$(das)_2]^+$ by acid followed by decomposition of the ruthenium(III) azide in a manner similar to $[Ru(NH_3)_5N_3]^{2+}$. In order to test this hypothesis, *trans*-$[RuN_3Cl(das)_2]$ was treated with an excess of bromine in methanol. A rapid reaction took place resulting in the formation of an unstable green solid. An ir spectrum of this material obtained as soon as possible after drying (5 min) initially consisted of three bands in the 2000-cm^{-1} region at 2125 (m), 2000 (s), and 1870 (vw) cm^{-1}. After the solution was allowed to stand for several hours, the color of this solid changed from green to yellow, and the ir band at 2000 cm^{-1} had disappeared, while the band at 1870 cm^{-1} had markedly increased in intensity. The bands can be identified as the ruthenium(III) azide (2000 cm^{-1}), ruthenium(II) dinitrogen complex (2125 cm^{-1}), and $[RuClNO(das)_2]^{2+}$ (1870 cm^{-1}). Thus the products from the oxidation with bromine differ markedly from those obtained from the reaction with HCl. Although this evidence is not conclusive, it strongly suggests that the action of HCl does not involve oxidation of the ruthenium(II) azide, and that eq 4 and 5 represent the most likely route for the formation of the dinitrogen complex.

The ion *trans*-$[RuClN_2(das)_2]^+$ is very stable. Numerous attempts were made to reduce this dinitrogen complex with a variety of reagents including $NaBH_4$, $LiAlH_4$, and $Na_2S_2O_4$. In every case, the dinitrogen complex was recovered unchanged. The complex cannot be oxidized with iodine and is stable toward displacements by various ligands including CO.

Preparation and Reactions of *cis*-$[Ru(N_3)_2(das)_2]$. To further explore the reactions of ruthenium(II) azide complexes, *cis*-$[Ru(N_3)_2(das)_2]$ was prepared by metathesis from the corresponding dichloride with NaN_3. The cis stereochemistry of these compounds was established by proton nmr spectra listed in Table I. The diazide does not undergo reactions analogous to those of *trans*-$[RuN_3Cl(das)_2]$. Reaction of the cis diazide with HCl in methanol gives the cis dichloro complex exclusively, while photolysis in dichloromethane also gives the dichloro complex. Reactions with NO^+ and NO_2^+ also did not lead to products containing the coordinated N_2 group.

Acknowledgments. The authors wish to thank Dr. P. Keller for his assistance with the vacuum line experiments, Miss M. Quinby for the preparation of the ^{15}N-substituted nitrosyl complexes, and Dr. J. Enemark for many helpful discussions. The financial support of this research by the National Science Foundation is also gratefully acknowledged.

Mechanism of Thermal Decomposition of Di-*n*-butylbis(triphenylphosphine)platinum(II)[1]

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Abstract: The thermal decomposition of di-*n*-butylbis(triphenylphosphine)platinum(II) (**1**) in methylene chloride to *n*-butane, 1-butene, and a complex of platinum(0) is proposed to take place by an intramolecular process involving an initial dissociation of 1 equiv of triphenylphosphine from **1** to yield a three-coordinate intermediate **5**, elimination of platinum hydride from one butyl group of **5** with concomitant transfer of the resulting 1-butene to the vacant coordination site, several cycles composed of rapid addition of platinum hydride to the coordinated butene and subsequent rapid reelimination of platinum hydride from the resulting butylplatinum complexes, and a final reductive elimination of *n*-butane from an intermediate having both hydride and butyl moieties bonded to platinum. Three significant conclusions concerning the mechanism of thermal decomposition of **1** have emerged from this study. First a vacant coordination site on platinum is a prerequisite for thermal decomposition under the conditions studied. Second, the identity of the rate-limiting step for the overall decomposition reaction depends upon the concentration of triphenylphosphine added to the solution: in the absence of added triphenylphosphine, the rate-limiting step is the dissociation of **1** to **5**; in the presence of *ca.* 1 equiv of added triphenylphosphine, the rate-limiting step is the reductive elimination of butane. Third, the olefins participating in the platinum hydride addition–elimination sequence are coordinated in the intermediate platinum complexes sufficiently firmly that they do not exchange with 1-butene free in solution.

Information concerning the mechanisms of thermal decomposition of alkyl derivatives of transition metals is pertinent both to theoretical discussions of the electronic structure of carbon–metal σ bonds and practical applications of transition metal organometallic compounds in organic synthesis and catalysis. Mechanisms involving both the homolytic scission of carbon–metal σ bonds and the β elimination of metal hydrides have been proposed for these thermal decompositions;[4,5] however, the latter course has been established as the more common for *n*-alkyl derivatives

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[1] Supported in part by The National Science Foundation, Grants GP-7266 and GP-14247.

[2] National Institutes of Health Predoctoral Fellow, 1967–1968; E. B. Herschberg Fellow, 1966–1967.

[3] National Institutes of Health Predoctoral Fellow, 1967–1970.

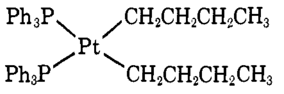
[4] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice Hall, New York, N. Y., 1954, Chapter 5.

[5] Reviews: (a) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. 2, 3rd ed, Methuen and Co., London, 1968, Chapter 7; (b) G. W. Parshall and J. J. Mrowca, *Advan. Organometal. Chem.*, **7**, 157 (1968); (c) F. A. Cotton, *Chem. Rev.*, **52**, 557 (1955); (d) I. I. Kritskaya, *Usp. Khim.*, **35**, 167 (1966).

of platinum(II),[6] rhodium(I),[7] and copper(I),[8] by identification of metal hydrides as products of the decompositions, and for derivatives of other metals by less direct techniques.[5,9] The nature of the factors determining both the rate of metal hydride elimination in the thermal decompositions of these classes of compounds and the reversibility of this elimination are unknown. The work reported in this paper deals with an examination of the mechanism of thermal decomposition of *cis*-di-*n*-butylbis(triphenylphosphine)platinum(II) (**1**), a representative alkyl derivative of a d^8 transition metal ion, whose physical properties make it amenable to detailed mechanistic examination. The purpose of this study was to substantiate a pathway for thermal decomposition of **1** involving platinum hydride elimination and to provide detail to the steps surrounding this elimination.

Results

Preparation and Characterization of Alkylplatinum(II) Compounds. Di-*n*-butylbis(triphenylphosphine)platinum(II) and di-*n*-octylbis(triphenylphosphine)platinum(II) (**2**) were prepared by reaction of the corresponding *n*-alkyllithium reagents with *cis*-dichlorobis(triphenylphosphine)platinum(II) in ether–hexane at 0°, using procedures developed by Chatt and Shaw.[10a] Deuterated derivatives of **1** were synthesized by analogous procedures using as starting materials 1-bromobutane-*1,1*-d_2 and 1-bromobutane-*2,2*-d_2 which were prepared following the reaction sequences outlined in Scheme I.[11] Di-*n*-butyl- and di-*n*-butyl-*2,2*-d_2-[1,1′-bis(diphenylphosphino)ferrocene]platinum(II) (**3** and **3**-*2,2*-d_2, respectively) were prepared by reaction of the corresponding lithium reagents with dichloro[1,1′-bis(diphenylphosphino)ferrocene]platinum(II).[13]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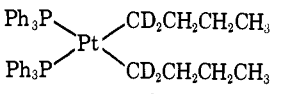
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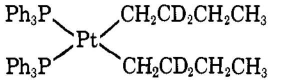
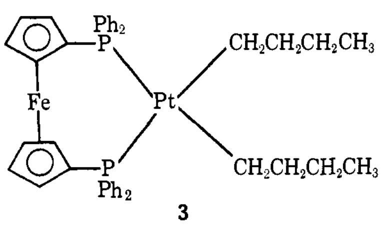

1-*2,2*-d_2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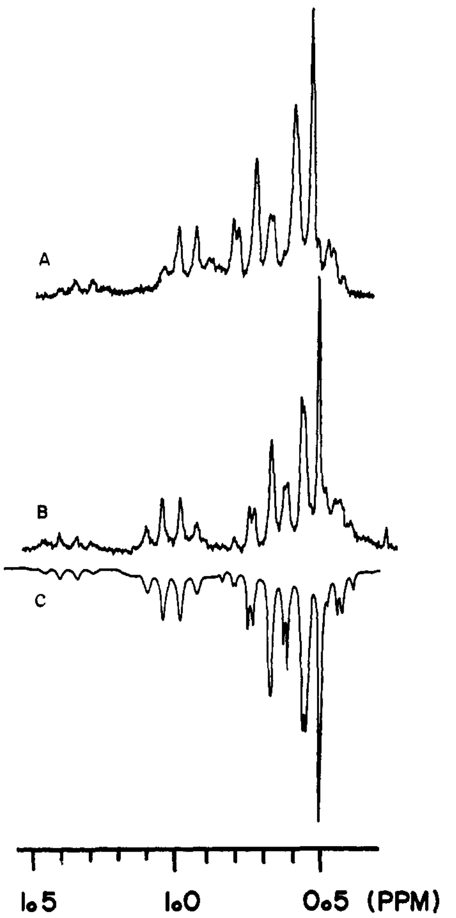

Figure 1. Observed 100-MHz deuterium-decoupled nmr spectra taken of *ca.* 0.25 *M* solutions in methylene chloride of: (A) di-*n*-butyl-2,2-d_2-[1,1′-bis(diphenylphosphino)ferrocene]platinum(II) (**3**); (B) di-*n*-butyl-*2,2*-d_2-bis(triphenylphosphine)platinum(II) (**1**); (C) calculated spectrum of di-*n*-butyl-*2,2*-d_2-bis(triphenylphosphine)platinum(II) (ref 14).

Scheme I. Synthesis of 1-Bromobutane-*2,2*-d_2 and 1-Bromobutane-*1,1*-d_2

$$CH_3CH_2CCl_2CN \xrightarrow[2.\ H_3O^+]{1.\ NaOEt,\ EtOH} \underset{75\%}{CH_3CH_2CCl_2CO_2Et} \xrightarrow{Zn-D_2O,\ DME}$$

$$CH_3CH_2CD_2CO_2Et \xrightarrow[2.\ HBr-H_2SO_4]{1.\ LiAlH_4} \underset{\sim 50\%;\ 97\%\ d_2,\ 3\%\ d_1}{CH_3CH_2CD_2CH_2Br}$$

$$CH_3CH_2CH_2CO_2Et \xrightarrow[2.\ HBr-H_2SO_4]{1.\ LiAlD_4} \underset{\sim 50\%;\ 98\%\ d_2,\ 2\%\ d_1}{CH_3CH_2CH_2CD_2Br}$$

The deuterium-decoupled ^1H nmr spectrum of **1**-*2,2*-d_2 was examined to establish the configuration of the alkyl and phosphine groups. The group of lines between ~0.4 and 0.9 ppm in the spectrum shown in Figure 1 can be assigned to the terminal ethyl groups

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

(7) R. Cramer, *Accounts Chem. Res.*, 1, 186 (1968); see also J. P. Collman, *ibid.*, 136 (1968).

(8) G. M. Whitesides, E. R. Stredronsky, C. P. Casey, and J. San Filippo, Jr., *J. Amer. Chem. Soc.*, 92, 1426 (1970). See also K. Wada, M. Tamura, and J. Kochi, *ibid.*, 92, 6656 (1970).

(9) R. F. Heck, *Accounts Chem. Res.*, 2, 10 (1969); L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience, New York, N. Y., 1966, Chapter 4; J. P. Candlin, K. A. Taylor, and D. T. Thompson, "Reactions of Transition-metal Complexes," Elsevier, Amsterdam, 1967.

(10) (a) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 705, 4020 (1959); 5075 (1962); (b) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969).

(11) We have found reduction of α-halo esters in a medium containing D_2O to be a much more efficient method of introducing deuterium α to the carbonyl group than the base-catalyzed exchange methods commonly used.[12]

(12) A. Murray and D. L. Williams, "Organic Synthesis with Isotopes," Interscience, New York, N. Y., 1958; M. Fetizon and J. Gramain, *Bull. Soc. Chim. Fr.*, 651 (1969).

(13) J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, and J. C. Smart, *J. Organometal. Chem.*, 27, 241 (1971). There is no evidence of interaction between the iron and platinum atoms in these compounds. We have used the ferrocene-1,1′-bis(diphenylphosphine)(fdpp) ligand in these studies because it is an easily prepared bidentate chelating phosphine whose dichloroplatinum(II) complex reacts cleanly with *n*-butyllithium.

of the alkyl chains; the four-line pattern at 1.04 ppm and the one visible ^{195}Pt satellite at 1.76 ppm arise from the methylene groups α to the platinum atom. Detailed analysis of the α-methylene "quartet" indicated that two distinct PPtCH coupling constants were required to simulate the spectrum[14] and confirmed that **1** has the cis configuration expected by analogy with related organoplatinum compounds.[10] The spectrum of **3**-*2,2-d*$_2$ (Figure 1) was not analyzed in detail; however, its qualitative similarity to that of **1**-*2,2-d*$_2$ suggests that the *P*Pt*P* and *P*PtC*H* coupling constants, and by inference the corresponding bond angles, are similar for these two compounds.

Products of the Thermal Decomposition of 1. Heating a 0.10 *M* solution of **1** at 60° for 24 hr in methylene chloride or benzene resulted in complete conversion of *n*-butyl moieties to an equimolar mixture of *n*-butane and 1-butene accompanied by transformation of the solution from its original pale yellow color to a dark red color. The relative yields of *n*-butane and 1-butene were independent of the extent of decomposition of **1**. No (<1% each) *cis*-2-butene, *trans*-2-butene, or octane was observed as a decomposition product. Product yields did not change when **1** was decomposed as a suspension in hexane or as the solid. Thermal decomposition of **2** under similar conditions yielded 50% *n*-octane and 50% 1-octene.

The observation that octane is not formed in the decomposition of **1** is sufficient evidence to exclude the possibility that butane and 1-butene are formed by disproportionation of free *n*-butyl radicals produced by homolysis of the platinum–carbon σ bonds of **1**. The rate constant for the coupling of *n*-butyl radicals is greater than that for their disproportionation by a factor of 4–6, both in the vapor phase and in solution.[15] Moreover, were *n*-butyl radicals intermediates in the thermal decomposition, free-radical abstraction of hydrogen or chlorine atoms from the methylene chloride solvent would be expected to be reflected in a difference between the yields of butane and butene, in contrast to the observed equality in yields. Indeed, decomposition of a solution of **1** in 1,5-hexadiene, a good hydrogen atom donor, resulted in a *decrease* in the yield of butane relative to that of butene (*vide infra*).

Additional qualitative evidence supporting the contention that free *n*-butyl radicals are not intermediates in the thermal decomposition of **1** was provided by the distribution of products observed when thermolysis was carried out in the presence of a fivefold excess of di-*tert*-butylnitroxyl (DTBNO). The butyl-derived products obtained under these conditions consist of butane (46%), 1-butene (50%), with only trace amounts (~1%) of octane and *N,N*-di-*tert*-butyl-*O*-*n*-butylhydroxylamine. The absence of a significant yield of the product of coupling of butyl radicals with DTNBO is entirely compatible with a mechanism for thermolysis of **1** *not* involving free *n*-butyl radicals. However, the pertinence of these data to discussions of the thermal behavior of **1** in the *absence* of DTBNO should be viewed with some reservations, since DTBNO forms complexes with a number of metals[16] and since a complex of **1** and DTBNO cannot be excluded as the species giving rise to the products obtained from decomposition of **1** in the *presence* of DTBNO on the basis of presently available evidence.[17]

In order to test explicitly the hypothesis that the hydrogen atoms incorporated into the *n*-alkane portion of the hydrocarbon products originated exclusively in the σ-bonded *n*-alkyl groups of the starting organometallic compound, and not in the solvent or the aryl groups of the coordinated triphenylphosphine ligands,[18] the octane formed as a product of the thermal decomposition of **2** in methylene-*d*$_2$ chloride, and of di-*n*-octylbis(triphenylphosphine-*d*$_{15}$)platinum(II) in methylene chloride, was isolated and its isotopic composition determined mass spectrometrically.[19] The low level of deuterium incorporation observed in these experiments establishes that the *n*-alkyl groups of the starting organoplatinum compounds are the only significant sources for the hydrogen found on the hydrocarbon products.

$$\mathbf{2} \xrightarrow[60°,\ 20\ \text{hr}]{CD_2Cl_2} \text{octane } (1.8\%\ d_1,\ 98.2\%\ d_0) + \text{octene}$$

$$[(C_6D_5)_3P]_2Pt(n\text{-octyl})_2 \xrightarrow[60°,\ 20\ \text{hr}]{CH_2Cl_2} \text{octane } (0.3\%\ d_1,\ 99.7\%\ d_0) + \text{octene}$$

Taken together, the foregoing observations are inconsistent with a free-radical mechanism for the thermal decomposition of **1**. However, they are compatible with a mechanism for its decomposition, anticipated by analogy with earlier studies,[6–8] involving an initial elimination of a platinum hydride with concomitant formation of 1 equiv of butene, followed by reduction of a carbon–platinum σ bond in some unspecified platinum alkyl by this platinum hydride to yield 1 equiv of butane.

It was possible to obtain *direct* evidence in support of an intermediate platinum hydride by examination of the products arising from thermal decomposition of **1** in 1,5-hexadiene solution. Thermolysis of a 0.07 *M* solution of **1** in this solvent resulted in formation of *n*-butane (~45%), 1-butene (~55%), 1-hexene (10 ± 5%), and two additional compounds, tentatively identified as *cis*- and *trans*-1,4-hexadiene (40 and 150%, respectively). Isotopic analysis of the hydrocarbons isolated from thermolysis of **1**-*2,2-d*$_2$ in 1,5-hexadiene established that approximately ~8% of one deuterium atom from a butyl group of the organoplatinum compound was incorporated into solvent-derived

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(14) G. M. Whitesides and J. F. Gaasch, *J. Organometal. Chem.*, **33**, 241 (1971). Spectral parameters obtained by matching of theoretical and experimental spectra were: $\delta_{CH_3} = 0.52$, $\delta_{CH_3CH_2} = 0.72$, $\delta_{CH_2Pt} = 1.04$ ppm; J_{PPtCH} (cis) $= \pm 13$, J_{PPtCH} (trans) $= \pm 19$, $J_{PP'} = 21$, $J_{HH'} = 1.5$, $J_{PtH} = 72$, $J_{CH_3CH_2} = 7.3$ Hz. The accuracy of these phosphorous–hydrogen and hydrogen–hydrogen coupling constants may not be high; however, the value of $J_{PP'}$ is in reasonable agreement with values reported recently by F. H. Allen and S. N. Sze, *J. Chem. Soc. A*, 2054 (1971).

(15) N. E. Morganrath and J. G. Calvert, *J. Amer. Chem. Soc.*, **88**, 5387 (1966); A. P. Stefani, *ibid.*, **90**, 1694 (1968); N. E. Morganrath and J. G. Calvert, *ibid.*, **88**, 5387 (1966); R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970), and references cited in each.

(16) See G. M. Whitesides and J. San Filippo, Jr., *ibid.*, **92**, 6611 (1970), for references.

(17) Preliminary examination of the *photolytic* decomposition of **1** in the presence and absence of DTBNO appears to be compatible with the production of free *n*-butyl radicals as intermediates (see the Experimental Section for details).

(18) For a review of reactions involving oxidative addition of aromatic C–H bonds to metals, see G. W. Parshall, *Accounts Chem. Res.*, **3**, 139 (1970).

(19) Compound **2** rather than **1** was used for these experiments because *n*-octane undergoes less fragmentation than *n*-butane at voltages required for ionization and is, as a result, the more tractable subject for accurate isotopic composition studies.

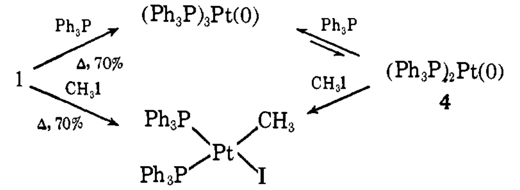
Table I. Mass Spectroscopic Deuterium Analysis of Products of the Thermal Decomposition of **1**-2,2-d_2 in 1,5-Hexadiene

Compound	Yield, %[a]	Isotopic analysis, % d_0	d_1	d_2
1-Hexene	10 ± 5[b]	86	13	1.6
cis-1,4-Hexadiene	40	94	6.3	
"*trans*-1,4-Hexadiene"[c]	150	97	2.8	

[a] Yields are based arbitrarily on the assumption that 1 mol of product per mole of **1** corresponds to a yield of 100%. [b] The experimental uncertainty in this datum reflects uncertainty concerning the quantity of residual 1-hexene present as a contaminant in the 1,5-hexadiene (see the Experimental Section). [c] *trans*-1,4-, *trans*-1,3-, and *cis*-1,3-hexadiene all had identical retention times under the conditions used for this glpc analysis.

products (Table I).[20] An intermediate platinum hydride would provide a plausible vehicle for the transfer of hydrogen from the butyl groups of **1**-*2,2*-d_2 to both the 1-hexene and the isomerized hexadienes.

The platinum originally present in **1** could be recovered as a red solid of unknown composition at the conclusion of thermal decompositions in either methylene chloride or benzene solution; thus, since the same substance is obtained from decompositions carried out in different solvents, it is presumed not to be derived from reaction of some intermediate organoplatinum compound with solvent. The stoichiometry of the decomposition suggests that a primary inorganic product might be 1-butenebis(triphenylphosphine)platinum(0) or bis(triphenylphosphine)platinum(0) (**4**).[21]



An analog of the former compound, ethylenebis(triphenylphosphine)platinum(0),[22] dissociates readily in solution to ethylene and **4**.[23] Both of these compounds are yellow crystalline solids that decompose upon heating to a red melt.[21,22] This last observation suggests that the red product isolated from the thermolysis of **1** might be a secondary product derived from **4**. However, the ir spectrum of the red solid after decomposition of **1** does not agree with that of the decomposition of product of **4**.[21]

It was possible to obtain indirect evidence indicating that either **4** or some material of very similar reactivity was indeed an intermediate in the thermal decomposition of **1** by isolating tris(triphenylphosphine)platinum(0) and iodomethylbis(triphenylphosphine)platinum(II) when thermolyses of **1** were carried out in the presence of triphenylphosphine and methyl iodide as trapping agents.[23,24] The yields of butane and butene were not affected by added triphenylphosphine; these yields were not determined for decompositions carried out in the presence of methyl iodide.

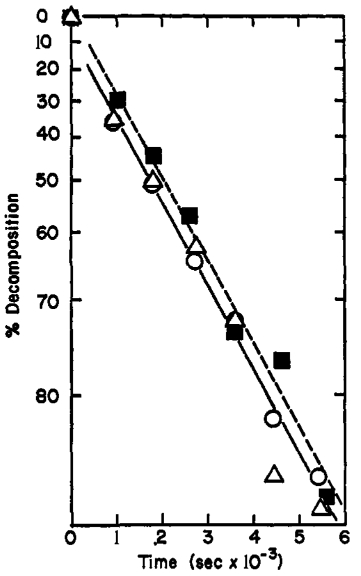


Figure 2. Plot of per cent decomposition of **1** *vs.* time in methylene chloride solution at 60.0°: (■) [**1**] = 0.280 *M* and (△) [**1**] = 0.030 *M*, determined from butane–butene areas; (○) [**1**] = 0.030 *M*, determined from concentrations of butane relative to a pentane internal standard.

Kinetics. The kinetics of thermal decomposition of **1** in methylene chloride was examined by following the appearance of 1-butene using glpc, after quenching samples with hydrochloric acid in methylene chloride. Points were obtained either by following the concentration of 1-butene relative to that of an added internal standard or by using as a reference the total concentration of butene and butane observed following protonolysis.

$$\%\ \text{decomposition} = [\text{butene}]_t/[\text{butene}] \times 100 = 2[\text{butene}]_t/([\text{butane}]_t + [\text{butene}]_t) \times 100$$

Typical data obtained by application of both methods are shown in Figure 2. The slight discrepancy between the intercepts at $t = 0$ obtained at the two concentrations shown is a fair reflection of the precision of the data. Decomposition was first order in **1**, with a rate constant at 60° of $k = 3.6 \times 10^{-4}\ \text{sec}^{-1}$. Comparison of the rates of decomposition of **1** and **1**-*2,2*-d_2 established that the thermolysis shows no significant β-deuterium kinetic isotope effect: $k_1/k_{1\text{-}2,2\text{-}d_2} = 0.97 \pm 0.05$.

The observation that **1** and di-*n*-octylbis(triphenylphosphine)platinum(II) (**2**) decompose at very similar rates ($k_2/k_1 = 1.11 \pm 0.05$) provides the basis for a simple demonstration that the formal hydrogen transfer involved in conversion of the two alkyl groups of **1** to butene and butane proceeds by an intramolecular process. Decomposition of a solution containing a mixture of approximately equimolar amounts of **1**-*2,2*-d_2 and **2** was carried out, the resulting octane isolated, and its isotopic composition determined by mass spectrometric analysis. If reduction of platinum–carbon bonds were to occur by an intermolecular

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[20] The extent of deuterium incorporation into C_6 products presumably reflects the relative rates of hydride addition to coordinated butene and displacement of butene by 1,5-hexadiene. Neither of these rates is known. However, assuming that the extent of deuterium scrambling in the butyl groups under the circumstances of these experiments compares with that during thermal decomposition in the absence of 1,5-hexadiene (*vide infra*), the maximum extent of deuterium incorporation into C_6 products should be ~15%.

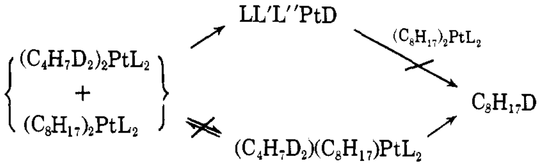
[21] R. Ugo, R. Cariati, and G. LaMonica, *Chem. Commun.*, 868 (1966).

[22] C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Lett.*, 3, 31 (1967).

[23] J. P. Birk, J. Halpern, and A. L. Pickard, *J. Amer. Chem. Soc.*, **90**, 4491 (1968); *Inorg. Chem.*, 7, 2672 (1968).

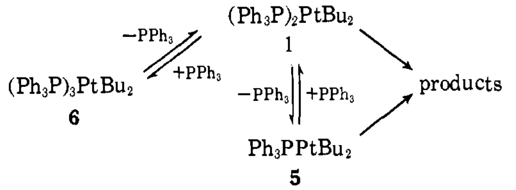
[24] Reviews: R. Ugo, *Coord. Chem. Rev.*, 3, 319 (1968); J. Halpern, *Accounts Chem. Res.*, 3, 386 (1970).

process, involving either an intermediate platinum hydride or a direct hydrogen transfer from the alkyl group of one molecule of organoplatinum compound to that of a second, this octane would contain deuterium originating in **1**-*2,2-d*$_2$. In fact, the octane contained no detectable deuterium (<1%). Hence, the hydrogen transfer must be an intramolecular reaction.[25] At the same time, this result establishes that no exchange of alkyl groups between platinum atoms occurs during the decomposition.



The addition of triphenylphosphine to solutions of **1** in methylene chloride strongly inhibits its thermal decomposition, although decomposition continues to follow approximately first-order kinetics. Thus, first-order rate constants for thermolysis of 0.030 *M* **1** in the presence of concentrations of triphenylphosphine ranging from 0.043 to 0.202 *M* appeared roughly equal, centered around a value of 5.5×10^{-6} sec^{-1}; *viz.*, a value approximately one-sixtieth of that observed in the absence of added triphenylphosphine. The limited solubility of triphenylphosphine in methylene chloride precluded rate measurements at higher concentrations. At concentrations below ~ 0.04*M*, the removal of triphenylphosphine from solution by coordination with the platinum(0) formed as a reaction product results in significant changes in the concentration of triphenylphosphine during the course of a kinetic run. Under these circumstances any kinetic data obtained would be useless without extensive corrections requiring a knowledge of the equilibrium constants for dissociation of platinum–ligand bonds; these data are not available.

Nonetheless, the qualitative observation of rate depression on addition of triphenylphosphine to solutions of **1** could in principle reflect one of two types of equilibria taking place during the thermal decomposition process: one involving *dissociation* of triphenylphosphine from **1** at some point before or during the rate-determining step for the reaction; or a second requiring a preequilibrium or rate-limiting *association* of triphenylphosphine. These two possibilities are exemplified by limiting cases involving preequilibrium formation of discrete three- or five-coordinate platinum complexes (**5** and **6**). Equilibria involving *addition* of triphenylphosphine to **1** could be excluded unambiguously by measuring the solubility of **1** in the presence of excess triphenylphosphine. If the rate suppression observed in the presence of triphenylphosphine reflected the operation of a parasitic equilibrium $\mathbf{1} \rightleftharpoons \mathbf{6}$,



more than 98% of the **1** originally present in solution would necessarily have to be in the form **6** in the presence of ~0.3 *M* triphenylphosphine to account for the observed rate decrease of a factor of 60. Thus, the solubility of **1** in pure methylene chloride solution should be less than that in solutions containing added triphenylphosphine. However, if the added triphenylphosphine influenced the rate by suppressing dissociation ($\mathbf{1} \rightleftharpoons \mathbf{5} + PPh_3$), and if the equilibrium constant for this dissociation lay far to the left, then added triphenylphosphine should have essentially no influence on the solubility of **1**. Experimentally, the solubilities of **1** in the presence and absence of added triphenylphosphine are indistinguishable. Hence, the added triphenylphosphine must affect the rate of thermal decomposition of **1** by affecting a *dissociative* equilibrium ($\mathbf{1} \rightleftharpoons \mathbf{5}$) rather than an associative one ($\mathbf{1} \rightleftharpoons \mathbf{6}$).

This conclusion is a surprising one, in that five-coordinate species of platinum(II) are well established both as discrete compounds[13,26–29] and as reaction intermediates,[30] while three-coordinate species of platinum(II) have not commonly been implicated.[31a] However, both three- and two-coordinate compounds of platinum(0) are well known,[24] and the usefulness of formal valence state terminology in rationalizing the behavior of organometallic compounds is debatable, since the strongly σ-donating alkyl or aryl ligands are capable of imposing a considerably higher charge density on the metal atom to which they are bonded than that usually encountered in coordination chemistry involving less basic ligands.[31b]

The influence of chelating diphosphine ligands on the stability of di-*n*-butyl derivatives of platinum(II) qualitatively confirms the requirement for dissociation of a phosphine ligand during the thermal decomposition. Heating methylene chloride solutions of either di-*n*-butyl[bis(diphenylphosphino)ferrocene]platinum(II) (**3**) or di-*n*-butyl(diphos)platinum(II) at 60° for 24 hr resulted in decomposition only to the extent of 1–4%, in contrast to the complete decomposition experienced by **1** under these conditions. The qualitative close similarity in the CH_2Pt regions of the nmr spectra of **1** and **3** (Figure 1) suggests that this difference in thermal stability is not the result of differences in the geometry

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[25] The evidence presented later that the deuterium and hydrogen atoms of intermediate platinum hydride derived from **1**-*2,2-d*$_2$ would be extensively scrambled during this experiment in no way vitiates this conclusion. Approximately 15% of the deuterium present in one butyl-*d*$_2$ moiety of **1**-*2,2-d*$_2$ (*i.e.*, ~0.3 deuterium atoms per $C_4H_7D_2$ group) is transferred to the second in forming butane (*vide infra*, Table II). Thus, since the rates of decomposition of **1**, **1**-*2,2-d*$_2$, and **2** are very similar, the octane isolated from the mixed decomposition of **1**-*2,2-d*$_2$ and **2** would be expected to be composed of ~15% *d*$_1$ and 85% *d*$_0$ material, provided that the deuterium kinetic isotope effect for the rates of reaction between platinum hydride (deuteride) and the carbon–metal bonds of octyl- and butylplatinum complexes were equal.

[26] R. D. Cramer, R. V. Lindsey, Jr., C. T. Prewitt, and U. G. Stolberg, *J. Amer. Chem. Soc.*, 87, 658 (1965).

[27] J. P. Fackler, Jr., W. C. Seidel, and J. A. Fetchin, *ibid.*, 90, 2707 (1968); C. M. Harris, R. S. Nyholm, and D. J. Phillips, *J. Chem. Soc.*, 4379 (1960); C. M. Harris and R. S. Nyholm, *ibid.*, 4375 (1956).

[28] L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 3, 453 (1964).

[29] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967, Chapter 5.

[30] C. H. Langford and H. B. Grey, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 2; P. Haake and R. M. Pfeiffer, *Chem. Commun.*, 1330 (1969).

[31] (a) Four-coordinate platinum(II) species in which one coordination site is loosely occupied by an easily displaced solvent molecule have been identified: *cf.* H. C. Clark and H. Kurosawa, *ibid.*, 957 (1971). The "three-coordinate" intermediate inferred from these solubility experiments may contain a weakly coordinating solvent molecule. (b) W. H. Riggs, *Anal. Chem.*, **44**, 830 (1972).

or electronic character of the metal–ligand bonds of chelating and nonchelating phosphines; hence, the most direct explanation of this difference is that the chelating phosphines exercise their stabilizing influence on the di-*n*-butylplatinum(II) moiety by inhibiting loss of one coordinated phosphine group during the rate-determining step for the decomposition.[32]

In a brief effort to determine the rate of interchange of triphenylphosphine free in solution with triphenylphosphine coordinated with **1**, the deuterium-decoupled, ^{1}H nmr spectra of solutions containing **1**-*2,2*-d_2 and triphenylphosphine were examined as a function of temperature. At the highest temperatures reached (~60°), there was no evidence of collapse of the pattern of the CH_2Pt protons due to *P*PtC*H* spin–spin coupling. In related experiments, the spectrum of a solution containing a mixture of **1**-*2,2*-d_2 and diphos was examined at 30° as a function of time. Slow replacement of the coordinated triphenylphosphine by diphos was readily evident, with the reaction being complete after several hours. No effort was made to establish the kinetic order of this process. Thus, although these experiments permit no quantitative conclusion, they do demonstrate that ligand exchange is slow on the nmr time scale and that substitution of one coordinated phosphine in **1** by another is possible without the destruction of the carbon–platinum bonds.

Deuterium Labeling and Scrambling Experiments. In order to establish the extent to which the platinum hydride elimination responsible for the formation of butene from **1** is reversible, a study was carried out of the deuterium distribution in products of thermal decomposition of **1**-*1,1*-d_2 and **1**-*2,2*-d_2, both in the presence and absence of added triphenylphosphine. The results of this study combine with those described previously to provide a detailed picture of the reaction profile for the thermal decomposition of **1**.

Comparison of the isotopic compositions of 1-butene isolated from thermal decomposition of **1**-*2,2*-d_2 and **1**-*1,1*-d_2 in methylene chloride solution established that a deuterium originating at the 1 or 2 position of the butyl groups would be lost with equal probability in formation of 1-butene (Table II) and thus demonstrated that complete scrambling of deuterium between the 1 and 2 positions of the butyl groups occurs during the thermal decomposition. To what extent scrambling extends beyond the 1 and 2 positions to the 3 and 4 positions is not clear from these data. If deuterium scrambling along the butyl chain were complete during the thermal decomposition, and if there were no deuterium kinetic isotope effect on the reaction sequence leading to butene, the probability that the butene would be formed by loss of deuterium would be 2/9 ~ 0.22; an isotope effect $k_H/k_D > 1$ would decrease this probability.[36] Since this probability is ~0.3 experimentally (Table II), the implication is that the distribution of deuterium atoms along the butyl chain is not quite statistical.

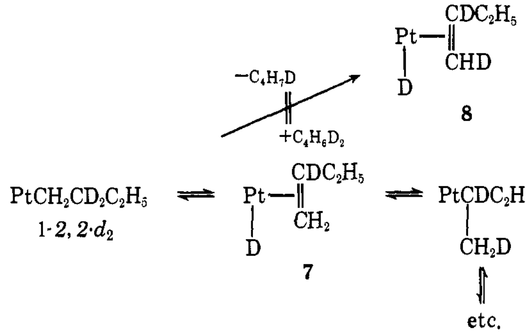
Table II. Isotopic Composition of 1-Butene from Thermal Decomposition of Di-*n*-butyl-*2,2*-d_2- and Di-*n*-butyl-*1,1*-d_2-bis(triphenylphosphine)platinum(II)

Compd	Isotopic compn, %[a] d_0	d_1	d_2	d_3
1-*1,1*-d_2[b]	2	31	66	1
1-*2,2*-d_2[b,c]	3	29	67	1
1-*2,2*-d_2[d]	1	27	71	1

[a] Precision is estimated to be ±1%. [b] Decomposition was carried out in methylene chloride solution at 60°. [c] The isotopic composition was established to be independent of conversion of **1**-*2,2*-d_2 to 1-butene (see the Experimental Section). [d] Decomposed without solvent at ~160°.

An unexceptional, reversible elimination and addition of platinum hydride is almost certainly responsible for the deuterium scrambling observed in **1**-*1,1*-d_2 and **1**-*2,2*-d_2 (Scheme II).[39] However, at least one unexpected conclusion concerning this platinum hydride elimination and readdition sequence emerges from the data in Table II: *viz.*, the observation that no appreciable quantity of 1-butene-d_3 is formed during these reactions indicates that the butene which is coordinated to platinum in the intermediate represented in Scheme II does *not* exchange with 1-butene free in solution (*e.g.*, **7** $\not\rightleftharpoons$ **8**). If exchange did occur, coordination of 1-butene-d_2 to a platinum(II) deuteride center, followed by deuteride addition and platinum hydride elimination, would provide an efficient route to 1-butene-d_3, and this substance is not observed as a

Scheme II. Platinum(II) Hydride Elimination–Addition Mechanism for Deuterium Scrambling



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[32] The exceptional thermal stability of other chelated transition metal organometallic compounds (*e.g.*, diisopropylcyclooctatetraeneplatinum(II),[33] diethyldipyridylnickel(II),[34] and alkyl cobaloximes)[35] and the enhanced stability of many phosphine-coordinated organometallic compounds in the solid state both probably have a similar mechanistic explanation. These observations suggest that isolation of other, presently unknown, organometallic species susceptible to metal hydride elimination may be possible by appropriate choice of chelating ligands.

(33) J. Müller and P. Göser, *Angew. Chem., Int. Ed. Engl.*, **6**, 364 (1967).

(34) T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji, and S. Ikeda, *J. Amer. Chem. Soc.*, **88**, 5198 (1966); A. Yamamoto and S. Ikeda, *ibid.*, **89**, 5989 (1967); T. Yamamoto, A. Yamamoto, and S. Ikeda, *ibid.*, **93**, 3350, 3360 (1971).

(35) G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968).

(36) The data of Chatt, *et al.*, suggest an isotope effect of k_H/k_D = 1.5–2.0 for loss of ethylene from $[(C_2H_5)_3P]_2PtBrCD_2CH_3$,[6] while the isotope effects for loss of copper hydride from $[CH_3CH_2CHDCH_2CuP(n\text{-}Bu)_3]_n$ (k_H/k_D = 4.7)[37] and of lithium hydride from *n*-butyllithium (k_H/k_D = 3–4)[38] are larger. However, these data are not directly applicable to considerations of the probable magnitudes of isotope effects in the data of Table II, since the step expected, on the basis of the mechanism of Figure 5, to determine an isotope effect would be reductive elimination of butane from a $L_2BuPtH(D)$ fragment.

(37) E. R. Stedronsky, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.

(38) R. A. Finnegan and H. W. Kutta, *J. Org. Chem.*, **30**, 4138 (1965).

(39) For reviews of evidence pertinent to metal hydride addition and elimination to olefins, see F. R. Hartley, *Chem. Rev.*, **69**, 799 (1969), and ref 6 and 7. Note that prior coordination of olefin to the metallic center cannot be assumed to be a prerequisite for addition of a metal hydride to the olefin, since such coordination is almost certainly not involved in at least one instance: *viz.*, the addition of $[HCo(CN)_5]^{3-}$ to olefins. *Cf.* J. Halpern and L. Wong, *J. Amer. Chem. Soc.*, **90**, 6665 (1968).

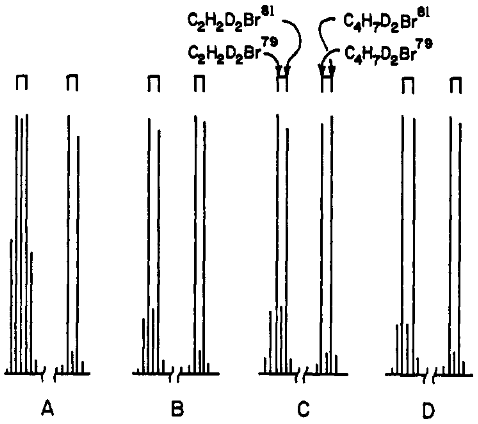

Figure 3. Mass spectra of deuterated 1-bromobutanes showing the molecular ion region and M − 29 ion region: A, *n*-butyl-d_2 bromide derived from **1**-2,2-d_2 after 1 half-life in the presence of added triphenylphosphine; B, *n*-butyl-d_2 bromide derived from **1**-*2,2*-d_2 after 1 half-life in the absence of added triphenylphosphine; C, *n*-butyl-*2,2*-d_2 bromide; D, *n*-butyl-*1,1*-d_2 bromide. Each region is normalized independently. The isotopic doublet for $C_4H_7D_2{}^{79}Br$ and $C_4H_7D_2{}^{81}Br$ (for M^+) and for $C_2H_2D_2{}^{79}Br$ and $C_2H_2D_2{}^{81}Br$ (for M − 29)$^+$ is indicated above each trace.

significant reaction product.[40] Thus, the rate of addition of the platinum hydride moieties, which are presumed to be intermediates in the scrambling process, to coordinated molecules of 1-butene, and the rate of the subsequent reductive elimination of butane from these intermediates, must be considerably more rapid than the rate of exchange of coordinated 1-butene with 1-butene free in solution.

Having established that the deuterium present in the 1-butene produced on thermal decomposition of **1**-*1,1*-d_2 and **1**-*2,2*-d_2 is extensively scrambled, we turned our attention to the complementary problem of determining the extent to which deuterium in the starting material is scrambled during thermolysis. The procedures used to effect this analysis are outlined Scheme III. Samples of **1**-d_2 were heated at 60° for *ca.* 1 half-life of the thermal decomposition reaction and then cooled and treated with molecular bromine. The 1-bromobutane-d_2 produced was isolated and its mass spectrum examined at low ionizing voltages. Examination of the mass spectra of 1-bromobutane-*1,1*-d_2 and 1-bromobutane-*2,2*-d_2 demonstrated that relatively little positional scrambling of deuterium occurs in the molecular ion prior to its fragmentation by loss of ethyl radical (Figure 3, Table III): *viz.*, only *ca.* 13–16% of one deuterium atom is lost from the C_1 and C_2 positions in the fragmentation of the molecular ion of 1-bromobutane-*1,1*-d_2 or -*2,2*-d_2 under the conditions used in obtaining these spectra. Thus, comparison of the isotope compositions of the M^+ and (M − Et)$^+$ peaks in the spectra of samples of 1-bromobutane obtained from partially decomposed samples of **1**-*2,2*-d_2 provides a measure of the manner in which the deuterium present in the molecule is divided between the first two and last two carbon atoms of the butyl group. The data in Table III indicate that 1-bromobutane-d_2 derived from partial thermal decomposition of **1**-*2,2*-d_2 in methylene chloride shows the same mass spectral isotopic distribution as 1-bromobutane-*2,2*-d_2. Hence, thermal decomposition of **1**-*2,2*-d_2 in the *absence* of added triphenylphosphine apparently does not take place with significant scrambling of deuterium along the alkyl chain in undecomposed starting material.

Scheme III. Determination of the Extent of Deuterium Scrambling in **1**-*1,1*-d_2 and **1**-*2,2*-d_2 Recovered Following Partial Thermolysis

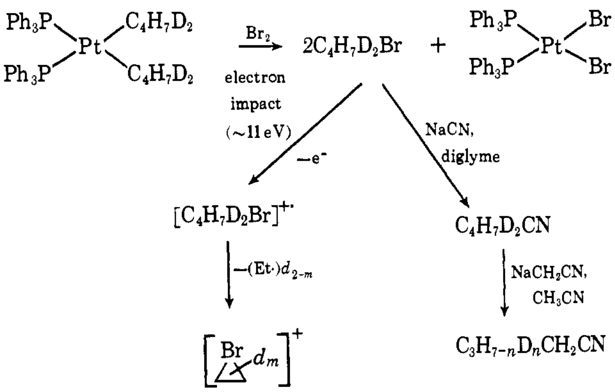

Table III. Isotopic Composition of Ions from 1-Bromobutane[a]

	M$^+$				(M − Et)$^+$			
Compound	d_0	d_1	d_2	d_3	d_0	d_1	d_2	d_3
$CH_3CH_2CH_2CD_2Br$	0	2	98	0	1	13	86	0
$CH_3CH_2CD_2CH_2Br$	0	3	97	0	2	16	82	0
n-$C_4H_7D_2Br$[b]	0	3	97	0	1	16	83	0
n-$C_4H_7D_2Br$[c]	0	2	98	0	24	49	26	0

[a] The nominal value of the ionizing voltage was 11 eV. Isotopic compositions are corrected for contributions from ^{13}C; precision is estimated to be ±1%. [b] 1-Bromobutane was obtained from partial thermal decomposition of **1**-*2,2*-d_2 (0.3 *M* in CH_2Cl_2). [c] 1-Bromobutane was obtained from partial thermal decomposition of **1**-*2,2*-d_2 (0.3 *M* in CH_2Cl_2) in the presence of added triphenylphosphine (0.3 *M*).

In contrast, comparison of the isotopic composition of M^+ and (M − Et)$^+$ for 1-bromobutane obtained from a sample of **1**-*2,2*-d_2 thermolyzed to *ca.* 1 half-life in a solution containing added triphenylphosphine indicates that extensive deuterium scrambling has occurred under these conditions. If two deuterium atoms are distributed entirely randomly along an *n*-butyl chain, the relative probabilities that the C_1,C_2 ethylene moiety will contain two, one, and zero deuterium atoms are 17:56:28, respectively.[41] Approximate corrections to these probabilities for the slight deuterium loss observed (Table III) from the C_1,C_2 ethylene moiety of 1-bromobutane-d_2 on fragmentation suggest that a statistical distribution of deuterium along the chain of 1-bromobutane-*2,2*-d_2 would lead to a distribution of isotopic compositions for the (M − Et)$^+$ fragment of d_0:d_1:d_2: 35:50:15. Thus, the observed distribution, 24:49:26, indicates qualitatively that thermolysis of **1**-*2,2*-d_2 in a solution containing added triphenylphosphine is accompanied by almost complete scrambling of the deuterium in the butyl groups of undecomposed starting material.

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(40) Chatt, *et al.*, apparently did not observe ethylene-d_3 as a product of thermal decomposition of solid ethyl-*1,1*-d_2-bromobis(triphenylphosphine)platinum(II).[6] This observation leads to conclusions concerning the relative rates of exchange of free and coordinated ethylene and platinum hydride addition to coordinated ethylene in the solid state or melt that are similar to those discussed here.

(41) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," Van Nostrand, Princeton, N. J., pp 431 ff.

The isotopic composition data in Table III demonstrate that thermal decomposition of **1**-*2,2*-d_2 in a solution containing no added triphenylphosphine does not result in interchange between deuterium at C_2 and hydrogen at C_3 or C_4; they do not permit any conclusions to be drawn concerning scrambling between C_1 and C_2. The extent of this scrambling was determined explicitly by converting the 1-bromobutane-d_2 obtained from recovered dibutyl-d_2-bis(triphenylphosphine)-platinum(II) to valeronitrile, washing out any deuterium in the position α to the nitrile group by treatment with base, and comparing the isotopic composition of the resulting exchanged valeronitrile with that of the 1-bromobutane from which it was made.[42] The 1-bromobutane had isotopic composition d_0, 0%; d_1, 2%; d_2, 98%; while that of the valeronitrile was d_0, 6%; d_1, 19%; d_2, 75%. Thus, *ca.* 13% of the deuterium originally present in the bromobutane can be exchanged following conversion to valeronitrile; this number provides a direct measure of the extent of scrambling of deuterium onto C_1 during the thermal decomposition of **1**-*2,2*-d_2.

The conclusions drawn from these mass spectrometric studies were confirmed independently by complementary nmr studies. Integration of the spectrum of 1-bromobutane-d_2 obtained from **1**-*1,1*-d_2 after incomplete thermolysis in methylene chloride solution containing no added triphenylphosphine indicated that the area of the $CH_{2-n}D_nBr$ peak at 3.15 ppm corresponded to 0.24 ± 0.1 protons (Figure 4). This estimate of transfer of *ca.* 0.24 protons from C_2 to C_1 during thermal decomposition of **1**-*1,1*-d_2 is in satisfactory qualitative agreement with the estimate, obtained by exchange and mass spectrometry, of transfer of 0.13 deuterons from C_2 to C_1 during thermolysis of **1**-*2,2*-d_2. Similarly, integration of the spectrum of 1-bromobutane-d_2 obtained from **1**-*2,2*-d_2 after incomplete thermolysis in methylene chloride solution containing 0.3 *M* triphenylphosphine indicated qualitatively that the deuterium originally localized at C_2 of the butyl group was statistically distributed along the alkyl chain. The error in this measurement is significant; however, within its limits of precision, it also points to approximately the same deuterium distribution as that inferred from the mass spectrometric studies.

In summary, these labeling experiments establish that deuterium scrambling in recovered starting material is restricted to a small (~13% of one hydrogen) interchange between C_1 and C_2, for thermal decomposition of **1** carried to 1 half-life in solutions containing no added triphenylphosphine; scrambling of deuterium during thermal decompositions of **1** carried to 1 half-life in solutions containing 0.3 *M* triphenylphosphine is essentially complete between all four carbon atoms of the *n*-butyl moiety.

Discussion

Six lines of evidence are directly pertinent to the mechanism of thermal decomposition of **1**.

(1) The products of the thermal decomposition, 1-butene, butane, and a compound of unknown composition containing platinum(0), are formed in a first-order, intramolecular process. No 2-butene is formed.

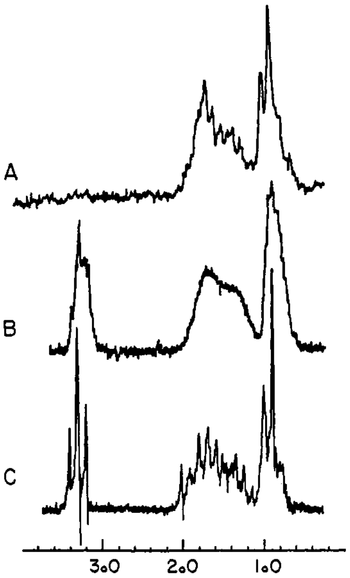

Figure 4. 60-MHz nmr spectra in carbon tetrachloride of: (A) 1-bromobutane-d_2 derived from **1**-*1,1*-d_2 after partial thermolysis in the absence of triphenylphosphine; (B) 1-bromobutane-d_2 derived from **1**-*2,2*-d_2 after partial thermolysis in the presence of triphenylphosphine; (C) 1-bromobutane-d_0.

(2) The rate of decomposition in methylene chloride solution is decreased by adding triphenylphosphine to the solution and by coordination of the dialkylplatinum(II) moiety to a chelating bidentate phosphine. Solubility experiments demonstrate that the effect of the added triphenylphosphine is that of inhibiting dissociation of a phosphine ligand from **1**.

(3) Deuterium present at C_1 or C_2 of **1** is extensively scrambled in the 1-butene product. The degree of scrambling appears to be independent of the extent of decomposition of the sample.

(4) During the platinum hydride elimination and addition reactions responsible for this deuterium scrambling, there is no exchange between 1-butene free in solution and 1- or 2-butene coordinated to platinum.

(5) Deuterium present at C_1 or C_2 of the butyl groups at the outset of decomposition carried out in solutions containing no added triphenylphosphine is found to be only slightly scrambled in starting material recovered after 1 half-life; deuterium present at C_2 is extensively scrambled in starting material recovered after 1 half-life in solutions containing added triphenylphosphine.

(6) There is no observable β-deuterium isotope effect on the rate of thermal decomposition of **1** carried out in solutions containing no added triphenylphosphine.

The most important features of the reaction profile characterizing the thermal decomposition of **1** in solutions containing no added triphenylphosphine are defined by three of these observations. First, the scrambling of deuterium in the 1-butene formed during decomposition of **1**-*1,1*-d_2 and **1**-*2,2*-d_2 indicates that the elimination of platinum hydride from butyl groups and its readdition to coordinated 1-butene are both more rapid reactions than the reductive elimination of *n*-butane from intermediates containing hydride and *n*-butyl groups σ bonded to platinum. Second, the

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[42] Independent experiments using authentic valeronitrile-*2,2*-d_2 established that ~98% of the deuterium present in this substance was lost during the exchange procedure.

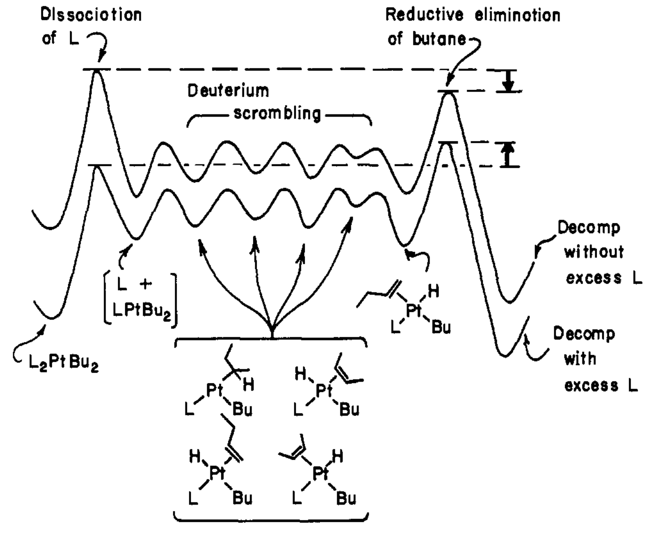

Figure 5. Schematic representation of the reaction coordinate describing the thermal decomposition of **1**. The separation between two curves is arbitrary, since one represents Gibbs free energy *G* for a solution containing no added phosphine while the second represents *G* for a solution containing added triphenylphosphine. L represents triphenylphosphine.

observation that the scrambling of deuterium does not extend to undecomposed starting material establishes that the starting material and those intermediates in which deuterium scrambling occurs are separated by a barrier *higher* than that for the reductive elimination step. Finally, since the highest barrier for thermal decomposition carried out in the absence of added triphenylphosphine appears to be that separating starting material from the hydrido- and *sec*-butylplatinum intermediates responsible for deuterium scrambling, and since the overall rate of the decomposition is decreased by either the presence of triphenylphosphine in solution or by chelating phosphines on the platinum atom, the rate-determining step in the absence of added triphenylphosphine can be assigned to a step involving dissociation of **1** into 1 equiv of triphenylphosphine and 1 equiv of a three-coordinate platinum complex, presumably having the composition $Ph_3PPt(n\text{-}Bu)_2$ (**5**). A reaction coordinate which accommodates these observations is represented in Figure 5.

A number of features of this diagram, and of the mechanism it implies, deserve amplification. First, the vertical axis in the diagram represents *G*, the Gibbs free energy, rather than *E* or *H*. Thus, added triphenylphosphine decreases the rate of the thermal decomposition by decreasing the magnitude of $\Delta S^{\ddagger}$ (and correspondingly of $\Delta G^{\ddagger}$) for the *recombination* of triphenylphosphine (called L in the diagram) with $LPtBu_2$ (**5**), rather than by *increasing* the magnitude of $\Delta G^{\ddagger}$ for the *dissociation* step. Since the magnitude of $\Delta G^{\ddagger}$ for the dissociation is not influenced by added L, the observed decrease in overall rate implies that some step other than dissociation of L from **1** becomes rate determining in the presence of added L. This implication is supported by the observation of extensive deuterium scrambling in **1**-d_2 recovered from samples partially decomposed in the presence of added L but not from samples decomposed in the absence of added L.[43] Second, we have no direct evidence for the existence of $LPtBu_2$ as a discrete intermediate along the reaction coordinate and certainly no evidence concerning its stability relative to that of the intermediates responsible for scrambling. In principle, extrusion of the olefin into the coordination site occupied by the leaving phosphine ligand could be concerted with phosphine–platinum bond breaking. However, the observation that there is no β-deuterium isotope effect on the rate of thermal decomposition of **1** in the absence of added triphenylphosphine suggests that β C–H bond breaking is not important in the dissociation step.[44] Third, the structure and relative energies of the intermediates responsible for deuterium scrambling, and the magnitudes of the barriers separating these species, are not known. The deuterium scrambling data suggest that exchange between C_1 and C_2 is more rapid than that between C_2 and C_3. Evidence taken from other studies suggests that complexes of 2-butene with platinum(II) should be less stable than analogous complexes of 1-butene.[7,39,45] These observations, although helpful in estimating qualitative stabilities for the intermediates involved in the deuterium scrambling, do not provide sufficient information to estimate relative concentrations.

We assume that the intermediate from which reductive elimination of butane takes place has hydride and alkyl groups cis[46] and that the reductive elimination step is concerted.[47]

This study, in establishing the basic mechanism for the thermal decomposition of **1**, points out certain principles which should be applicable in practice to the synthesis of organometallic compounds of platinum, and presumably of other transition metals, having high thermal stability. Thus, in particular, alkyl

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[43] The observation of a small amount of scrambling between C_1 and C_2 in recovered starting material in the absence of added L suggests that the energies of the transition states leading to loss of L from **1**, and to reductive elimination of butane, in fact differ by ~1 kcal/mol.

[44] Another alternative, involving extrusion of olefin to give a five-coordinate intermediate complex i in a preequilibrium step occurring

$$\begin{array}{l} L_2Pt(n\text{-}Bu)_2 \rightleftharpoons \\ L_2PtH(n\text{-}Bu)(1\text{-butene}) \xrightarrow[\text{rate determining}]{-L} LPtHBu(1\text{-butene}) \\ \quad\updownarrow\, i \\ L_2Pt(n\text{-}Bu)(sec\text{-}Bu) \end{array}$$

before dissociation of a molecule of triphenylphosphine, is also formally compatible with our evidence, *provided* that platinum–hydride addition to the coordinated 1-butene in i only takes place to regenerate starting material. However, since platinum hydride addition to 1-butene can clearly occur to give either primary or secondary carbon–platinum bonds during the reactions involved in deuterium scrambling, it is not clear why both directions of addition also should not occur in an intermediate such as i.

[45] R. J. Cvetanovic, F. J. Duncan, W. E. Falconer, and R. S. Irwin, *J. Amer. Chem. Soc.*, **87**, 1827 (1965); R. Cramer, *ibid.*, **89**, 4621 (1967); F. R. Hartley and L. M. Venanzi, *J. Chem. Soc. A*, 333 (1967), and references cited in each.

[46] Concerted trans reductive elimination is possible but seems unlikely: *cf.* F. R. Jensen and B. Knickel, *J. Amer. Chem. Soc.*, **93**, 6339 (1971); J. A. Labinger, R. J. Braus, D. Dolphin, and J. A. Osborn, *Chem. Commun.*, 612 (1970); R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970); J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *ibid.*, **94**, 4043 (1972); and G. M. Whitesides and D. J. Boschetto, *ibid.*, **93**, 1529 (1971), for brief discussions of the stereochemistry of oxidative addition of alkyl halides to transition metals.

[47] Free alkyl radical intermediates have been excluded in a related reductive elimination involving a palladium alkyl: E. Vedejs and M. F. Salomon, *ibid.*, **92**, 6965 (1970). See also G. M. Whitesides, J. San Filippo, Jr., E. R. Stedronsky, and C. P. Casey, *ibid.*, **91**, 6542 (1969).

derivatives of platinum(II) in which metal hydride elimination is blocked, either by incorporation of ligands which render the metal coordinatively saturated or by using σ-alkyl groups so constructed that metal hydride elimination from them is impossible, should be more stable than **1**.

In a more general vein, it appears that rationalizations of the thermal instability of transition metal alkyls that are based on considerations of the relative energies of carbon–metal σ and σ^* orbitals[48] have only small pertinence to the thermal decompositions of many, or perhaps most, derivatives of d^8–d^{10} metals studied to date, since metal hydride elimination rather than homolytic carbon–metal bond scission seems to provide the lowest energy pathway for thermal decomposition available for alkyl derivatives of those metals capable of forming strong bonds to hydrogen.[49] The high stability associated with methyl, neopentyl, and aryl derivatives of these metals is thus attributable to the absence of β hydrogens which can be eliminated as metal hydride.

For compounds of the d^8–d^{10} metals in which metal hydride elimination has been blocked as a pathway for thermal decomposition, it is not obvious what reaction type will emerge as preferred for decomposition. Mechanisms involving homolytic scission of carbon–metal bonds provide one possibility;[50] bimolecular decompositions, or reactions occurring between organic ligands on a common metal center or on the surface of a metal atom cluster, provide a second.[51] If radical mechanisms *do* intervene, increasingly the polarity of the carbon–metal bond should increase the stability of the compound toward thermal decomposition, and the stability of organometallic derivatives of fluorocarbons,[52] metal acetylides, and the recently reported derivatives of trimethylsilyllithium[53] can each be rationalized on the grounds that these substances cannot decompose by elimination of metal hydrides and that low-energy polar resonance structures for their carbon–metal bonds render homolytic bond scission energetically unfavorable. If, however, nonradical reactions leading, *e.g.*, to organic dimers prove to provide the lowest energy pathway for thermal decomposition,[51] devising a successful, rational formula for the protection of organometallic compounds against thermal decomposition will depend on an understanding of the details of the mechanisms involved.

Experimental Section[54]

***cis*-Dichlorobis(triphenylphosphine)platinum(II)**, prepared from potassium tetrachloroplatinite and triphenylphosphine in ethanol, according to the method of Jensen,[56] had mp 305° dec (lit.[56] mp 308° dec).

***cis*-Dichlorobis(triphenylphosphine-d_{15})platinum(II)** was prepared using triphenylphosphine-d_{15} having mass spectral isotopic analysis: 90% d_{15}, 9% d_{14}, 1% d_{13}.[57] Recrystallization from CH_2Cl_2–heptane gave material having mp 305° dec.

Dichloro[1,1′-bis(diphenylphosphino)ferrocene]platinum(II). A solution of 2.0 g (4.8 mmol) of potassium tetrachloroplatinite in 30 ml of water was treated with 1.0 g (10 mmol) of diethyl sulfide. The reaction mixture was stirred for 3 hr and extracted with two 20-ml portions of methylene chloride.[58] The extract was added to a solution of 3 g (4.8 mmol) of 1,1′-bis(diphenylphosphino)ferrocene[13,59] in 80 ml of methylene chloride. After the reaction mixture was stirred for 1 hr, 75 ml of heptane was added, and the resulting solution was slowly concentrated at room temperature by stirring using reduced pressure (100 Torr) to *ca.* 70 ml. The resulting solid was filtered and dried at 0.01 Torr. The bright yellow powder had mp 335° dec (lit.[13] mp > 315° dec) and weighed 3.8 g (90%): ir (KBr) 3050 w, 1430 sp, 1160 mb, 1100 mb, 750 sb, 650 w, 500 b cm^{-1}.

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[48] For reviews, see ref 5a,b and J. Chatt and B. L.Shaw, *J. Chem. Soc.*, 1718 (1960).

[49] Alkylsilver(I) compounds might be expected to be less likely to decompose by a pathway involving metal hydride elimination than are alkylcopper(I) compounds, since silver(I) hydride appears to be somewhat less stable than copper(I) hydride. Thus, efforts to prepare silver hydride using techniques previously proved successful in the preparation of copper hydride[16] have resulted in the formation of uncharacterized materials of very low thermal stability that decomposed rapidly even at −78°, with formation of silver(0) and evolution of hydrogen. (Note, however, that AgH has been detected in the vapor phase and inferred in solution: B. Siegel, *J. Chem. Educ.*, **38**, 496 (1961); J. Halpern, *Advan. Catal.*, **11**, 301 (1959); J. Halpern, G. Czapski, J. Jortner, and G. Stein, *Nature* (*London*), **186**, 619 (1960)). In keeping with this expectation, examination of the mechanism of thermal decomposition of *n*-butyl(tri-*n*-butylphosphine)silver(I) has in fact provided good evidence that a silver hydride is not an intermediate in this reaction: P. E. Kendall, unpublished.

[50] See, for example, G. M. Whitesides, E. J. Panek, and E. R. Stedronsky, *J. Amer. Chem. Soc.*, **94**, 232 (1972), and references cited therein.

[51] Vinylic and arylcopper(I) and -silver(I) compounds produce the dimers of the organic ligands on thermal decomposition, by mechanisms that do *not* involve organic free radicals: G. M. Whitesides, C. P. Casey, and J. K. Krieger, *ibid.*, **93**, 1379 (1971); A. Cairncross and W. A. Sheppard, *ibid.*, **93**, 247 (1971); A. Cairncross, H. Omura, and W. A. Sheppard, *ibid.*, **93**, 248 (1971).

[52] Reviews: R. S. Nyholm, *Quart. Rev., Chem. Soc.*, **24**, 1 (1970); M. I. Bruce and F. G. A. Stone, *Angew. Chem., Int. Ed. Engl.*, **7**, 747 (1968).

[53] G. Yagupsky, W. Mowat, A. Shortland, and G. Wilkinson, *Chem. Commun.*, 1369 (1970); F. Hug, W. Mowat, A. Shortland, A. C. Skapski, and G. Wilkinson, *ibid.*, 1079 (1971); M. R. Collier, M. F. Lappert, and M. M. Truelock, *J. Organometal. Chem.*, **25**, C36 (1970); M. R. Collier, B. M. Kingston, and M. F. Lappert, *Chem. Commun.*, 1498 (1970).

[54] Melting points were determined using a Thomas-Hoover capillary melting point apparatus in tubes sealed under reduced pressure (80 Torr) and are uncorrected. Boiling points are uncorrected. Infrared spectra were taken in sodium chloride cells or potassium bromide pellets as noted using a Perkin-Elmer Model 237 or 237B grating spectrophotometer. Band positions are reported in reciprocal centimeters with the following notations: vs, very strong intensity; s, strong; m, medium; w, weak; b, broad; sh, shoulder; and sp, sharp. Mass spectra used for compound identification were determined on a Hitachi Perkin-Elmer RMU-6D mass spectrometer at 70 eV; spectra used in isotopic analysis were taken at the lowest ionizing voltages compatible with adequate signal intensities.[55] Product mixtures were analyzed by glpc on an F & M Model 810 flame ionization instrument equipped with a Disc integrator. Products were collected for mass spectra by glpc using a F & M Model 720 thermal conductivity instrument. The following columns were used: column A, 6 ft × 0.25 in. 3% Apiezon M on 40:60 alumina operated at 80°; column B, 8 ft × 0.25 in. 20% UCW98 on 60:80 Chromosorb P operated at 80°; column C, 8 ft × 0.375 in. 20% SE-30 on 60:80 Chromosorb P operated at 50°; column D, 8 ft × 0.25 in. 10% XF 1150 on 60:80 Chromosorb P operated at 80°; column E, 10 ft × 0.25 in. 20% saturated solution of $AgNO_3$–tetraethylene glycol on 60:80 aqueous bicarbonate-washed Chromosorb operated at 40°; column F, 6 ft × 0.25 in. 10% saturated solution of $AgNO_3$–benzyl cyanide on 60:80 aqueous bicarbonate-washed Chromosorb P operated at −10°; column G, 10 ft × 0.25 in. 10% Carbowax 20M on 70:80 Chromosorb P operated at 100°. Nmr spectra were taken using Varian A-60, T-60, or HA-100 spectrometers. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind.

[55] K. Biemann "Mass Spectrometry-Organic Chemical Applications," McGraw-Hill, New York, N. Y., 1962, pp 223 ff.

[56] K. A. Jensen, *Z. Anorg. Allg. Chem.*, **229**, 242 (1936).

[57] Triphenylphosphine-d_{15} was generously provided by Dr. W. J. Ehmann, Jr.: *cf.* G. M. Whitesides and W. J. Ehmann, *J. Amer. Chem. Soc.*, **92**, 5625 (1970); and W. J. Ehmann, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1969.

[58] Reported preparations of halophosphine–platinum(II) complexes have usually involved adding aqueous potassium tetrachloroplatinite to a hot solution of phosphine in a solvent, such as ethanol or 2-propanol, that does not dissolve either potassium tetrachloroplatinite or the product complex. This procedure frequently leads to impure products. Dichlorobis(diethylsulfido)platinum(II) is readily soluble in methylene chloride, and the diethyl sulfide ligand is readily displaced by phosphines. The use of this platinum complex as an unisolated intermediate leads to homogeneous reactions and to product of high purity.

[59] G. P. Sollot, J. L. Snead, S. Portnoy, W. R. Peterson, and W. E. Metway, U. S. Department of Commerce, Office of Technical Services, Report A. D. 611869; *Chem. Abstr.*, **63**, 18147*a* (1965).

***cis*-Di-*n*-butylbis(triphenylphosphine)platinum(II) (1).** To a stirred suspension of 2.0 g (2.5 mmol) of *cis*-dichlorobis(triphenylphosphine)platinum(II) in 20 ml of dry ether at 0° was added 4 ml (6.2 mmol) of a 1.6 *M* solution of *n*-butyllithium in hexane. The reaction mixture was allowed to warm to 25° over 30 min and 10 ml of water was added. The resulting solid was collected and washed in succession with 5-ml portions of water, ethanol, and ether. After drying at 100 Torr, the product weighed 2.0 g (95%) and had mp 125° dec (lit.[60] mp 132–134°). Precipitation of the sample from *ca.* 20 ml of methylene chloride by adding an equal volume of heptane and removing methylene chloride at reduced pressure[20°(100mm)], followed by recrystallization from methylene chloride, yielded a colorless crystalline analytical sample (90%), having ir (KBr) 3050 m, 2950 sh, 2920 s, 2860 sh, 1480 sp, 1440 sp, 1190 m, 1160 m, 1100 s, 740 vs, 700 vs, 540 sh, 515 vs, 500 sh, 420 cm^{-1}, and nmr (CD_2Cl_2) δ 0.5–1.3 (m, 18) and 7.1–7.7 (m, 30).

Anal. Calcd for $C_{44}H_{48}P_2Pt$: C, 63.37, H, 5.80; P, 7.43. Found: C, 63.11; H, 5.85; P, 7.29.

The complexes **1**, **2**, and **3** were microcrystalline powders when precipitated from methylene chloride by heptane. When recrystallized slowly from a single solvent, they were macrocrystalline solids. These materials are stable when solid toward water and oxygen, stable in solution toward water, slightly oxygen-sensitive in solution, and somewhat light sensitive both when solid and in solution. They are insoluble in saturated hydrocarbon solvents and water, slightly soluble in ethyl ether and ethanol, and moderately soluble in methylene chloride and toluene.

***cis*-Di-*n*-octylbis(triphenylphosphine)platinum(II) (2).** To a stirred suspension of 1.6 g (2 mmol) of *cis*-dichlorobis(triphenylphosphine)platinum(II) in 20 ml of ether at 0° was added 3 ml (6 mmol) of a 2 *M* solution of *n*-octyllithium in hexane. After the addition, the reaction mixture was allowed to warm to room temperature over 30 min and 1 ml of methanol was added. The solution was concentrated under reduced pressure, and the resulting solid partitioned between a mixture of 20-ml each of water and methylene chloride. The layers were separated and the organic layer was dried ($MgSO_4$). After the addition of 20 ml of heptane, the methylene chloride was slowly removed (20°, 100 Torr). After drying at 30° and 0.1 Torr, the resulting off-white microcrystalline product weighed 1.6 g (85%), and had mp 70° dec. Recrystallization twice from acetone at −30° gave crystalline colorless material having mp 76° dec and ir (KBr) 2900 vs, in addition to absorptions at 3050, 1430, 1160, 1100, 750, 700, 650 cm^{-1} that are found in L_2PtCl_2: nmr (CD_2Cl_2) δ 0.4–1.6 (m, 36), 7.1–7.8 (m, 30).

Anal. Calcd for $C_{52}H_{64}P_2Pt$: C, 66.43; H, 6.87; P, 5.94. Found: C, 66.38; H, 6.84; P, 6.21.

***cis*-Di-*n*-octylbis(triphenylphosphine-*d*$_{15}$)platinum(II)**, prepared from *cis*-dichlorobis(triphenylphosphine-*d*$_{15}$)platinum(II) and *n*-octyllithium, had mp 75° dec after recrystallization from acetone.

Di-*n*-butyl[1,1′-bis(diphenylphosphino)ferrocene]platinum(II) (3). To a stirred suspension of 0.87 g (1 mmol) of dichloro[1,1′-bis(diphenylphosphino)ferrocene]platinum(II) in 20 ml of ether at 0° was added 2 ml (3 mmol) of 1.5 *M* *n*-butyllithium in hexane solution. After 20 min the reaction mixture was centrifuged, and the supernatant solution was separated and concentrated to yield a yellow solid. This solid was dissolved in 20 ml of methylene chloride, the solution was filtered, 10 ml of heptane was added, and methylene chloride was removed at room temperature (100 Torr) to yield a powder which was isolated by filtration and dried at 60° (1 Torr): mp (dec) 172.5–173.5°; ir (KBr) 2900 s, 3050, 1430, 1160, 1100, 750, 700, 650, and 600 cm^{-1}; nmr ($CDCl_3$) δ 0.5–1.3 (m, 18), 6.5–6.7 (m, 8), 7.1–7.5 (m, 24). An analytical sample was obtained by recrystallization from methylene chloride.[61]

Anal. Calcd for $C_{42}H_{48}FeP_2Pt$: C, 58.41; H, 5.40; P, 7.18. Found: C, 57.91, 57.95; H, 5.53, 5.61; P, 7.00, 7.11.

Ethyl 2,2-Dichlorobutyrate. To a solution prepared from 5 g (0.22 g-atom) of sodium metal in 500 ml of dry ethanol in a three-necked 1-l. flask containing a magnetic stirring bar and equipped with a dropping funnel and dry nitrogen inlet was added at 0° over 1 hr 140 g (1 mol) of 2,2-dichlorobutyronitrile.[62] After standing for 1 hr, the solution was added slowly, with constant stirring, to a mixture of 800 g of ice and 150 ml (1.8 mol) of concentrated hydrochloric acid. The resulting mixture was extracted with three 100-ml portions of 1 *M* sodium bicarbonate, dried ($MgSO_4$), and distilled carefully using a 40-cm Teflon spinning-band column. Analysis by glpc (column G) showed that early distillation fractions contained ethyl 2-chlorobutyrate, derived from a small quantity of 2-chlorobutyronitrile in the starting material. The ethyl 2,2-dichlorobutyrate (140 g, 76%) obtained had bp 75–76° (18 Torr) [lit.[63] bp 71° (16 Torr)].

1-Butanol-*2,2-d*$_2$. Powdered zinc metal (200 g) was activated by washing with 200 ml of 5% hydrochloric acid followed by three 200-ml portions of water. The activated powder was collected by filtration and placed in a three-necked 2-l. flask equipped with a mechanical stirrer and Dean-Stark trap. Benzene (200 ml) was added and the mixture was refluxed until all water was removed. Most of the benzene was removed by distillation and 250 ml of 1,2-dimethoxyethane (DME), freshly distilled from benzophenone sodium dianion, was added. A reflux condenser and dropping funnel were fitted to the flask. The dropping funnel was charged with 145 g (0.8 mol) of ethyl 2,2-dichlorobutyrate, 80 g (4 mol) of deuterium oxide (99.5% *d*$_2$), and 300 ml of dry DME. This two-phase mixture was agitated while being added over 2 hr to the stirred, refluxing suspension of zinc in DME.[64] After an additional 8 hr at reflux temperature no dichloro or monochloro ester remained, as determined by glpc (column G). After cooling, the solids were filtered and washed with two 150-ml portions of dry ether. The combined filtrates were added slowly over 12 hr to a mixture of 80 g (2 mol) of lithium aluminum hydride in 250 ml of dry ether in the same apparatus. On completion of the reduction, cautious addition of 80 ml of saturated sodium sulfate solution produced a semisolid mass that was extracted four times with 100-ml portions of ether. The dried ($MgSO_4$) extract was distilled using a Teflon spinning-band column to yield 44 g (73%) of 1-butanol-*2,2-d*$_2$, having bp 116°.

1-Butanol-*1,1-d*$_2$ was prepared by reduction of methyl *n*-butyrate using lithium aluminum deuteride.

1-Bromobutane-*1,1-d*$_2$ and 1-bromobutane-*2,2-d*$_2$ were prepared from the corresponding alcohols by treatment with concentrated hydrobromic acid in concentrated sulfuric acid.[65] The former had isotopic composition 98% *d*$_2$, 2% *d*$_1$; the latter had isotopic composition 97% *d*$_2$, 3% *d*$_1$.

Di-*n*-butyl-*1,1-d*$_2$-bis(triphenylphosphine)platinum(II), di-*n*-butyl-*2,2-d*$_2$-bis(triphenylphosphine)platinum(II), and di-*n*-butyl-*2,2-d*$_2$-(1,1′-bisdiphenylphosphinoferrocene)platinum(II) were prepared and purified using methods identical with those used in the preparation of nondeuterated materials using *n*-butyllithium-*1,1-d*$_2$ and *n*-butyllithium-*2,2-d*$_2$. The melting points of the purified samples were identical with those of nondeuterated samples.

Reaction of Di-*n*-butyl-*2,2-d*$_2$-bis(triphenylphosphine)platinum(II) (1-*2,2-d*$_2$) with 1,2-Diphenylphosphinoethane (diphos). A 0.20 *M* solution of **1**-*2,2-d*$_2$ was prepared and the nmr spectrometer tuned. A 0.25-equiv portion of solid diphos was dissolved in the sample and a spectrum of the solution immediately taken.[66] Change in the composite spectrum could be observed in 10 min. Spectra were taken at regular intervals over 6 hr, after which time subsequent spectra showed no change. The nmr spectrum of this solution was compatible with a formulation of the resulting complex as di-*n*-butyl-*2,2-d*$_2$-(diphos)platinum(II). This solution was heated at 60.0° for 24 hr, treated with hydrochloric acid, and analyzed by glpc. The per cent decomposition of the complex, as determined by butane-butene areas as described in the Kinetics Studies section, was 4%.

Products of Thermal Decomposition of *cis*-Di-*n*-butylbis(triphenylphosphine)platinum(II). Solutions of **1** in sealed tubes decomposed in *ca.* 3 hr at 60° to give a red solution. The organic products of the decomposition were determined by glpc analysis (column A) using pentane as internal standard and column F using heptane as internal standard. Together the columns separate *n*-butane, 1-butene, *cis*- and *trans*-2-butene, and octane. The products of decomposition of 0.1 *M* solutions of **1** in methylene chloride or benzene, as a suspension in hexane, and as a solid (at *ca.* 120°), were 50 ± 1% butane, 50 ± 1% 1-butene, and less than 1% of *cis*-

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(60) B. A. Morrow, *Can. J. Chem.*, **48**, 2192 (1970).

(61) Compound **3** includes solvent of crystallization tenaciously. This analytical sample was prepared by Dr. Terry Newirth.

(62) 2,2-Dichlorobutyronitrile was obtained as a gift from the Dow Chemical Co.

(63) J. von Braun, F. Jostes, and W. Munch, *Justus Liebigs Ann. Chem.*, **453**, 136 (1927).

(64) Agitation was accomplished by passing a stream of nitrogen through the mixture; agitation was sufficiently vigorous that the amount of D_2O and ethyl dichlorobutyrate added to the zinc suspension were roughly proportionate, despite the heterogeneous nature of the mixture.

(65) O. Kamm and C. S. Marvel, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1941, p 25.

(66) Diphos was prepared from triphenylphosphine by the procedure of J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).

or *trans*-2-butene or octane. Products were identified by comparison of glpc retention times and mass spectra with those of authentic samples (Matheson).

An inorganic product was isolated by heating a saturated (at 60°) solution of **1** in benzene or methylene chloride for *ca.* 3 hr, allowing the tube to stand at room temperature overnight, collecting by filtration, washing the resulting red solid with hexane, and drying. From 0.30 g of **1** in 2 ml of benzene was obtained 0.21 g of material, mp 242° dec (with change in form at 139°); from 0.3 g of **1** in 0.5 ml of methylene chloride was obtained 0.22 g of material, mp 240° dec (with change in form at 139°): ir (KBr) 3050 mb, 1480–1470 s doublet, 1430 sp, 1380 mb, 1120 wsh, 1095 s, 735 s, 685 vs cm^{-1}.

Anal. Found: C, 55.20; H, 3.95; P, 9.31.

We were not successful in identifying this substance (*vide supra*).

Tris(triphenylphosphine)platinum(0) was prepared according to the method of Ugo, *et al.*, by reduction of potassium tetrachloroplatinite in ethanol in the presence of triphenylphosphine.[67] The yellow solid obtained had mp (in air) 120–125° [lit.[67] (in air) 125–135°], mp (1 mm) 192–198° (red liquid) [lit.[67] mp (1 mm) 205–206° (red liquid)]. Recrystallization under nitrogen from acetone[67] gave pale yellow platelets which darkened instantly to a bronze color upon exposure to air. Even in a nitrogen-filled glove bag the color changed slightly during transfer to a melting point capillary: mp (1 mm) 195–200°; ir (KBr) 1430 vs, 1175 vs, 1150 mn, 1075 vs, 1020 s, 990 s, 740 vs, 700 vs cm^{-1}.

Iodomethylbis(triphenylphosphine)platinum(II) was prepared according to the method of Chatt[10a] by reaction of tris(triphenylphosphine)platinum(0) and methyl iodide. After recrystallization from benzene, the material had mp 272–275° (lit.[67] mp 270–274°): ir (KBr) 3050 w, 2950 w, 1480 sp, 1440 sp, 1100 sb, 745 sb, 690 vs cm^{-1}.

The solubility of di-*n*-butylbis(triphenylphosphine)platinum(II) in methylene chloride was determined with and without 0.1 *M* triphenylphosphine present. A mixture of excess solid platinum complex and methylene chloride or of excess complex and a solution of triphenylphosphine in methylene chloride was stirred at 22° for 10 min and filtered into a 1-ml volumetric flask, and the solvent was removed under vacuum to constant weight. The solubilities were determined to be 228 mg of complex per milliliter of methylene chloride; 230 mg of complex per milliliter of methylene chloride that was 0.1 *M* in triphenylphosphine; and 205 mg of complex per milliliter of methylene chloride that was 0.3 *M* in triphenylphosphine. After washing with a small volume of hexane, the residue from filtration of the solution containing 0.3 *M* triphenylphosphine had a melting point identical with that of **1**. A saturated solution of **1** at 22° in methylene chloride is 0.28 *M*.

Thermolysis of 1 in the Presence of Triphenylphosphine. A sealed tube containing a degassed solution of 0.80 g of **1** and 0.30 g of triphenylphosphine in 2 ml of methylene chloride was heated at 60° for 72 hr. The tube was cooled and opened, and 4 ml of hexane was added. The resulting solid was collected by filtration, boiled in 10 ml of ethanol under nitrogen for 2 hr, filtered, washed with ethanol, and dried (0.1 Torr, 25°) to yield 0.70 g (70%) of a yellow solid identified as tris(triphenylphosphine)platinum(0) by its mp (1 Torr) 191–198°; mp [of an authentic sample (*vide supra*) (1 Torr)] 192–198° (lit.[66] mp 205–206°), by the identity of its ir spectrum (KBr) to that of authentic material; and by its conversion to iodomethylbis(triphenylphosphine)platinum(II) (80%). After recrystallization from benzene the iodomethyl complex had mp 270–273°, mmp 271–273° (lit.[67] mp 270–274°), and an ir spectrum indistinguishable from that of authentic material.

Thermolysis of 1 in the Presence of Methyl Iodide. A sealed tube containing a degassed solution of 0.80 g of **1** and 2 ml of methyl iodide was heated at 60° for 3 hr. The resulting solid (0.75 g, 70%) was collected, recrystallized from benzene, and identified as iodomethylbis(triphenylphosphine)platinum(II): mp 270–274°; mmp 271–274° (lit.[67] mp 270–274°); and spectrum indistinguishable from that of authentic material.

Thermolysis of 1 in 1,5-Hexadiene. 1,5-Hexadiene (99.9%), obtained from Chemical Samples Co., was purified by preparative glpc (column E); the material used as solvent contained less than 0.001% 1-hexene. In a representative experiment, a sample containing 55.8 mg (0.067 mmol) of **1**, 1 μl (0.78 mg) of *cis*-1,2-dimethylcyclohexane as an internal glpc standard, and 1.0 ml of 1,5-hexadiene was degassed and sealed in a Pyrex tube, heated at 80° for 6 hr, cooled, opened, and analyzed by glpc (column E). Besides butane, 1-butene, internal standard, and solvent there were three peaks respectively assigned to 1-hexene (0.8 mg, 0.01 mmol, 10 ± 5% based on the assumption that production of 1 equiv of 1-hexene from thermal decomposition of 1 equiv of **1** would constitute 100%), *cis*-1,4-hexadiene (structure assigned by comparison of glpc retention time and mass spectrum with that of an authentic sample), and a compound whose retention time corresponded with those of *trans*-1,4-, *cis*-1,3-, and *trans*-1,3-hexadiene. Samples of 1-hexene used for isotopic analysis following thermal decomposition of **1**-*2,2*-d_2 in 1,5-hexadiene were collected from glpc (column E).

Reaction of 1 with Hydrochloric Acid. Into a flame-dried centrifuge tube was weighed 50 mg (0.017 mmol) of **1**. A no-air stopper was fitted to the tube and the solid dissolved at 0° in 1 ml of methylene chloride containing pentane as internal standard. At 0°, 1 ml of concentrated aqueous hydrochloric acid was added and the tube was shaken for 5 min. The product mixture was centrifuged and the methylene chloride layer was analyzed by glpc using columns A and B. The yield of butane was 100%; no (<1%) butene or octane was formed. The upper aqueous layer was discarded and 5 ml of pentane added to the remaining mixture. The solid was collected, washed with pentane, and dried to give 50 mg of dichlorobis(triphenylphosphine)platinum(II), mp 303° dec, mmp 303° dec.

Kinetics Studies. General Methods. Solutions of **1** used for kinetics studies were prepared by weighing **1** into a volumetric flask and adding dry methylene chloride that had been distilled and stored over 5A Linde Molecular Sieves. Aliquots (0.25 ml) of this solution were transferred to Pyrex tubes (8 mm) that had been washed with dilute hydrochloric acid, rinsed with distilled water, soaked in dilute ammonia solution, and dried in a vacuum oven; the tubes were degassed at 0.05 Torr and sealed. The tubes were immersed in a 60 ± 0.1° oil bath (except as noted), removed at intervals, and stored at liquid nitrogen temperature until quenched. Quenching was carried out by opening the tube at 0°, adding *ca.* 0.2 ml of concentrated hydrochloric acid, fitting a no-air stopper to the tube, and mixing the two layers by shaking. All samples were quenched at the same time and stored at −20° during glpc analyses. As a control, one tube in each set was not heated but was otherwise treated in the same manner as the thermolyzed samples. Analysis of this tube showed no olefin (<1)% due to spurious decomposition.

Since undecomposed **1** produced only butane on quenching, and **1** produced equimolar amounts of 1-butene and butane on thermal decomposition, it was possible to determine the extent of decomposition of **1** from the relative areas of the peaks due to 1-butene and butane in the glpc traces of the protonolyzed samples without need of an internal standard. However, to verify the accuracy of this method, an internal standard (pentane) was used in representative decomposition reactions. As an internal check, two points were computed from the glpc trace of each sample in these reactions: one from the ratio of areas of the butene and pentane peaks (100 minus per cent yield butene), the other from the butene–butane areas: 100 minus two times the butene area divided by (butene area + butane area). Typical data obtained using each method are plotted in Figure 2. The agreement between these procedures is satisfactory: first-order rate constants were estimated to be $3.6 \pm 0.1 \times 10^{-4} sec^{-1}$.

Thermal Decomposition of 1 in the Presence of Added Triphenylphosphine. The concentration of **1** was held constant at 0.03 *M* while the concentration of phosphine was varied over 0.20, 0.13, 0.086, and 0.043 *M* solutions. The corresponding rate constants obtained in these experiments were 5.5, 5.6, 5.2, and $5.8 \times 10^{-6} sec^{-1}$, respectively, from data that extended through 2 half-lives.

Thermal decomposition of di-*n*-butyl-2,2-d_2-bis(triphenylphosphine)platinum(II) (1-*2,2*-d_2) (0.03 *M* in methylene chloride) yielded a rate constant of $3.7 \times 10^{-4} sec^{-1}$.

Thermal decomposition of di-*n*-octylbis(triphenylphosphine)platinum(II) (2) (0.3 *M*) was carried out in methylene chloride solution. The combined yield of octane and octene was determined to be 99% by glpc (column B) using *n*-nonane as internal standard. The relative amounts of *n*-octane and 1-octene were determined by collecting the single octane–octene peak by glpc from column B, dissolving the material in pentane, and reanalyzing on column E. After 20 hr at 60° the ratio of octane to octene was 51:49. Kinetic data obtained using techniques described above yielded a first-order rate constant for thermal decomposition of **2** of $4.0 \times 10^{-4} sec^{-1}$.

Thermal decomposition of di-*n*-butyl[1,1′-bis(diphenylphosphino)ferrocene]platinum (II) (3) (0.03 *M* in methylene chloride) produced a red solution and a black metallic "mirror." The inorganic products of this reaction were not determined; butane and 1-butene were produced in yields of 40 and 60%, respectively. The rate

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[67] R. Ugo, F. Cariati, and G. LaMonica, *Inorg. Syn.*, 11, 106 (1968).

constant for decomposition was determined to be 1.9×10^{-4} sec^{-1} at 120 ± 2°.

Deuterium Labeling Studies. General Methods. Solutions of deuterated platinum complexes were prepared and thermolyzed following procedures outlined in the Kinetics section; except where noted solutions were heated for *ca.* 6 half-lives. In purifying material by glpc for deuterium analyses, care was taken to collect as much of the peak as possible to avoid isotopic fractionation.[55] Hydrocarbons were collected at liquid nitrogen temperature (column A) and their isotopic composition determined using a nominal ionizing voltage of 10 eV.[68] Results of these studies are given in the text.

Preparation and Mass Spectral Analysis of 1-Bromobutane from Di-*n*-butyl-2,2-d_2-bis(triphenylphosphine)platinum(II) Recovered Following Partial Thermal Decomposition. A solution of 250 mg of the platinum compound in 2 ml of methylene chloride contained in an 8-mm Pyrex tube was degassed at 0.001 Torr, sealed, and heated at 60.0° for 20 min. The tube was opened, the volatiles were swept off with a stream of nitrogen, and the resulting solid was evacuated to 0.05 Torr for 30 min. After 2 hr, 2 ml of chlorobenzene was added and the resulting red mixture was stirred at room temperature while being treated with an excess of bromine which was swept slowly over the mixture in a stream of nitrogen. The solid product was separated by centrifugation and the 1-bromobutane was collected by glpc from the supernatant solution (column C); the yield of bromide was ~50%. The mass spectrum of this substance at 11 eV was examined for the isotopic compositions of the molecular ion (M^+) and of $(M - Et)^+$: M^+, 0% d_3, 97% d_2, 3% d_1, 0% d_0; $(M - Et)^+$, 0% d_3, 83% d_2, 16% d_1, 1% d_0.

A similar analysis was performed on 1-bromobutane from a solution originally containing 250 mg of the **1**-*2,2*-d_2 and 80 mg of triphenylphosphine in 2 ml of methylene chloride: M^+, 0% d_3, 98% d_2, 2% d_1, 0% d_0; $(M - Et)^+$, 0.6% d_3, 26% d_2, 49% d_1, 24% d_0.

Conversion of 1-Bromobutane to Valeronitrile. A micromagnetic stirring bar was sealed into a small bulb fashioned from 8-mm tubing together with a mixture of *ca.* 2 mg of 1-bromobutane, 50 mg of sodium cyanide, and 0.25 ml of dry diglyme. The reaction mixture was heated at 65° for 12 hr with stirring. The tube was cooled and opened; valeronitrile (~70% yield) was collected using glpc (column B).

Exchange of α Hydrogens of Valeronitrile. The exchange of hydrogen for deuterium was carried out in a solution of $NaCH_2CN$ in acetonitrile prepared by cautiously adding 20 ml of acetonitrile (distilled from P_2O_5) to *ca.* 0.2 g of sodium amide (Matheson Coleman and Bell) at 0°, stirring for 30 min at room temperature, and separating insoluble material by centrifugation. The supernatant liquid had a yellowish color that disappeared upon exposure to water. Only samples displaying this yellow color were considered to contain active base.

Valeronitrile was collected from glpc directly into a flame-dried 3-mm Pyrex tube cooled to −78°. One end of the tube was sealed, the other end was closed with a no-air stopper, and the valeronitrile was forced into the sealed end of the tube by centrifugation. The tube was flushed with dry nitrogen, and *ca.* 150 μl of the acetonitrile solution of $NaCH_2CN$ was added using a syringe. The tube was sealed, completely immersed in a 70° oil bath for 12 hr, then cooled, and opened. Valeronitrile was purified by glpc (column C) for isotopic analysis (15-eV nominal ionizing voltage). After valernonitrile that had been prepared from 1-bromobutane-*1,1*-d_2 (98% d_2) was subjected to this exchange and analysis procedure, its isotopic composition was found to be 0.7% d_2, 2.7% d_1, 96.6% d_0. After valeronitrile that had been prepared from 1-bromobutane obtained from **1**-*2,2*-d_2 after partial thermolysis without added triphenylphosphine as described above was subjected to this procedure, its isotope composition was found to be 75% d_2, 19% d_1, 6% d_0.

Photolysis of *cis*-Di-*n*-butylbis(triphenylphosphine)platinum(II). A degassed 0.021 *M* solution of **1** in methylene chloride containing pentane and undecane as internal standards was irradiated in a Pyrex cell for 8 hr at room temperature using a 3600-Å Hanovia medium-pressure mercury lamp. The resulting yellowish solution was analyzed by glpc using columns A (butane and butene) and B (octane). The yield of butane was 54%, of butene was 3%, and of octane was <1%.

Thermolysis and Photolysis of Solution Containing *cis*-Di-*n*-butylbis(triphenylphosphine)platinum(II) and Di-*tert*-butyl Nitroxide in Methylene Chloride. A solution of 70.8 mg (0.085 mmol) of **1** and 68.3 mg (0.47 mmol) of di-*tert*-butyl nitroxide[69] was dissolved in 4.0 ml of methylene chloride containing pentane and undecane as internal standards. A portion of this solution was heated to 80° and held at that temperature for 1 hr. Another portion was irradiated for 8 hr in a Pyrex cell with 3500-Å lamps in a Rayonet reactor. Analysis for butane and butene was carried out by glpc using column A. Analysis for *N,N*-di-*tert*-butyl-*O*-*n*-butylhydroxylamine (DTBNO-*n*-butyl) and octane was carried out using column B. The product yields observed in these experiments are summarized in Table IV.

Table IV. Hydrocarbon Products from Thermolysis and Photolysis of **1** in the Presence of DTBNO

	Products (yields, %)			
	Butane	1-Butene	Octane	DTBNO *n*-butyl
Thermolysis	46	50	~1	~1
Photolysis	2	13	44	42

A solution of *ca.* 50 mg of di-*n*-butylbis(triphenylphosphine)platinum(II) and *ca.* 30 mg of di-*tert*-butyl nitroxide in methylene chloride after standing at room temperature 5 days shows ir absorptions at 1670, 1200–1100, and 970 cm^{-1} in addition to bands characteristic of the two starting materials.

***N,N*-Di-*tert*-butyl-*O*-*n*-butylhydroxylamine.** To a flame-dried 50-ml round-bottomed flask equipped with a side arm, condenser, magnetic stirring bar, and nitrogen inlet tube were added 3.6 g (25 mmol) of di-*tert*-butylnitroxyl, 30 ml of dry dimethoxyethane, and 2.3 g (large excess) of sodium metal. The mixture was allowed to reflux under nitrogen, with stirring, overnight. The resulting colorless solution was transferred by cannula to a dry 50-ml round-bottomed flask, equipped with a magnetic stir bar and reflux condenser, containing 4.6 g (25 mmol) of 1-iodobutane. The solution was allowed to stir for 2 hr under nitrogen and was quenched with water, the aqueous layer was saturated with sodium chloride, the organic layer was separated, and the aqueous phase extracted several times with ether. The combined ether phase was washed with water, dilute hydrochloric acid, water, saturated salt solution, dried ($MgSO_4$), and concentrated. Unreacted 1-iodobutane was separated from the product by distillation. The resulting pale orange oil was passed through a silica gel G column (11 × 1 cm) eluting with cyclohexane to give 0.95 g (19%) of *n*-butyl-di-*tert*-butylhydroxylamine: ir (CCl_4) 3000, 2970, 2930, 2875, 1500, 1485, 1470, 1460, 1370, 1250, 1205, 1075, 1050, 1025 cm^{-1}; nmr (CCl_4) δ 3.65 (t, 2 H), 1.15 (t, 18 H), 1.1 (m, 7 H).

Anal. Calcd for $C_{12}H_{27}NO$: mol wt, 201.209. Found: mol wt, 201.208.

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(68) For details of the collection and analysis procedure, see J. F. Gaasch, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1970.

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