

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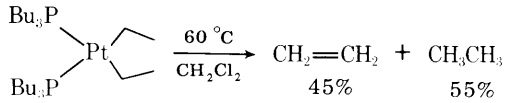
Abstract: Thermal decomposition of a series of platinacycloalkanes $L_2\overline{Pt(CH_2)_nCHR}$ [L = n-Bu_3P, Et_3P; L_2 = $Me_2PCH_2CH_2PMe_2$, 2,2′-bipyridyl; R = H, n = 3,4; R = Me, n = 3] in dichloromethane and dibromomethane solutions generated both cycloalkanes and alkenes derived from the metallacyclic moiety and homologous cycloalkanes and alkenes formed by incorporation of a solvent-derived methylene group. Thermal decompositions of platinacycloalkanes in hydrocarbon or ethereal solutions yielded only alkenes having the same carbon number as the metallacyclic group. These products reflect two competing reaction paths. Olefins are formed by β-hydride elimination. Cycloalkanes and homologated products are generated by decomposition of platinum(IV) intermediates, produced by oxidative addition of dihalomethane to platinum(II) metallacycles. The thermolytic behavior of two model systems [*cis*-$(Bu_3P)_2Pt(CH_2)_4(CF_3)I$ and $(bipy)Pt(CH_2)_4(CH_2Cl)Cl$] support these contentions.

Introduction

Metallacycles[3] are emerging as an important class of intermediates in organic reactions involving transition metals, with characteristic patterns of reactivity significantly different from those of acyclic metal alkyls.[4-9] One major factor contributing to the difference between the reactivity of analogous acyclic and cyclic organometallic substances is the relative rates of β-hydride elimination from them: because this reaction is effectively suppressed in five- and six-membered metallacycles,[6] other types of reactions—normally obscured in alicyclic organometallic compounds—determine the products derived from them. We have reported previously that the thermal decomposition of diethylbis(tri-n-butylphosphine)platinum(II) and 1,4-tetramethylene(tri-n-butylphosphine)platinum(II) in methylene chloride solution illustrates one such characteristic difference in reactivity.[6] The former reaction generates approximately the 1:1 mixture of olefin and alkane characteristic of the formation and decomposition of an intermediate hydridoalkylplatinum species, presumably by initial β-hydride elimination (eq 1).[10,11] The latter reaction produces



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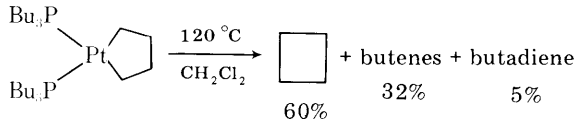

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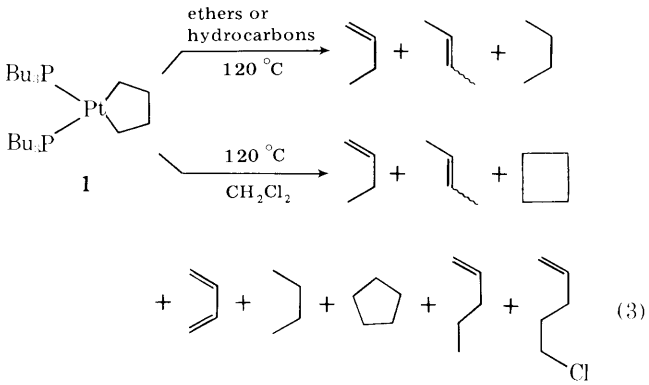
significant quantities of cyclobutane (eq 2). Carbon–carbon bond formation by reductive elimination from transition-metal alkyls is an important reaction in organometallic synthesis and catalysis,[12] but one whose mechanistic determinants are poorly understood. This paper describes an investigation designed to clarify the mechanism of the reaction represented by eq 2. The major conclusion from this work is that oxidative addition of methylene chloride to platinum(II) and generation of a platinum(IV) intermediate precedes reductive elimination of cyclobutane. Thus, the principal result of inhibition of β-hydride elimination is, in this instance, reaction of the tetramethyleneplatinum(II) moiety with methylene chloride.

Results

Products and Kinetics of the Thermal Decomposition of 1,4-Tetramethylenebis(tri-n-butylphosphine)platinum(II) (1) and Derivatives. Thermal decomposition of **1** at 120 °C in nonhalogenated solvents (Et_2O, THF, n-hexane, cyclohexane) yielded only butenes and butane; no detectable cyclobutane was formed (eq 3, Table I). Both the extent of decomposition



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and the product distribution varied slightly with solvent, but the qualitative character of the decomposition remained unchanged. By contrast, decomposition of **1** in methylene chloride solution proceeded more rapidly (by one to two orders of magnitude) and yielded, in addition to linear C_4 products, significant quantities of cyclobutane, cyclopentane, 1-pentene, and 5-chloro-1-pentene (eq 3, Table I). The product distribution was insensitive not only to the starting concentration of **1** over the range of 0.025 to 0.23 M but also to the thermolysis temperature between 80 and 120 °C. Thermal decomposition of **1** in methylene dibromide afforded similar products, although the yield of C_5 materials was significantly higher, and that of cyclobutane lower, than in methylene chloride. The use of 1,2-dibromoethane and carbon tetrachloride as solvents for thermolysis did not yield either cyclobutane or C_5 compounds as detectable products.

The product distribution arising from thermal decomposition of the triethylphosphine analogue of **1** demonstrates the generality of these phenomena. Replacement of the monodentate ligands by 1,2-bis(dimethylphosphino)ethane or 2,2′-bipyridyl produced significant changes in product distribution; in both cases, high yields of C_5 products were generated and the sole platinum-containing species detected was the corresponding dichloride. The 1,5-cyclooctadiene derivative evolved only linear C_4 hydrocarbons in both methylene chloride and hexane (Table I).

Studies of the decomposition of **1** in methylene-d_2 chloride established that the C_5 products in this solvent were dideuterated (≥95%) and that the C_4 products were deuterium free. Protolysis of a solution of **1** during or shortly after completion

[Reprinted from the Journal of the American Chemical Society, **100**, 5808 (1978).]

Table I. Products of Thermal Decomposition of 1,4-Tetramethyleneplatinum(II) Derivatives, $L_2Pt(CH_2)_4$[a]

compd	L	solvent	additive (equiv)	Yield (mol/mol of Pt) × 100[b]											
				□	⬠	⬡	⬡	⬡	⬡	⬠	⬡	⬡	⬡	⬡	CH_4
1	Bu_3P	CH_2Cl_2[c]		35	43	9	4	3	1	7	3			<1	(14)[d]
		CH_2Br_2		4	25	2	3	<1	<1	23	24			12	<1[d]
		$BrCH_2CH_2Br$[e]		1	61	3	11	12	<1						
		CCl_4		3	<1				35						<1[d]
		Et_2O			55	18	10		3(22)[d]						<1[d]
		THF			49	4	7		16(51)[d]						
		n-hexane			17	2	2		1(85)[d]						
		cyclohexane			5	<1	<1		<1(98)[d]						
		Bu_3P			82	9	3		3						
		CH_2Cl_2	Bu_3P (2.0)		76	14	4		18		10			1	
			Et_4NCl (2.0)		69	16	4		1		6			2	
			MAH[f] (10.0)		35	40	20								
			PBQ[f] (10.0)	3	30	20	12								
			Me_3Al (2.0)		27	21	38		5	6	<1				
			L_2NiBr_2 (0.1)	9	58	10	3	2	1	4	6			6	
			$FeCl_3$ (0.1)	32	40	7	3	2	1	6	4				(17)[d]
			H_2O (satd)	12	46	28	5		5	2	2				
	Et_3P		none	24	34	5	2	6	1	11	4			8	(14)[d]
4	bipy[f,g]			4	2	3	<1		1	2	82	2	6		
	dmpe[f]				6	2	3	<1	4	22	25	3	7		
	COD[f,h]				37	35	34		<1						

[a] Decompositions were carried out at 120 ± 0.2 °C for 17 ± 0.25 h using solutions originally 0.025 M in organoplatinum compound, unless indicated otherwise. [b] A blank in the table signifies that the indicated product was sought explicitly but was not observed. (Yields of 0.1% would have been detected.) [c] 5-Chloro-1-pentene (3%) was also detected as a product. Very similar product distributions were observed in CD_2Cl_2, except that the C_5 products contained two deuterium atoms. [d] Yields detected following treatment of the reaction mixture with 12 N aqueous HCl; methane yields quoted are maxima observed. [e] 1-Hexene (2%), 1,5-hexadiene (3%), and cyclohexane (2%) were also detected as products. [f] Abbreviations: dmpe, bis(1,2-dimethylphosphino)ethane; COD, 1,5-cyclooctadiene; bipy, 2,2′-bipyridyl; MAH, maleic anhydride; PBQ, *para*-benzoquinone. [g] Decomposition at 180 °C. [h] The cyclooctadiene recovered from this reaction was 100% 1,3-isomer (61 mol %, based on platinum). A platinum mirror was produced.

of decomposition generated appreciable methane. The triethylphosphine analogue behaved similarly.

The decomposition of **1** in methylene chloride followed first-order kinetics for close to two half-lives ($k_{120} = 1.0 \times 10^{-4} s^{-1}$; $\tau_{1/2} = 1.9$ h). The evolution of cyclobutane and butenes was first order during this period. After two half-lives, the decomposition accelerated, and butenes were the only further products generated. For comparison, the decomposition of 1,4-tetramethylenebis(triphenylphosphine)platinum(II) in methylene chloride at 120 °C—a reaction which generated no significant C_5 products (<1% 1-pentene)—followed first-order kinetics with $k_{120} = 0.54 \times 10^{-4} s^{-1}$.[6]

It was not practical to examine the influence of added tri-*n*-butylphosphine on the course of decomposition of **1**. Addition of 2 equiv of phosphine to a solution of **1** suppressed the formation of cycloalkanes, slightly increased the yield of butane and 1-pentene, and accelerated the rate of decomposition by a factor of ten (Table I). Independent studies established, however, that tri-*n*-butylphosphine reacted rapidly with methylene chloride at 120 °C and released, among other products, 1 equiv of chloride ion. The presence of 2 equiv of tetraethylammonium chloride in decomposing solutions of **1** in methylene chloride produced changes in rates and products distribution similar to those observed on addition of tri-*n*-butylphosphine. Thus, there is no simple way of distinguishing the influence of added phosphine from that of chloride ion generated by reaction of phosphine with methylene chloride. Addition of an excess (tenfold) of maleic anhydride or benzoquinone to a methylene chloride solution of **1** did not increase the yield of cyclobutane observed on thermolysis, as might have been expected by analogy with the behavior of related 1,4-tetramethylenenickel(II) species.[13,14] Instead, like tri-*n*-butylphosphine (or chloride ion), these electron-withdrawing olefins wholly or partially suppressed the formation of cyclobutane and also of the C_5 products and led to butenes as the

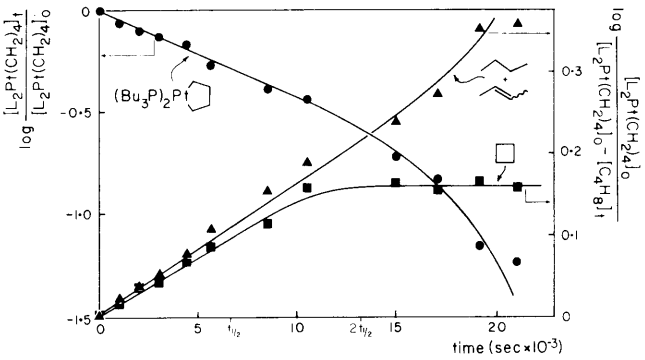
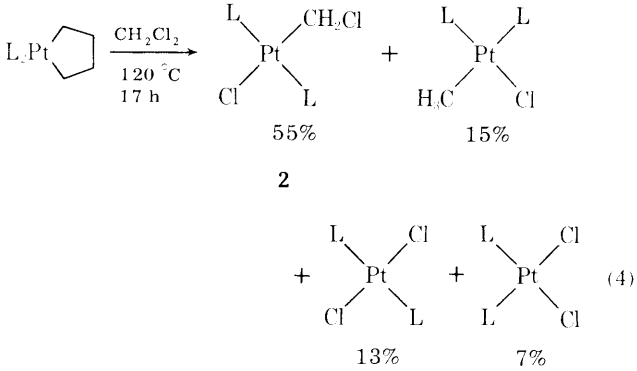


Figure 1. First-order plot for thermal decomposition of **1** in methylene chloride at 120 °C.

major or exclusive products. The product distribution was identical in dry methylene chloride which had been saturated with dioxygen before thermolysis. There was, similarly, no significant change in product distribution upon inclusion of anhydrous iron(III) chloride (0.1 equiv) in the thermolysis mixture, but introduction of bis(tri-*n*-butylphosphine) dibromonickel(II) (0.1 equiv) produced a marked decrease in the yield of cyclobutane. Two equivalents of trimethylaluminum also suppressed cyclobutane formation in favor of butene. When **1** decomposed in methylene chloride saturated with water, the yields of *n*-butane and *cis*-2-butene increased and that of cyclobutane decreased. Labeling studies indicated extensive incorporation of water-derived hydrogen in product butenes, but none was detected in cyclobutane. Prior hydrolysis of methylene chloride may be partly responsible for these observations. Thermal decomposition of **1** in pure tri-*n*-butylphosphine yielded mainly 1-butene.

Phosphorus and proton NMR spectroscopic examination

of solutions derived from thermolysis of **1** in methylene chloride indicates the presence of the four platinum-containing species shown in eq 4; no other phosphorus-containing species were

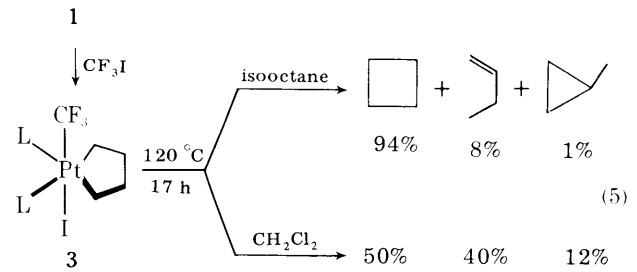


(4)

detected in quantities greater than 2%. The chloromethylplatinum(II) compound **2** was not isolated, but its structure was inferred on the basis of spectroscopic parameters and chemical behavior detailed in the Experimental Section. This compound decomposed over the course of several weeks at room temperature to a mixture of *cis*- and *trans*-L_2PtCl_2. The fate of its methylene unit has not been established, although small yields of ethylene (2–4%, based on platinum) are generally observed on thermolysis of **1** in methylene chloride.

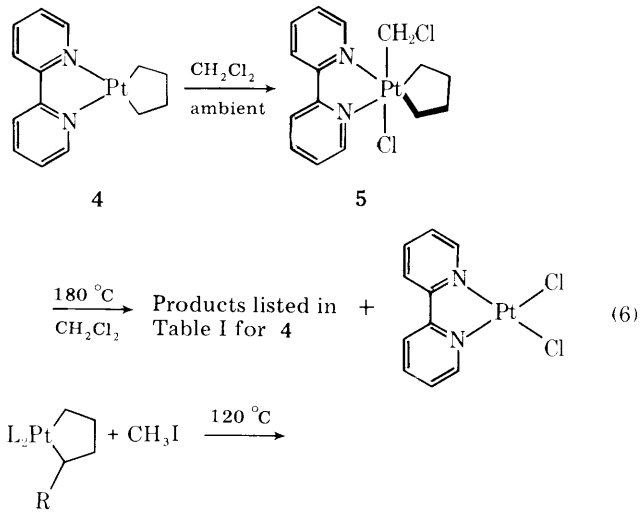
Oxidative Addition of Alkyl Halides to 1 and 4 and Products of Thermal Decomposition of the Resulting Platinum(IV) Organometallics. The generation of cyclobutane in methylene chloride, the incorporation of solvent-derived fragments into products, and the suppression of both of these reaction by coordinating species suggest that oxidative addition of solvent to **1** may precede cyclobutane formation. We have never detected a product having the composition expected from oxidative addition of methylene chloride to **1**. We have, however, been able to prepare and isolate two model substances and to show that their thermal decompositions take place by reductive elimination of carbon–carbon bonds and yield products consistent with those obtained from **1** in methylene halide solutions.

Reaction of **1** with trifluoromethyl iodide generated the platinum(IV) species **3**. Thermal decomposition of this compound generated cyclobutane as the major product (eq 5). No



(5)

product incorporating either trifluoromethyl or iodo moieties was detected; *trans*-$(Bu_3P)_2Pt(CF_3)I$ was the predominant platinum-containing product.[15] Similarly, reaction of 1,4-tetramethylene(bipyridyl)platinum(II) (**4**) with methylene chloride at ambient temperature readily yielded **5** (eq 6). This compound was stable in solution at 120 °C but decomposed at 180 °C to yield the array of products listed for **4** in Table I. These products include little cyclobutane but a high yield of pentenes; 2,2′-bipyridyldichloroplatinum(II) was also formed. Related qualitative results were obtained on thermal decomposition of platinacyclopentanes in the presence of methyl iodide, a material which undergoes rapid oxidative addition to many low-valent metals (eq 7).[15,17] The low yield of pentenes observed when this reaction is carried out in hexane presumably reflects the slow rate of oxidative addition of methyl iodide



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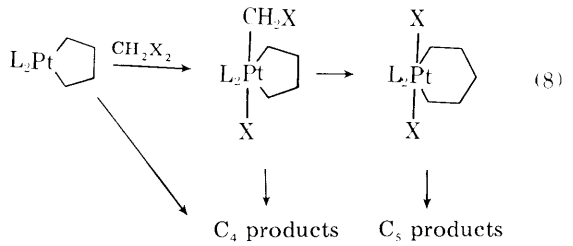
butenes +	pentenes +	hexenes;	solvent	L	R
37%	56%		CH_2Cl_2	Ph_3P	H
11%	85%			Bu_3P	
58%	26%		C_6H_{14}		
	52%	48%	CH_2Cl_2		Me

(7)

to platinum(II) in a nonpolar solvent and the corresponding importance of thermal decomposition of **1** by β-hydride elimination before oxidative addition.[18]

These studies indicate that reductive elimination of two alkyl groups from platinum(IV) with carbon–carbon bond formation occurs under the conditions used for the thermolysis of **1**. We defer the problem of rationalizing the partitioning of products between cycloalkanes and linear alkenes until the Discussion. Oxidative addition of methylene chloride to **4** is clearly an integral step in the formation of the products listed in Table I, since the intermediate **5** can be isolated. The oxidative adduct of **1** and methylene chloride has not been detected directly, but **1** does add trifluoromethyl iodide (and apparently methyl iodide) readily.

Thermal Decomposition of 1,5-Pentamethylenebis(tri-*n*-butylphosphine)platinum(II) (6) and Derivatives. A possible route from **1** to products would follow eq 8. To check the plausibility



(8)

of this sequence, we have examined several reactions of 1,5-pentamethylenebis(tri-*n*-butylphosphine)platinum(II) (**6**). Decomposition of **6** itself in methylene chloride yields a spectrum of products analogous to those observed for **1** (Table II). Low yields (≤5%) of C_4 products are also observed. It has not been determined whether these are derived from the butyl groups of the phosphine or from the fragmentation of the pentamethylene unit, although the former seems more likely. In isooctane, decomposition is more sluggish and no cyclopentane is formed. Thus, direct thermal decomposition of **6** does not appear to offer a plausible mechanism for the generation of cyclopentane, but does indicate that the reactivity observed for the platinacyclopentane is also characteristic of a platinacyclohexane.

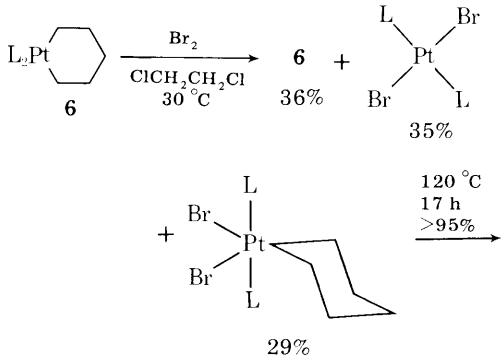
Treatment of **6** with 1 equiv of molecular bromine generates the mixture of compounds shown in eq 9. Treatment of this reaction mixture with an additional 1.4 molar equiv of bromine destroyed the residual **6** and afforded a reaction mixture

Table II. Products of Thermal Decomposition of Five- and Six-Membered Platinacycles Related to **6**[a]

compd	solvent	Yield (mol/mol of Pt) × 100[b]											
		⬠	□	⬡	⬡	⬡	⬡	⬡	⬢	⬢	⬢	⬢	CH_4
6	CH_2Cl_2	48		28	3	2	2	3	4		10		(15)[c]
	i-C_8H_{18}			12	<1	<1		<1 (89)[c]					
8	CH_2Cl_2		9	39	11	25	<1	<1		1	5[d]	1	(12)[c]

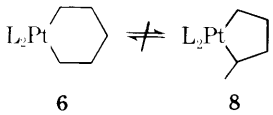
[a] Decompositions were carried out at 120 ± 0.2 °C for 17 ± 0.25 h, using solutions originally 0.025 M in organoplatinum compound, unless indicated otherwise. [b] A blank in this table signifies that the indicated product was checked for explicitly but was not detected. [c] Yields following treatment with 12 N aqueous HCl. [d] Includes 2-methyl-1-pentene.

containing **7** (25–30%) as the only organometallic species. Thermolysis of **7** (prepared by this sequence, used without isolation) for 17 h at 120 °C resulted in its quantitative conversion to cyclopentane.



(9)

To determine whether five- and six-membered platinacycles were in equilibrium (via β-hydride elimination–readdition), the products of thermolysis of 1-methyl-1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II) (**8**) were determined under conditions used for the decomposition of **6** (Table II). The very different array of products observed from **6** and **8** suggests that the equilibrium represented by eq 10 is not important in these systems. Thermolysis products from **8** ascribable to prior oxidative addition by solvent (e.g., methylcyclobutane) are formed only in low yield. Decomposition of **8** in the presence of iodomethane also generates low yields of C_6 products. Steric hindrance to oxidative addition by the α-methyl substituent is probably responsible for the difference in reactivity of **1**, **6**, and **8** toward methylene chloride.[19]

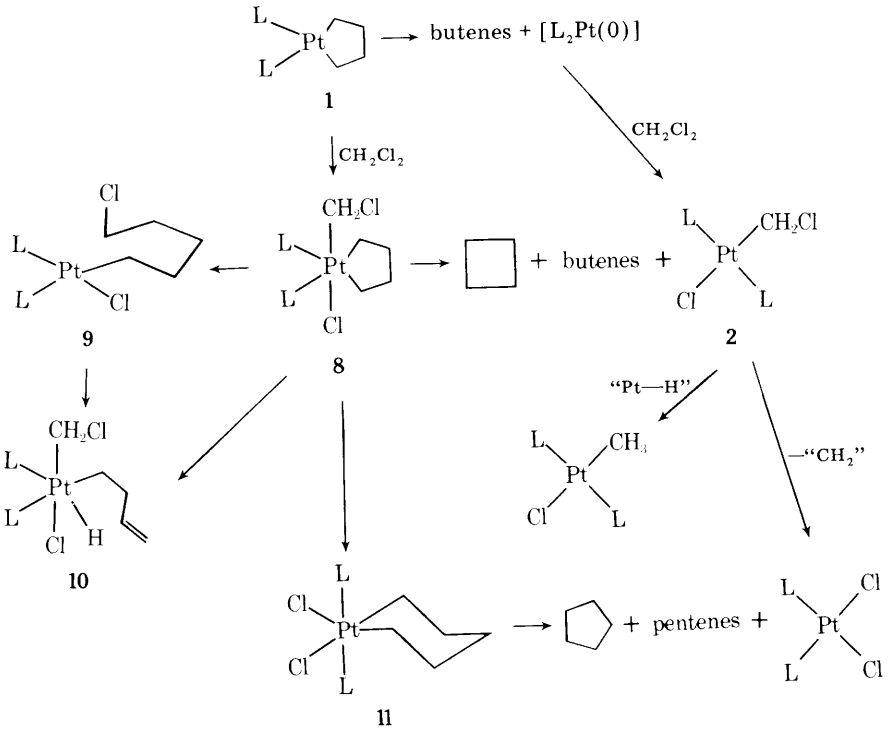


(10)

Discussion

Scheme I organizes the available experimental information and our current speculation about the course of the thermal decomposition of 1,4-tetramethylenebis(tri-n-butylphosphine)platinum(II) (**1**) and related species in methylene chloride solution. The major pathway leading from **1** to cyclobutane, cyclopentane, and pentenes—formation of **8** by oxidative addition of methylene chloride to **1** and decomposition of **8** by reductive elimination of carbon–carbon bonds—is supported by five types of evidence. First, formation of cyclobutane and C_5 materials does not take place in the absence of a solvent capable of oxidative addition. In unreactive solvents, thermal decomposition of **1** generates only acyclic products: butenes predominate, and butane and butadiene are minor products. Second, the C_5 products obtained in methylene-d_2 chloride incorporate methylene units derived from solvent.

Scheme I. Possible Reactions Contributing to the Products of Thermolysis of **1** in CH_2Cl_2



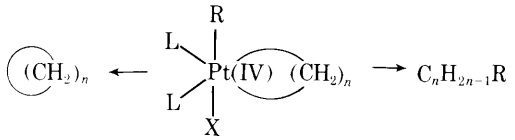
Third, thermal decomposition of **3** and **5**—isolable models for the proposed adduct **8**—generate cyclobutane and pentenes (respectively) in good yields. Fourth, the oxidative adduct **5** from methylene chloride and (bipy)$Pt(CH_2)_4$ (**4**) can be isolated and established as an intermediate in the thermolysis of **4.** Fifth, species which might be expected to hinder oxidative addition to the platinacyclopentane, either by occupying coordination sites on platinum (chloride ion, maleic anhydride) or by steric hindrance (coordinated triphenylphosphine, an α-methyl substituent on the metallacyclic ring) suppress the formation of cyclobutane and C_5 products and enhance the production of butenes. Differing electronic properties of the ligands may also influence the tendency of the platinacycle to undergo oxidative addition and the subsequent course of decomposition of the adduct, although the ESCA data[19] suggest that electron densities on the platinum do not correlate with reactivity in oxidative addition.

It is probable, although not rigorously established, that conversion of **8** to cyclopentane proceeds through the ring-expanded platinacyclohexane **11.** An authentic sample of **7** (the dibromo analogue of **11**), prepared in situ, generated cyclopentane on thermal decomposition. The pentenes certainly arise via **8,** since analogous behavior is observed in the thermal decomposition of the isolable example (**5,** L_2 = 2,2′-bipyridyl). The pathway for this transformation is not, however, entirely clear. These alkenes are not produced in appreciable quantities upon decomposition of authentic **7** under the conditions we explored, but that does not preclude their generation from **11,** produced as an intermediate, under the prevailing thermolytic conditions. Alternatively they may arise from other modes of decomposition of **8** (for example, to **9** or **10**).

Our observations are consistent with direct carbon–carbon bond formation by reductive elimination from Pt(IV) precursors. More convoluted explanations are, however, conceivable. Sequential oxidative addition/reductive elimination steps might, for example, generate transient isomers of the original Pt(II) complex with stereochemical or electronic features which favor carbon–carbon bond formation.[20] The simpler arguments currently seem more justifiable for these platinum organometallic compounds.

The origin of the platinum-containing products is ambiguous. *trans*-Methylchlorobis(tri-*n*-butylphosphine)platinum(II) may, plausibly, be generated by reduction of the chloromethyl group of **2** by a hydridoplatinum species present in solution. The quantities of dienes and 5-chloropentene generated are generally sufficient to account for the quantities of hydride required. Earlier reduction of the chloromethyl groups of **8** seems less likely, since the methyl groups of the adduct **1** and methyl iodide are converted primarily to pentenes. Compound **2** could be generated both from **8** and by oxidative addition of methylene chloride to a platinum(0) species, in turn produced directly from **1.** The thermal decomposition of **2** appears to yield L_2PtCl_2.

The reactions inferred in this scheme suggest two generalizations about organoplatinum chemistry. First, it appears that reductive elimination of two alkyl groups and formation of a carbon–carbon bond occurs readily from platinum(IV)[21-23] but not from platinum(II). [Diaryl- and divinylplatinum(II) analogues, by contrast, yield biaryls or butadienes during thermal decomposition.][22] The β-hydride elimination reaction dominates the chemistry of platinum(II) dialkyls in the absence of competing oxidative addition processes. This difference between the reactivity of dialkylplatinum(II) and dialkylplatinum(IV) compounds cannot presently be rationalized theoretically but should be useful empirically. Second, the partitioning of trialkylplatinum(IV) species containing a metallacyclic group between linear alkenes and cycloalkanes seems to be very sensitive to the structure of the starting complex. This partitioning probably reflects several factors, especially the strain involved in the formation of cyclobutane rings, and the enhanced energy of σ bonds between platinum and electronegatively substituted carbon.[24] Thus, on the basis of limited evidence, it appears that production of cycloalkane is favored if the group R is electron withdrawing (CF_3[23]) but



that formation of acyclic products is favored if R is electron donating (CH_3).

Experimental Section

General and Instrumental. Melting points were determined in open capillaries using a Thomas-Hoover apparatus and are uncorrected. Gas chromatographic analyses were performed on Perkin-Elmer Models 990 and 3920 B instruments, equipped with electronic integrators (Spectra Physics Minigrator). GLC–MS measurements were carried out using a modified Perkin-Elmer 990 chromatograph interfaced with a Hitachi-Perkin-Elmer RMU-6E mass spectrometer. ^1H NMR data were obtained in chloroform-d_1 at 60 MHz with a Varian T-60. Chemical shifts are presented in ppm relative to tetramethylsilane. ^{31}P NMR spectra (^1H decoupled) were recorded at 36.4 MHz on a modified Bruker HFX-90 instrument. ^{31}P chemical shifts are relative to external 60% phosphoric acid (downfield shifts positive). Infrared spectra were recorded on a Perkin-Elmer 567 spectrophotometer. Assignments of chemical identity based on spectra were made by comparison with those of authentic materials and/or reference to the literature. X-ray photoelectron spectra (ESCA) were measured on a Hewlett-Packard 5950 A instrument using an Al(K2α) anode X-ray source. Samples were examined as solid films on gold plates with overlaid gold windows to minimize surface charging effects. $Pt(4f_{7/2})$ binding energies were corrected relative to those of C(1s) = 285 eV.[19] Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J. Preparation of organometallic materials was carried out under argon or nitrogen, according to established inert-atmosphere procedures.[25] Solvents for organometallics were purified by distillation through a 1-m column of glass helices under argon. Diethyl ether and tetrahydrofuran were distilled from disodium benzophenone dianion. Pentane, hexane, and cyclohexane were dried and deolefinated with concentrated sulfuric acid, treated with anhydrous sodium carbonate, and distilled from a suspension of sodium benzophenone ketyl. Dichloromethane, 1,2-dichloroethane, 1,2-dibromoethane, and dibromomethane were distilled from phosphorus pentoxide. Iodomethane was passed through a 10-cm column of Woelm Activity I alumina and distilled under vacuum. Tri-*n*-butylphosphine was distilled under vacuum. Maleic anhydride was purified by vacuum sublimation and *p*-benzoquinone was recrystallized. 1,2-Bis(dimethylphosphino)ethane was prepared by the method of Parshall.[26] Organoplatinum complexes were, with three exceptions (vide infra), stored in the dark at ambient temperature in glass-stoppered vessels initially filled with argon. Prior to analyses or thermolytic studies, each was dried in vacuo for at least 16 h at ambient temperature.

Preparation of DiGrignard Reagents. 1,4-Butane-, 1,5-pentane- and 1,4-pentanedi(magnesium bromide) were prepared according to previously described procedures.[6] Their concentrations were determined by titration against 2-butanol in xylenes, using the purple-red 1,10-phenanthroline–organomagnesium complex as indicator.[27]

(1,5-Cyclooctadiene)-1,4-tetramethyleneplatinum(II). Slight modification of apparatus and technique allowed the ready isolation in quantity and in good yield of complexes (COD)$Pt(CH_2)_n$, previously employed as unisolated intermediates in platinacycloalkane syntheses.[6] (COD)PtC_4H_8 was obtained from (COD)PtI_2 (6.2 g, 11.1 mmol) and 1,4-butanedi(magnesium bromide) in 160 mL of ca. 1:1 ether–THF by first quenching the reaction by passage through a 25-cm chromatography column prepared in ether under argon to the following specifications: lowest 5 cm, silica-gel F-1; central 15 cm, silica gel/activated charcoal dispersion (ca. 3:1, w/w); highest 5 cm, silica gel F-1. These adsorbents were contained in a 2-cm diameter fritted glass column with a Teflon stopcock, equipped with an 8-cm diameter glass jacket which was ultimately filled with ice-water coolant. A fragment

of dry ice sunk to the bottom served, by effervescence, to maintain a constant column temperatures of 0–1 °C. The pale amber reactant mixture was transferred in aliquots to the column by forced syphon via a needle-tipped Teflon catheter. These portions were swept through the column at positive pressure and emerged via a hypodermic needle as an entirely colorless solution which was collected at 0 °C in a septum-capped flask. The reaction vessel and column were then rinsed with successive portions of ether (4 × 50 mL). The solvent was removed at reduced pressure, leaving a cream-white, extremely ether-soluble residue with a characteristic acrid odor. Fine white needles (mp 74 °C, sharp, no decomposition below 150 °C) were recovered via successive recrystallizations by dissolution in a minimum volume of ether, addition of ca. 4 mL of methanol, and gradual evaporation by an argon stream, maintaining a temperature of 0 °C [3.16 g, 79% based on $(COD)PtI_2$]. The material is thermally unstable in ether–methanol if not refrigerated, but when dry it appears to be indefinitely stable in air at ambient temperature: ^1H NMR ($CDCl_3$) δ 4.85 [alkene, 4 H, J (^{105}Pt–^1H) = 39 Hz], 2.29 (methylenic, unresolved, 12 H), 1.40 (methylenic unresolved, 4 H).

Anal Calcd for $C_{12}H_{20}Pt$: C, 40.10; H, 5.61. Found: C, 39.86; H, 5.70.

(1,5-Cyclooctadiene)-2-methyl-1,4-tetramethyleneplatinum(II) was isolated analogously (in 60% yield) as a pale-yellow, almost translucent oil at ambient temperature. It was soluble in ether but not in methanol in which it formed a milky emulsion: ^1H NMR δ 4.83 [1:4:1 triplet, alkene, 4 H, J (Pt–H) = 38 Hz]; 2.33 (methylenic, unresolved 12 H), 1.20 (methylenic, unresolved; superimposed, 1:4:1 triplet of 1:1 doublets, methyl, J (H–H) = 7 Hz, J (Pt–H) = 65 Hz; total ca. 7 H). Elemental analysis of this compound was not obtained but its NMR spectrum and good yield on conversion to bis(phosphine)platinacycles indicated reasonable purity.

(1,5-Cyclooctadiene)-1,5-pentamethyleneplatinum(II) was obtained in 65% yield as off-white, fine needles from ether–methanol by slow evaporation (mp 35 °C sharp). The solid undergoes appreciable yellowing at ambient temperature but is stable at −20 °C under argon: ^1H NMR ($CDCl_3$) δ 4.06 (broad 1:4:1 triplet, alkene, 4 H; J (Pt–H) = 38 Hz), 2.27 (broad triplet, cyclic methylenic, 10 H), 1.55 (broad singlet, methylenic, 8 H). Due to the thermal instability of this material, elemental analyses were not sought.

Preparation of $L_2Pt(CH_2)_n$. General. 1,4-Tetramethylenebis(tri-*n*-butylphosphine)platinum(II) (**1**) and 1,4-tetramethylenebis(triphenylphosphine)platinum(II) (**2**) were prepared and characterized as described previously[6] (for ^{31}P NMR parameters, see Table III); satisfactory elemental analyses were obtained. Homologous divalent platinacycloalkanes and derivatives with other ligands were prepared similarly by methathetical replacement of 1,5-cyclooctadiene in appropriate metallacyclic precursors. These transformations were effected under argon and, unless otherwise specified, in diethyl ether solutions.

1,4-Tetramethylenebis(triethylphosphine)platinum(II). To a rapidly stirred solution of recrystallized $(COD)Pt(CH_2)_4$ (0.30 g, 0.84 mmol) in ether (40 mL) at −78 °C, distilled Et_3P (0.25 mL, 20.3 mg, 1.72 mmol) was added dropwise from a syringe. The reagents were stirred for 4 days at 0 °C without visible change, although there remained no residual odor of phosphine. Solvent was removed at reduced pressure, leaving a colorless oil. This oil was dissolved in ether (5 mL), an equivalent volume of methanol was added, and the solution was cooled under argon to −78 °C. Slow concentration by a rapid flow of argon led to gradual precipitation of a white solid. Two subsequent recrystallizations yielded granular white crystals (3.56 g, 87% based on Pt) which melted over a 1 °C range at 58 °C without decomposition: IR (5% KBr dispersion) 2960, 2910, 2875, 2820 (vs), 1450 (s), 1425 (m), 1375 (m), 1320, 1300 (mw), 1250 (m), 1195 (mw), 1065, 1055 (vs), 760, 720 (vs), 630 (m), 545, 530 (mw) 455, 415 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.7–1.4 (multiplet methylic, 18 H); 1.4–2.2 (multiplet, methylenic, 20 H); ^{31}P NMR data appear in Table III.

Anal Calcd for $C_{16}H_{38}P_2Pt$: C, 39, 42; H, 7.86. Found: C, 39.16; H, 7.94.

1,4-Tetramethylene-1,2-bis(dimethylphosphino)ethaneplatinum(II). To 50 mL of an agitated ether solution of $(COD)Pt(CH_2)_4$ (0.64 g, 1.78 mmol) at −50 °C was cautiously added a solution of dmpe (0.50 g, 2.66 mmol) in ether (5 mL). The homogeneous mixture acquired a pale-yellow color during 5 days at 0 °C. The solvent was removed at low pressure, leaving a yellowish white solid crust. Three recrystallizations by dissolution in ether and gradual evaporation under argon at 0 °C yielded well-formed white plates which melted sharply with decomposition at 172 °C (yield 0.51 g, 71% based on Pt): ^1H NMR ($CDCl_3$), δ 1.5–2.2 [unresolved, methylenic), on which is superimposed a triplet of 1:1 doublets at 1.50, phosphine methyl, J (P–H) = 9 Hz; J (t–H) = 20 Hz]. ^{31}P NMR characteristics appear in Table III: IR (KBr dispersion) 2970, 2860, 2820, 2780 (br, vs), 1420 (br, vs), 1300 (m), 1285 (vs), 1245, 1235 (ms), 940 (br, vs), 900 (vs), 835 (s), 745 (s), 715 (vs), 660 (s), 545, 535 (ms), 640 (ms) cm^{-1}.

Anal Calcd for $C_{10}H_{24}P_2Pt$: C, 29.93; H, 6.03. Found: C, 29.60; H, 6.17.

Table III. ^{31}P NMR Parameters for $L_2Pt(CH_2)_n$[a]

Complex	J (^{195}Pt–^{31}P), ±2 Hz	$\delta_{^{31}P}$(±2)
$(Ph_3P)_2Pt(CH_2)_4$	1842	27.6
$(Bu_3P)_2Pt(CH_2)_4$	1775	2.7
$(Bu_3P)_2Pt(CH_2)_5$	1723	2.7
$(Bu_3P)_2Pt(CH_2)_3CHCH_3$	1552, 1885[b]	1.4
$(Et_3P)_2Pt(CH_2)_4$	1782	11.0
$(dmpe)Pt(CH_2)_4$	1620	26.2

[a] Spectra were obtained using ca. 0.03 M solutions in CH_2Cl_2; chemical shifts are in ppm downfield from 60% H_3PO_4 external standard. [b] The smaller coupling constant is probably due to phosphorus trans to the secondary carbon. [c] Recorded in $CHCl_3$.

1,4-Tetramethylene-2,2′-bipyridylplatinum(II) (4). 2,2′-Bipyridyl (0.98 g, 6.28 mmol) and $(COD)Pt(CH_2)_4$ (2.25 g, 6.26 mmol), dissolved in 60 mL of hexane under argon in a septum-capped vessel, were allowed to react at ambient temperature in the absence of light.[28] Over a period of 3 weeks, the solution gradually assumed a pink hue, and ruby-red needles began to separate, in addition to quantities of fine orange-yellow powder. From the 4th to the 8th week, weekly crops of crystals were recovered, and the reaction was allowed to continue until no further deposition was apparent. Recrystallization of the red material was best effected from a filtered, hot solution in 1:1 ethanol–acetone. By cooling (to ambient) and evaporation by a stream of nitrogen, beautiful blood-red needles were obtained, which decomposed to a black residue from 186 °C without melting (up to 320 °C) (yield, 1.31 g, 51% based on Pt): IR (4% KBr dispersion) 3100, 3080, 3040 (m), 2920–2800 (br, vs), 2770 (vs), 1605 (vs), 1468, 1465 (vs), 1430 (s), 1310 (s), 1250 (s), 1200, 1160 (s), 775 (br, s), 747 (br, vs), 548 (br, s), 417 (ms) cm^{-1}. The visible spectrum in dichloromethane displayed prominent absorption at 470 nm, assigned to the first MLCT bond,[28] which gradually disappeared ($\tau_{1/2} \simeq 30$ min). Because of the poor solubility of **4** in solvents with which it does not react, reliable ^1H NMR data were difficult to obtain. The spectrum of a freshly prepared chloroform-d_1 solution revealed complex multiplets at δ 9.1, 8.0, and 7.5 [ascribable to 6-, 3-, and 4-, and 5-bipyridyl hydrogens, respectively; J (Pt–H_{ortho}) $\simeq$ 21 Hz] and spanning 0.8–3.4 (prominent maxima at 1.4 and 2.6, platinacyclic hydrogen).

Anal Calcd for $C_{14}H_{16}N_2Pt$: C, 41.27; H, 3.96; N, 6.88. Found: C, 40.82; H, 4.03; N, 6.96.

1,5-Pentamethylenebis(tri-*n*-butylphosphine)platinum(II) (6). To a stirred ether solution of $(COD)Pt(CH_2)_5$ (6.34 g, 0.91 mmol) at −20 °C, tri-*n*-butylphosphine (0.46 mL, 0.37 g, 1.85 mmol) was added dropwise via a syringe. The mixture was stored for 48 h at 0 °C, with no visible alteration. Removal of solvent at low pressure afforded a pale-yellow oil. This oil was taken up in a minimum volume of ether and ca. 5 mL of methanol was added. Slow concentration at 0 °C under an argon stream led to the separation of a milky oil. During 36-h storage at −20 °C this material became large translucent colorless cuboids. These were recovered and washed with cooled methanol, and the process was repeated twice prior to drying in vacuo. The material had mp 30–31 °C without decomposition (yield 0.51 g, 87% based on Pt): ^1H NMR ($CDCl_3$) spectrum consisted of a broad-based sharp resonance δ 0.9 (methyl, 18 H), 1.0–2.2 (unresolved, methylenic, 46 H); ^{31}P NMR data appear in Table III. This material was stored at −4 °C in an argon-filled desiccator.

Anal. Calcd for $C_{29}H_{64}P_2Pt$: C, 52.00; H, 9.63. Found: C, 51.93; H, 9.74.

1-Methyl-1,4-tetramethylenebis(tri-*n*-butylphosphine)platinum(II) (8). To a solution of $(COD)Pt(CH_2)_3CHMe$ (2.49 g, 6.67 mmol) in ether at 0 °C was cautiously introduced an ether solution (10 mL) of tri-*n*-butylphosphine (2.70 g, 13.35 mmol), with continuous swirling. The mixture was allowed to stand at 0 °C for 72 h in the absence of

light, during which there was no visible indication of reaction. Solvent removal left a pale-yellow oil which was dissolved in ether (ca. 5 mL). Addition of an equal volume of methanol caused precipitation of a waxy, cream-colored solid. This solid was dissolved by addition of a minimum of ether, and the solution was slowly cooled to −30 °C. Over 30 min, fine white needles deposited. These were separated and washed with methanol. The liquors were further concentrated by slow evaporation, and an additional crop of well-formed crystals was recovered. Two successive recrystallizations yielded snow-white material which after vacuum drying melted sharply at 60 °C without decomposition (yield, 4.36 g, 98% based on Pt): ^{1}H NMR ($CDCl_3$) δ 2.4 (small broadened hump, methine 1 H), 1.3 [methylenic and exocyclic methyl, total 45 H; J (Pt–H) = 74 Hz, J (P–H) = 6 Hz], 0.9 (sharp, terminal methyl, 18 H). Details of the ^{31}P NMR spectrum appear in Table III.

Anal. Calcd for $C_{29}H_{64}P_2Pt$: C, 52.00; H, 9.63. Found: C, 52.00; H, 9.77.

Bis(tri-*n*-butylphosphine)(1,4-tetramethylene)trifluoromethyl)-iodoplatinum(IV) (3). In a heavy-walled glass bomb (ca. 10-cm^3 capacity) was placed a solution of $(Bu_3P)_2Pt(CH_2)_4$ (0.33 g, 0.50 mmol) in dichloromethane (1 mL). The vessel was attached to a vacuum system ($\leq 5 \times 10^{-3}$ Torr), the contents were degassed through two freeze–thaw cycles, and trifluoroiodomethane was condensed in via a gas burette (180 cm^3 at atmospheric pressure and 292 K; 7.51 mmol). The bomb was sealed under vacuum at 77 K. After warming to ambient temperature, the contents were shaken continuously for 4 days in the absence of light, during which time they acquired a pale lemon coloration. The vessel was opened at −78 °C, the solution was removed, and the solvent was evaporated at reduced pressure, leaving a viscous yellow oil. Although ^{31}P NMR analysis suggested that the major component (>90%) was $(Bu_3P)_2Pt(CH_2)_4(CF_3)I$ (vide infra), it could not be induced to crystallize. TLC on silica gel using 4:1 pentane–dichloromethane as eluent resolved six components, the most abundant of which had R_f 0.40–0.58. Two successive elutions on preparative scale plates yielded, after drying in vacuo, a pale-yellow, slightly opaque and viscous fluid (3.53 g, 83% based on Pt): IR (thin film) 2800–3010 (vs, br), 1460 (s), 1410 (m), 1380 (m), 1250 (m), 1210 (ms), 1155 (m), 980–1120 (vs, br) (CF), 720 (ms) cm^{-1}; ^{1}H NMR ($CDCl_3$) consisted of δ 2.0 (platinacycle methylenic), 1.47 (methylenic, ligand substituents), and 0.97 (sharp, ligand methyl) (ratio ca. 4:19:9). The ^{31}P NMR spectrum consisted of 1:3:3:1 quartets which appeared in 1:4:1 triplet: J (^{195}Pt–^{31}P) = 996 Hz, J (^{19}F–^{31}P) = 12.5 Hz δ (^{31}P) = −35.1 ppm (to higher field than H_3PO_4). These spectroscopic parameters are consistent only with a structure for **3** with *cis*-phosphine ligands and mutually *trans*-trifluoromethyl and *trans*-iodo substituents (see text eq 5) and compare well with those obtained for related dimethylplatinum(IV) derivatives.[29] The major impurity from the preparation was identified as *trans*-$(Bu_3P)_2PtI_2$. The material was stored at −4 °C in an argon-filled desiccator.

Anal Calcd for $C_{29}H_{62}F_3IP_2Pt$: C, 40.89; H, 7.33. Found: C, 40.86; H, 7.32.

Treatment of $(Ph_3P)_2Pt(CH_2)_4$ with CF_3I under analogous conditions for 21 days at room temperature resulted in no reaction.

(2,2′-Bipyridyl)(chloromethyl)chloro-1,4-tetramethyleneplatinum(IV) (5). (Bipy)$Pt(CH_2)_4$ (0.11 g, 0.28 mmol) was dissolved in dichloromethane (30 mL) and the mixture stirred for 16 h at ambient temperature under argon. The solution, initially wine red, became pale lemon yellow, and a ivory-white solid precipitated. This solid was separated by filtration and further deposition was induced by slow solvent removal. Almost colorless, translucent needles were obtained by dissolving this material in dichloromethane and concentrating it slowly (0.13 g, 94%). The material exhibited no melting point below 300 °C, but rapidly decolorized to bright red-orange and yellow needles from 135–145 °C, subsequently becoming russet and finally dun-brown by 300 °C: ^{1}H NMR ($CDCl_3$) δ 8.65 [1:4:1 triplet of broadened doublets, bipyridyl H_6, 2 H; J (Pt–H) = 22 Hz], 7.6–8.2 (bipyridyl H_3 and H_4, 4 H), 7.4 (unsymmetrical triplet, bipyridyl, H_5, 2 H), 3.73 [sharp 1:4:1 triplet, chloromethylene, 2 H;, J (Pt–H) = 51 Hz], 0.7–3.0 (platinacyclic methylenic, 8 H); IR (KBr) 3105–2980 (5 sharp bands, ms), 2930, 2900, 2840 (vs), 1630 (vs), 1495, 1475 (s), 1445 (vs), 1320, 1310 (s), 1255 (s), 1204 (s), 1190, 1170 (ms), 110 (s), 1030, 1022 (s), 770 (br, vs), 738 (vs), 670–640 (5 bands (s) cm^{-1}; there was in addition a sharp isolated absorption of medium intensity at 370 cm^{-1}, attributable to ν (Pt–Cl). A dideuterated analogue was prepared by an analogous procedure using CD_2Cl_2. Its infrared spectrum displayed [in addition to analogous ν (Pt–Cl) at 368 cm^{-1}] new sharp absorptions of moderate intensity at 2160 and 2255 cm^{-1} [ν(C-D)]. Apart from lessening of complexity in the region 1210–1150 cm^{-1} the spectrum was otherwise indistinguishable from that of the unlabeled derivative. This was also the case, except for the absence of the triplet at 3.73 ppm, for the ^{1}H NMR spectrum. The stereochemistry of coordination cannot be certainly assigned, but the *transoid* structure for **5** (text, eq 6) is believed most likely.

Anal. Calcd for $C_{15}H_{18}Cl_2N_2Pt$: C, 36.59; H, 3.69; N, 5.69; Cl, 14.40. Found: C, 36.48; H, 3.78; N, 5.60; Cl, 14.56.

Thermolytic Studies. Solutions of platinacycloalkanes (25 mM) were prepared, degassed, and thermally decomposed in clean, dry, glass vessels according to procedures described previously.[7] Unless otherwise specified in the text, decomposition was accomplished by immersion for 17 ± 0.25 h in stirred oil whose temperature was thermostatically regulated to 120 ± 0.2 °C.[30] Decomposed samples were stored at −78 °C prior to analysis. The extent of decomposition could be determined by injecting aliquots of residual solution, from a precooled syringe, onto an appropriate GLC column. It was established that none of the complexes studied underwent decomposition at temperatures ≤100 °C and so the GLC injection port was maintained at this level. Subsequent to chemical quenching with HCl,[6] the samples were reanalyzed to verify that total hydrocarbon evolution corresponded satisfactorily with predictions. Although neither of the Pt(IV) derivatives was susceptible, all divalent platinacycloalkanes ultimately yielded quantitative *n*-alkane on HCl treatment. (The rate of proteolysis was solvent dependent; at −78 °C, reaction in dichloromethane was complete in as little as 3 h, whereas reaction in hexane required up to 130 h.) Comparison of product distributions before and after quenching allowed estimation of the extent of decomposition. Absolute product yields were calculated by comparison of peak areas with those of internal standards; normally, *n*-pentane for C_4 and C_5 products and isooctane or methylcyclopentane (where it was not itself a product) for C_5 and C_6 products were used. It was established that *n*-pentane was neither a product of thermal decomposition nor did its presence in any way affect the ultimate product distribution from $L_2Pt(CH_2)_4$ in methylene chloride. Assumption of 1:1 correspondence of detector response per unit weight was found to give satisfactory results for hydrocarbons; mass balances for unequivocally platinacycle-derived products were generally within 100 ± 5%. Response factors for halocarbons were evaluated from authentic materials. Products were identified by their retention characteristics (predetermined from authentic samples) on two GLC columns of different packing. A number of columns were employed: A, tandem column; 8 m, 20% dibutyl maleate on Chromosorb P (NAW; 60–80 mesh) in series with 4.3-m, 10% bis(2-(2-methoxyethoxy)ethyl)ether on Chromosorb P (NAW; 60–80 mesh);[31] B, tandem column, 10 m, 25% of a saturated solution of $AgNO_3$ in tetramethylene glycol on Chromosorb W (80–100 mesh) in series with 3.3 m, 15% tris(cyanoethoxy)propane (TCEOP) on F-1 Alumina (80–90 mesh); C, 8 m, 20% propylene carbonate on F-1 alumina (80–100 mesh); D, 4 m, 20% SE-30 on Chromosorb P (80–100 mesh). Column A was found to be especially satisfactory for the separation of hydrocarbons from C_1 to C_6 with particularly good baseline resolution of C_4 products. Column B was employed for C_4 and C_5 analyses, while column C served for C_5 and C_6 characterizations. Column D was mainly of use in halocarbon identification. Columns A–C were operated isothermally at ambient (30–35 °C) temperatures with carrier flow rates of 30 mL min^{-1}.

Kinetic analysis of decomposition of **1** was accomplished by monitoring the disappearance of **1** as revealed by the absolute yield of *n*-butane following HCl quenching of samples withdrawn and cooled (−78 °C) at noted intervals. Internal *n*-pentane was also included to allow observation of relative levels of decomposition products as decay proceeded, as well as a check on overall mass balances.

Evaluation of Thermal Decomposition of $(Bu_3P)_2Pt(CH_2)_4Br_2$ (7). This process was observed by ^{31}P NMR spectroscopy. Two 1,2-dichloromethane solutions were prepared under argon containing (a) **6** (0.085 M) and (b) bromine (0.086 M). Solution b (1.0 mL) was added dropwise to a stirred equal volume of solution a. After 20 min, the ^{31}P NMR spectrum of an aliquot (0.4 mL) was recorded, revealing the presence only of **6** (36 mol %[32]), *trans*-$(Bu_3P)PtBr_2$ (35 mol %[32]) [δ_P −2.7 ppm, J (Pt–P) = 2332 Hz; lit.[33] = 2334 Hz], and a species identifiable by subsequent reaction as *trans*-$(Bu_3P)_2Pt(CH_2)_4Br_2$ (**7**) (29 mol %[33]) [δ_P 18.8, J (Pt–P) = 2066 Hz; cf. for isostructural $(Ph_2MeP)_2Pt(CH_3)_2Br_2$, J = 1970 Hz[34]]. This mixture is consistent with the consumption of 0.99 equiv of bromine. To the remaining 1.6

mL of a was added 1.15 mL of additional bromine solution, affording final concentrations of 0.025 M for platinum and 0.061 M for added bromine (Br_2/Pt = 2.44). Aliquots of the golden liquors were withdrawn after 10 min stirring and sealed into thermolysis vessels in the normal manner (vide supra). The remainder of the solution was meanwhile subjected to ^{31}P NMR analysis. At this stage the mixture contained *trans*-$(Bu_3P)_2PtBr_4$ (72 mol %[32]) [δ_P −18.3 J (Pt-P) = 1474 Hz; cf. *trans*-$(Bu_3P)_2PtCl_4$ = 1462 Hz[33]] and **7** (28 mol %[32]). Thermolytic treatment (120 °C, 17 h) of this mixture was found to yield cyclopentane (28 ± 2 mol %, absolute yield based on original Pt) and yellow solutions.

Examination of Residual Products from 1 in CH_2Cl_2. More concentrated solutions of **1** (0.23 M) were prepared and thermally decomposed according to standard procedures. Hydrocarbon production was checked by GLC, and the residual solution was immediately analyzed by ^{31}P NMR spectroscopy. The solvent was then quickly removed and replaced by chloroform-d_1, prior to ^1H NMR analysis. On the basis of these two techniques, four dissolved components could be identified: *cis*-$(Bu_3P)_2PtCl_2$ [J (Pt-P) = 3511 Hz, lit[35] = 3502 Hz] and *trans*- $(Bu_3P)_2PtCl_2$ [J (Pt-P) = 2393 Hz, lit[35] = 2400 Hz] were readily identifiable (ca. 7 mol and 13 mol %, respectively[32]). A third minor product (ca. 15 mol %[32]) was *trans*-$(Bu_3P)_2PtMeCl$. The ^{31}P NMR evidence (δ_P 7.6, J (Pt-P) = 2789 Hz, cf. for *trans*-$(Et_3P)_2$-PtMeCl = 2816 ± 15 Hz[34]) was supported by ^1H NMR observations: δ 0.32 (1:2:1 triplet, one satellite obscured J (P-H) ≃ 80 Hz; ca. 1% of total resonance for Bu_3P; methylplatinum substituent).[36] The ^{31}P NMR spectrum of the major (ca. 55 mol %[32]) component [δ_P 14.7; J (Pt-P) = 2714 Hz] is characteristic of a further *trans*-bis(phosphine)organoplatinum(II) derivative. That this is *trans*-$(Bu_3P)_2$-$Pt(CH_2Cl)Cl$ seems certain from the presence in the ^1H NMR spectrum (ca. 2% of total Bu_3P resonance) of a set of signals comprising a 1:2:1 triplet with flanking satellites of ca. one-fourth intensity, centered at δ 3.70 [J (Pt-H) = ca. 50 Hz, J (P-H) = 8 Hz]. Those parameters compare well with those attributable to the chloromethylplatinum substituent of **5** (vide supra). This latter species does not survive 4 weeks storage even at 0 °C. Bimolecular elimination of ethylene affording $(Bu_3P)_2PtCl_2$ seems a likely explanation, and this was indeed the major compound observed after protracted storage (ca. 1-3 mol % ethylene is also a product of decomposition from **1** and **4-6** in CH_2X_2).

Although up to 14 mol % methane was observed upon treatment of residual solutions with aqueous 12 N HCl—presumably from *trans*-$(Bu_3P)_2Pt(Me)Cl$—no chloromethane was detected. Upon treatment with neat trifluoromethanesulfonic acid, however, chloromethane was produced in 18% yield (at ca. 70% decomposition).

Thermal decomposition of $(Ph_3P)_2Pt(C_2H_4)$ in CH_2Cl_2 at 120 °C led to a complex mixture of products among which—in addition to ethylene—benzene (ca. 40 mol %) and biphenyl (ca. 13 mol %) were prominent.[22] [These are also minor secondary products of thermal decomposition of $(Ph_3P)_2Pt(CH_2)_4$ in CH_2Cl_2.]

Acknowledgments. The award of a NATO Fellowship by the British Science Research Council (to G.B.Y.) is gratefully acknowledged. Dr. Cathy E. Costello and Professor Klaus Biemann provided GLC/MS data (NIH Grant No. RR 00317). Mr. Harold R. Rogers provided ^{31}P NMR spectra. Mr. Thomas D. Y. Chung, Professor Ed Solomon, and Mr. Paul Foley performed ESCA measurements (Grant NIH AM20406).

References and Notes

(1) Supported by the National Science Foundation, Grant MPS 74-20946.
(2) British Science Research Council (NATO) Postdoctoral Fellow, 1975–1977.
(3) Nomenclature: Organometallic compounds derived by substitution of a metal for a carbon center in a cycloalkane are called metallacycloalkanes in accordance with IUPAC recommendations on heterocyclic nomenclature. Prefixes "cis-" and "trans-" refer to the phosphine ligands when applied to octahedral bis(phosphine)-platinum(IV) complexes.
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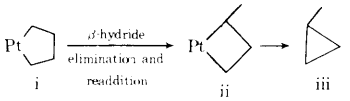

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