of a well-defined scattering mechanism.

On the Nature of NiPcI_x Stoichiometries Where $x \neq 1$. As noted earlier, powdered samples of NiPcI_x can be prepared for a wide range of x. The resonance Raman and iodine Mössbauer results indicate that iodine is present predominantly if not exclusively as I_3^- up to $x \sim 3.0$. For $x \lesssim 1.0$, there is some evidence from the optical spectra that unoxidized NiPc may be present. However, from such results it is not clear whether starting bulk NiPc or discrete NiPc molecules (or groups of molecules) integrated into a NiPcI_x lattice are being observed. Indeed, the spectral data provide no information on whether a single phase with a continuously varying iodine content or phases of discrete stoichiometries (or ranges of stoichiometries) might be present. This problem was investigated by X-ray powder diffractometry on NiPcI_x samples where $x = 0, 0.55, 1.0, 1.1, 2.64$, and 4.01. Although the data were only evaluated in a semiquantitative fashion, the following conclusions could be reached. First, for $x < 1.0$, quantities of bulk, unoxidized NiPc were clearly present. The only other phase which could be detected was the $x = 1.0$ material. The presence of unoxidized NiPc is in accord with the optical spectra. Second, the materials with $x > 1$ contain no detectable NiPc. However in addition to varying amounts of the $x = 1.0$ material, they exhibit an additional phase with a new crystal structure, distinctly different from the $x = 1.0$ phase. No attempt was made to index this cell. Iodine oxidation of the related macrocycle Ni(OMTBP) has so far produced crystals with two stoichiometries, $x \approx 1$ and $x \approx 3$.[4a,d] The present powder diffraction results for NiPcI_x suggest that there also may be only two phases with $x < 3$, one at $x = 1$, the other at $x \approx 3$.

Conclusions

Partial oxidation of metallophthalocyanines with iodine has provided an extensive new class of molecular conductors. As illustrated in the present case with nickel phthalocyanine, the properties of the resulting solid-state array of π-cation radicals include electrical conductivity which is comparable with that of the best known stacked molecular conductors. A particularly intriguing feature of $\mathrm{NiPcI}_{1.0}$ charge transport is a transition from metallic to semiconducting behavior which apparently is not reflected in the magnetic properties of the carriers. It is tempting to speculate that this behavior reflects a change in carrier mobility brought about by some subtle structural rearrangement.

In a broader perspective, the iodinated metallophthalocyanines, such as those reported here, represent the first entry into a widening area of conductive materials based upon the ligand π systems of mixed-valent metallomacrocyclic arrays. Clearly the insights gleaned and the methodology developed will lead to an ever-deepening understanding of those molecular characteristics which facilitate charge conduction and which optimize materials performance.

Acknowledgments. This research was generously supported by the NSF-MRL program through the Materials Research Center of Northwestern University (Grant DMR76-80847A01), by the NSF (Grant DMR77-26409 to B.M.H. and Grant CHE76-10335 to J.A.I.), and by the Office of Naval Research (to T.J.M.). We thank Professor J. B. Cohen for assistance with the diffuse scattering measurements and Mr. J. Martinsen for assistance in the static susceptibility measurements. We thank Dr. Stanley L. Ruby of the Physics Division of Argonne National Laboratory for recording the iodine Mössbauer spectrum of $\mathrm{NiPc^{129}I_{2.16}}$.

Supplementary Material Available: The root-mean-square amplitudes of vibration (Table IV) and a listing of structure amplitudes (4 pages). Ordering information is given on any current masthead page.

Mechanism of Thermal Decomposition of Dineopentylbis(triethylphosphine)platinum(II): Formation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane[1]

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Abstract: The thermal decomposition of dineopentylbis(triethylphosphine)platinum(II) (**1**) in cyclohexane solution at 157 °C yields bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**4**) by a reaction which involves dissociation of 1 equiv of triethylphosphine, intramolecular oxidative addition of the C–H bond of a neopentyl methyl group to platinum (**3**), and reductive elimination of neopentane. Carbon–carbon bond formation resulting in production of dineopentyl is a detectable side-reaction. The overall reaction has Arrhenius activation parameters: $E_a \simeq 49$ kcal mol^{-1}, $\log A \simeq 20$. The activation energy for phosphine dissociation is 27–35 kcal mol^{-1}. Transfer of a hydrogen atom from the triethylphosphine group to a neopentyl moiety occurs at a rate approximately 3% that of transfer of hydrogen from the methyl of one neopentyl group to the methylene of the other. Any processes which abstract α-methylene hydrogens from the neopentyl group occur at less than 1% the rate of processes which abstract hydrogens from the neopentyl methyl groups. Substitution of deuterium for hydrogen in either the neopentyl methyl groups or the triethylphosphine groups slows the decomposition reactions ($k_H/k_D \simeq 3.0$). The mechanism proposed for generation of **4** is based in part on deuterium-labeling experiments: comparison of results by using different labeling patterns for **1** demonstrates the special utility of "inverted" experiments in which *hydrogen* transfer from a specific site is examined in a system which is otherwise perdeuterated. The driving force for the conversion of **1** to **4** is not obvious: it may be relief of steric strain in **1**, changes in electronic energy due to reorganization of ligands around platinum, or changes in entropy.

Introduction

The cleavage of unactivated aliphatic C–H bonds by reaction with transition metals occurs in a number of useful heterogeneous catalytic processes; reforming,[2] dehydrogenation,[3] and probably platinum-catalyzed oxidation[4] provide examples. Current efforts to develop *homogeneous* catalysts for C–H bond activation are justified on the basis that such catalysts might functionalize hydrocarbons selectively and that they might be amenable to detailed

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(1) Supported by the National Science Foundation, Grants MPS 74-20956 and 7711282 CHE.

(2) Sinfelt, J. H. *Prog. Solid State Chem.* **1975**, *10*, 56–69; *Science (Washington, D.C.)* **1977**, *195*, 641–646.

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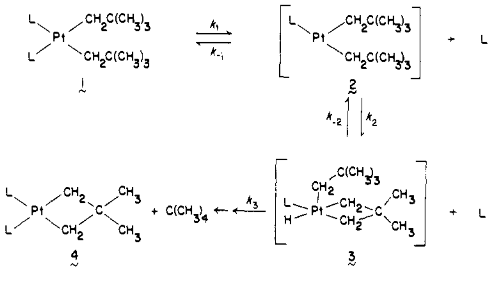
Scheme I. Postulated Mechanism for Conversion of 1 to 4 (L = Et_3P)



mechanistic studies. Intermolecular catalytic reactions which cleave alkane C–H bonds (apparently) homogeneously are restricted to those which result in exchange with acids in the presence of several transition-metal salts.[5] A number of *intramolecular* cyclometallations break C–H bonds of ligands attached to transition-metal complexes in facile stoichiometric reactions.[6,7] Although these reactions cleave C–H bonds which are "unactivated" in the sense of having no adjacent unsaturated groups of heteroatoms, their facility may in some way reflect the energetic or entropic contribution of prior coordination of the ligand to the metal center. This paper describes a study of the mechanism of one such reaction: the conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (**4**) and neopentane (Scheme I).[8] This study establishes that a vacant coordination site on the metal facilitates cleavage of the C–H bond and suggests structural characteristics for platinum(II) complexes which might make C–H activation rapid. Although it does not rigorously establish whether the conversion of **2** to **3** or the loss of neopentane from **3** is overall rate limiting, the high entropy of activation for the reaction favors the latter possibility. In either event a rate law of the same form describes the reaction (eq 1 for **2** → **3** rate limiting, eq 2 for **3** → **4** rate limiting), provided that the steady-state assumption holds for intermediate **2** (eq 1) or intermediates **2** and **3** (eq 2).

$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1k_2[\mathbf{1}]}{k_2 + k_{-1}[\mathrm{Et_3P}]} \qquad (1)$$

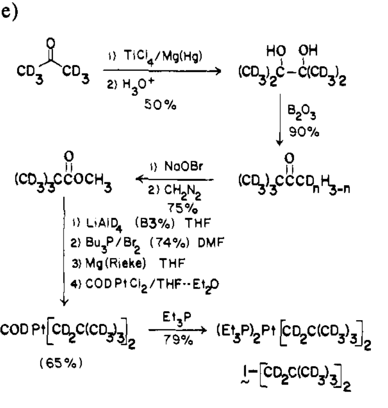
$$-\frac{d[\mathbf{1}]}{dt} = \frac{k_1k_2k_3[\mathbf{1}]}{k_2k_3 + k_{-1}(k_{-2} + k_3)[\mathrm{Et_3P}]} \qquad (2)$$

This work is based on studies of isotopically labeled compounds. These compounds are named as derivatives of the analogous nondeuterated parent: for example, bis(neopentyl-*1,1*-d_2)bis(triethylphosphine)platinum(II) is represented as **1**-$[CD_2C(CH_3)_3]_2$. This designation only *labels* the isotopically substituted compounds: it indicates the major isotopic species present, not the true isotopic composition. "L" refers to triethylphosphine and "L_D" to $P(C_2D_5)_3$.

Results

Preparation of 1 and Isotopic Derivatives. The same general procedure was used to synthesize **1** and its deuterated derivatives. Scheme II outlines a synthesis of **1**-$[CD_2C(CD_3)_3]_2$; obvious modifications of this synthesis generated other isotopic substitution patterns on the neopentyl group. Isotopically substituted tri-

Scheme II. Synthesis of **1**-$[CD_2C(CD_3)_3]_2$ (COD = 1,5-Cyclooctadiene)



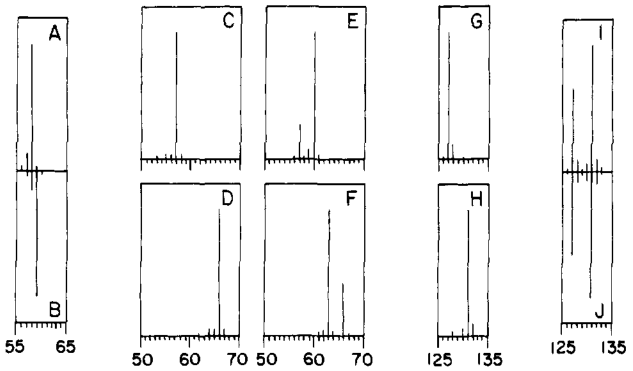


Figure 1. Ion clusters used in mass spectroscopic isotopic analyses: A, butane; B, butane-d_n from *n*-butylmagnesium chloride and DCl; C, $C(CH_3)_4$; D, $C(CD_3)_4$; E, $C(CH_3)_3CD_3$; F, $C(CH_3)(CD_3)_3$; G, $(CH_3)_3CCH_2CH_2C(CH_3)_3$; H, $(CH_3)_3CCD_2CD_2C(CH_3)_3$; I, a mixture of dineopentyls generated by treatment of a mixture of **1** and **1**-$[CD_2C(CH_3)_3]_2$ with cyanogen; J, calculated intensities for the mixture in I, based on the yields described in the text.

ethylphosphines were prepared by reaction of the appropriate Grignard reagent with triethyl phosphite.[9]

Isotopic Analyses of Hydrocarbons: Characterization of Organoplatinum Compounds. We have relied heavily on gas chromatography/mass spectroscopy (GC/MS) for analysis of the deuterated alkanes. A number of types of error—isotopic impurities in reagents, adventitious isotopic exchange processes, instrumental artifacts, and competing side reactions—can be significant in these types of analyses. This section outlines methods used to estimate isotopic distributions and to evaluate their accuracy. We note at the onset that even with close attention to experimental detail, 3% uncertainty in isotopic analysis was routine, and in certain instances we were unable to establish the origin of isotopic species detected at the level of 10%.

Organoplatinum compounds were assayed for C–Pt bonds by treatment with DCl/D_2O and analysis of the hydrocarbons generated by GC/MS for deuterium incorporation. We preferred not to establish the isotopic yield in this deuterolysis procedure using neopentane-*d* from **1**, since neopentane does not give a molecular ion. Instead, *n*-butylmetal compounds were examined: butane gives a molecular ion with abundance 50% of the base peak. Figure 1 summarizes the distribution of ion intensities observed on treating samples of *n*-butylmagnesium bromide (from which butane present from preparation and handling had been previously removed) with H^+ and D^+ sources; Table IA in supplementary material for this article summarizes numerical data for ion intensities. Experimentally indistinguishable data were obtained on treating di-*n*-butylbis(triphenylphosphine)platinum(II) with H^+ or D^+. Comparison of these spectra suggests that the butane generated by deuterolysis of each organometallic compound was

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[8] Preliminary account: Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732–2733.

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a mixture of butane-d_1 (96–97%) and -d_0 (4–3%), on the assumption that loss of H^+ (D^+) from C_4H_9D on electron impact is statistical.[10] Proton sources present on the surface of the glassware used to manipulate samples must be eliminated by exchange with deuterium to achieve this level of deuterium incorporation, and other precautions outlined in the experimental section must be followed.

Most of our work was concerned with analysis of mass spectra of neopentane. Neopentane does not give a molecular ion on electron impact: the base peak is [M – methyl]$^+$ ($C_4H_9^+$, *m/e* 57), with smaller amounts of $C_3H_5^+$ (*m/e* 41) (Figure 1). Isotopic analyses were based on the cluster of ions from *m/e* 55–58 (and corresponding clusters at higher mass for deuterated species). The spectra anticipated for neopentane-d_1, -d_2, and -d_3 were derived from that observed for neopentane-d_0 by making two assumptions: first, that there was no deuterium kinetic isotope effect on the loss of a methyl group (that is, that loss of CH_3 and CH_nD_{3-n} were equally probable); second, that the processes resulting in loss of H and H_2 in addition to methyl from neopentane (that is, processes generating ions with *m/e* 56 and 55) also occurred in the deuterated neopentanes with no discrimination between H and D. These calculated distributions are listed in Table IA (supplementary material for this paper), together with observed distributions.

The good agreement between calculated and observed intensities for neopentanes-d_{1-3} establishes that no intramolecular scrambling of hydrogen (deuterium) between carbon atoms occurs in neopentane-d_n before fragmentation. The minor discrepancies observed are compatible with a secondary isotope effect involving preferential loss of methyl radical rather than methyl-d_n radical on fragmentation.[11] These experimental ion intensities are not useful in establishing whether the hydrogen-loss processes are also subject to kinetic isotope effects. Even with the assumption of an isotope effect of $k_H/k_D = 6$, however, the influence of changes in the intensities of the low-intensity ions from such an isotope effect would sum to only ca. 0.9% of [M – methyl]$^+$ and would thus be smaller than the uncertainty in measuring this intensity.[12] Detailed comparison of calculated and observed intensities for neopentanes-d_{9-12} is not worthwhile, since the available experimental samples were all isotopic mixtures. The ion intensities listed in Table IA for these species are all approximate. They entirely neglect isotope effects in both methyl- and hydrogen-loss processes and are almost certainly in error to some extent. The purpose of experiments based on these species was, however, normally qualitative: that is, to establish whether hydrogen or deuterium was transferred in a particular reaction. Semiquantitative information concerning isotopic compositions was adequate for this purpose.[13]

Estimation of the composition of all isotopic mixtures was based on unsophisticated analysis.[14] The major species present were identified on the basis of knowledge of the starting material and reaction and observation of the major peaks in the mass spectrum. The calculated ion distributions listed in Table IA were used to correct the intensities of the base peaks of overlapping spectra, and the isotopic composition was inferred from the relative intensities of the base peaks.[15]

Several other experimental details were found to be important in obtaining reproducible isotopic analysis. First, isotopic fractionation in GLC is well-known[16] and was evident in our spectra.[17] Isotopic analyses reported here are based on an average of approximately 50 individual spectra taken over the full width of the GLC peak. Second, injection of platinum-containing solutions onto the GLC led to the deposition of platinum in the injection port. This platinum was capable of causing isotopic scrambling. To minimize this problem, we changed injection port liners after 10 injections.

The success of these procedures can only be judged empirically. Compound **1** was converted to neopentane-*d* by treatment with commercial (99% *d*) DCl/D_2O—a reaction which we believe (but have not proved) to proceed without isotopic exchange in the alkyl groups. GC/MS analysis of this neopentane indicated a mixture of d_1 (97%) and d_0 (3%). This result is in adequate agreement with similar experiments carried out by using *n*-butylmetal compounds.

A second MS analysis was also essential to this work. Treatment of L_2PtR_2 with cyanogen (N≡C–C≡N) yields the coupled dimer R–R. Although the yield of this reaction is only ~30%, it provided a very useful method for identifying the two alkyl groups present on a single platinum atom.[18] GC/MS analysis of the dineopentyl generated from **1**-d_n by treatment with cyanogen also relied on a prominent [M – methyl]$^+$ peak (*m/e* 127 for d_0 material): Figure 1 shows representative mass spectra, and Table IA lists ion distributions in the region used for analysis.[19] The cyanogen-induced coupling reaction is cleanly intramolecular. Treatment of a mixture of **1** and **1**-$[CD_2C(CH_3)_3]_2$ with cyanogen generates no significant intensity at *m/e* 129 above that expected for the unmixed dineopentyls (eq 3).

$$\mathbf{1} + \mathbf{1}\text{-}[CD_2C(CH_3)_3]_2 \xrightarrow[\substack{CH_2Cl_2\\ 80\ °C\\ \sim 30\%}]{NCCN} \underset{\sim 1}{[(CH_3)_3CCH_2]_2} + \underset{\sim 1}{[(CH_3)_3CCD_2]_2} + \underset{<0.02}{(CH_3)_3CCH_2CD_2C(CH_3)_3} \tag{3}$$

Thermal Decompositions of 1: Products. Most decompositions were carried out under argon in sealed tubes starting with 0.08 M solutions of **1** in cyclohexane containing 0.02 M triethylphosphine (eq 4; yields are based on **1**). Addition of triethylphosphine prevented a rapid increase in the rate of decomposition of **1** after 1.5–2.0 half-lives which was observed for reactions carried out in the absence of added triethylphosphine; it slowed the reaction (see below) but had no effect on product yields. All reaction mixtures appeared homogeneous throughout. The starting solution was colorless; the final mixture was pale yellow-orange. Hydrocarbon product yields did not change when the initial

$$\mathbf{1} \xrightarrow[\substack{C_6H_{12}\\ 0.02\ M\ El_3P}]{157\ °C,\ 2.25\ h} \underset{98-102\%}{(CH_3)_4C} + \underset{5-10\%}{[(CH_3)_3CCH_2]_2} + \underset{85-90\%}{\mathbf{4}} + \underset{trace}{(Et_3P)_3Pt^0} \tag{4}$$

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(10) For a discussion of techniques useful in careful analysis of deuterium distribution in hydrocarbons, see: Katz, T. J.; Rothchild, R. *J. Am. Chem. Soc.* **1976**, *98*, 2519–2526.

(11) Analysis of the intensities in Table IA, on the assumption that deviations between calculated and observed patterns are due entirely to secondary isotope effects in fragmentation, suggests that the relative rates of loss of deuterated and nondeuterated methyl groups are $k_{CH_3}/k_{CD_3} = 1.30$, $k_{CH_3}/k_{CHD_2} = 1.15$, and $k_{CH_3}/k_{CH_2D} = 1.00$. This phenomenon has been observed in other systems: Field, F. H.; Franklin, J. L. "Electron Impact Phenomena"; Academic Press: New York, 1957; pp 204–217; McLafferty, F. W.; McAdoo, D. J.; Smith, J. D.; Kornfield, R. *J. Am. Chem. Soc.* **1971**, *93*, 3720–3730; Mandelbaum, A.; Weisz, A. *J. Chem. Soc., Chem. Commun.* **1978**, 521–522.

(12) Isotope effects on electron impact ionization cross-sections should be unimportant at 70-eV ionizing voltage: Myerson, S.; Grubb, H. M.; Vabder Haar, R. W. *J. Chem. Phys.* **1963**, *39*, 1445–1446.

(13) Calculations based on the fragmentation patterns of neopentanes-d_{9-12} shown in Table IA for the analysis of mixtures of neopentanes would represent the maximum ^1H incorporation possible for experiments incorporating ^1H as a minor component of a process predominately involving D transfer.

(14) Brauman, J. In "Spectral Analysis"; Blackburn, J. A., Ed., Marcel Dekker: New York, 1970.

(15) No corrections were made in the analysis of mixtures for ^1H impurities in the deuterated starting materials.

(16) Biemann, K. "Mass Spectrometry-Organic Chemical Applications"; McGraw-Hill: New York, 1962; pp 223 ff. Possanzini, M.; Pela, A.; Liberti, A.; Cartoni, G. P. *J. Chromatogr.* **1968**, *38*, 492–497.

(17) Typically, the isotopic composition of a 1:1 mixture of neopentane-d_0 and neopentane-d_1 would change from a 3:2 d_1–d_0 at the leading edge of a GLC peak to a 2:3 d_1–d_0 mixture at the tail of the peak. These changes were larger with broad peaks.

(18) This reaction probably occurs by oxidative addition of cyanogen to platinum(II) (or nonadditive oxidation), yielding a transitory dialkylplatinum(IV) species which spontaneously reductively eliminates dialkyl. For previous descriptions of reactions of cyanogen with transition-metal complexes see: Tolman, C. A.; Lukosius, E. *J. Inorg. Chem.* **1977**, *16*, 940–943; Gauthier, R.; Chastrette, M. *J. Organomet. Chem.* **1979**, *165*, 139–149.

(19) Analysis of isotopic mixtures of dineopentyl were performed by comparison of these mixtures with the dineopentyl obtained from reaction of cyanogen with **1** or **1**-$[CD_2C(CH_3)_3]_2$.

Table I. Isotopic Composition of Neopentane Derived from Thermal Decomposition of Deuterated Analogues of 1[a]

entry	$(CH_3)_3C$[b]	CH_2Pt[c]	C_2H_5P[d]	solv[e]	isotopic comp of neopentane (%)[f]		inference[g]
1	D	D	D	D	D (89)	H (11)	not solvent
2	D	D	D	H	D (88)	H (12)	
3	D	H	D	H	D (83)	H (17)	little or no α
4	D	H	H	H	D (79)	H (21)	γ
5	D	D	H	H	D (79)	H (21)	some L (<γ)?
6	H	H	D	H	H (97)	D (3)	
7	H	D	H	H	H (98)	D (2)	
8	H	D	D	D	H (92)	D (8)	γ
9	H	H	H	D	H (99)	D (1)	

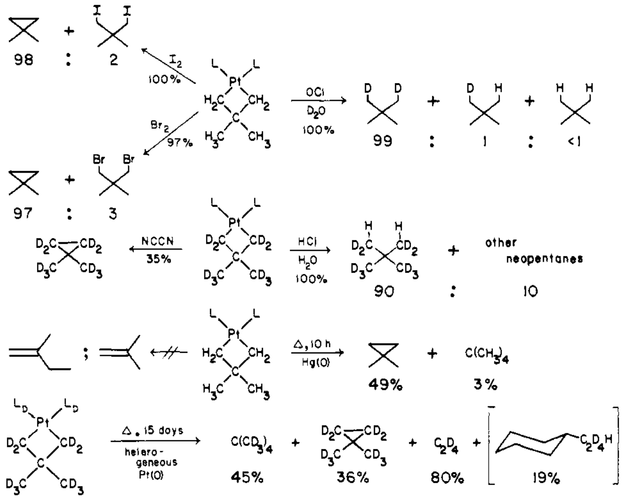
[a] Reaction mixtures were originally 0.08 M in platinum organometallic and contained 0.02 M of the corresponding triethylphosphine. Decompositions were carried to completion at 157 °C (>2 h). Isotopic compositions reported are not corrected for isotopic impurities in the starting materials and represent the absolute isotopic enrichment. [b] The entries in this column indicate whether the indicated position is protonated or deuterated: entry 3 is $[(CD_3)_3CCH_2]_2Pt[P(C_2D_5)_3]_2$ in C_6H_{12}. [c] The isotopic purities of the starting platinum complexes were analyzed by examination of the neopentanes produced by treatment with HCl/H_2O or DCl/D_2O: $(CH_3)_3CCD_2$- (96% d_2, 4% d_1); $(CD_3)_3CCH_2$- (93% d_9, 7% d_8); $(CD_3)_3CCD_2$- (94% d_{11}, 6% d_{10}). [d] Estimated isotopic composition was 92% d_{15} and 8% d_{14}, as inferred from the ethyl-d_5 bromide from which it was made. [e] The solvent used was cyclohexane or cyclohexane-d_{12} (99% *d*), except entry 7 which was dodecane. [f] These data summarize the isotopic composition of the neopentanes produced. For example, for entry 1, $(CD_3)_4C$ (89%) and $(CD_3)_3CCD_2H$ were the two major species detected. Only these two major neopentane species are listed. These estimates are derived *directly* from the MS data: they are not corrected for isotopic impurities present in the starting materials. [g] This column summarizes the conclusion drawn from the neopentane isotopic compositions concerning the origin of the hydrogen transferred to the neopentyl group: α refers to the CH_2 position of the neopentyl group; γ refers to the methyl portion of the neopentyl group.

concentration of **1** was varied,[20] when benzene-d_6, diethyl ether, or decane was substituted for cyclohexane as solvent, or when mercury(0) was added. Mercury(0) would have been expected to modify the activity of bulk or colloidal platinum(0) by amalgamation. The observation that it had no effect supports the belief that the reaction is homogeneous and not catalyzed by traces of bulk platinum metal. The distribution of hydrocarbon products was independent of the extent of decomposition.

Compound **4** was isolated as an air-stable white solid. Its assigned structure rests on a combination of spectroscopic evidence (summarized in the Experimental Section) and on the chemical transformation summarized in Scheme III.[21] In particular, GC/MS analysis indicated that treatment of **4** with DCl introduced deuterium into the 1,3-positions of the neopentane produced; little or no 1,1-disubstitution was observed. Dimethylcyclopropane was observed as a major product on treatment of **4** with diiodine, bromine, or cyanogen. Thermolysis of **4** is complicated by the deposition of platinum metal and by reactions apparently catalyzed by this metal. Thermolysis of perdeuterated **4** generates a dark reaction mixture containing platinum(0), neopentane-d_{12}, and 1,1-dimethylcyclopropane-d_{10}, in addition to ethylene-d_4 (from triethylphosphine-d_{15}) and a compound tentatively identified by GC/MS as ethylcyclohexane-d_4. Thermolysis of **4** in the presence of mercury(0) results in clear reaction mixtures containing no obvious precipitated platinum(0) and a simpler spectrum of products; amalgamation of the platinum(0) with the mercury(0) suppresses platinum(0)-catalyzed reactions.[22] Under these conditions, dimethylcyclopropane is the major product of thermal decomposition, and formation of the products (neopentane and ethylene) suggesting hydrogen transfer from the triethylphosphine ligand to the metallacycle is inhibited. In no instance do we observe 2-methylbutene, 2-methylbutane, isobutylene, isobutane, or other products, suggesting carbon skelton rearrangement or fragmentation.[23]

The molecular weight of **1** in benzene is consistent with a monomeric structure (calculated 501, found 515). The inference that there are no significant dimeric organometallic species in solution is reinforced by the observation that reactions which induce carbon–carbon bond formation (treatment with dicyanogen, thermolysis) generate no detectable products containing two moieties derived from neopentyl groups: in particular, 1,1,4,4-tetramethylcyclohexane or other C_{10} products were not observed.

Scheme III. Chemical Reactions Used in Characterizing 4[a]



a Yields for the reactions of 4-d_{10} and 4-d_{40} are based on initial 1 used to generate 4. L_D is $P(C_2D_5)_3$; Δ = 157 °C, C_6H_{12} solution. Thermal decompositions of 4 carried out in the presence of a small amount of mercury(0) deposited no bulk platinum(0); those carried out in its absence formed a platinum(0) mirror. Ethylcyclohexane is formed only in the presence of platinum metal and reflects a *heterogeneous* platinum-catalyzed reaction of undefined course.

The presence of small quantities of $(Et_3P)_3Pt^0$ among the reaction products was inferred from ^{31}P NMR spectroscopy. During the disappearance of **1** (0.08 M) in cyclohexane containing Et_3P (0.12 M, δ −19.9) the ^{31}P NMR signal for free Et_3P broadened markedly. At the conclusion of the reaction, a new, low-intensity ^{31}P signal appeared at δ +41.9. This signal and the exchange broadening are consistent with the assignment of this new peak to $(Et_3P)_3Pt^0$.[24]

Deuterium-Labeling Studies. Table I summarizes experiments which establish that a methyl group of the neopentyl moiety is the primary source of the hydrogen (deuterium) which is transferred to the newly formed molecule of neopentane, that there is significant incorporation of hydrogen from the alkyl group of

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[20] A set of sealed tubes containing **1** (0.046–0.24 M) in cyclohexane with $(C_2H_5)_3P$ (0.05 M) were decomposed at 157 °C for 1.6 h (1 half-life). Identical yields of neopentane and dineopentyl were obtained in all tubes.

[21] The structure of **4** has been confirmed by a single-crystal X-ray diffraction study: Ibers, J., private communication.

[22] Results in the presence of mercury(0) were obtained by Karen Root. A more detailed study of the influence of mercury(0) on this and related thermal decomposition reactions will be described later.

[23] These fragmentations have been observed for an analogous nickelacycle: Grubbs, R., private communication.

[24] $(Et_3P)_3Pt^0$ is reported to have δ +41.5 in hydrocarbon solvents (Gerlach, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Muetterties, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543–3544).

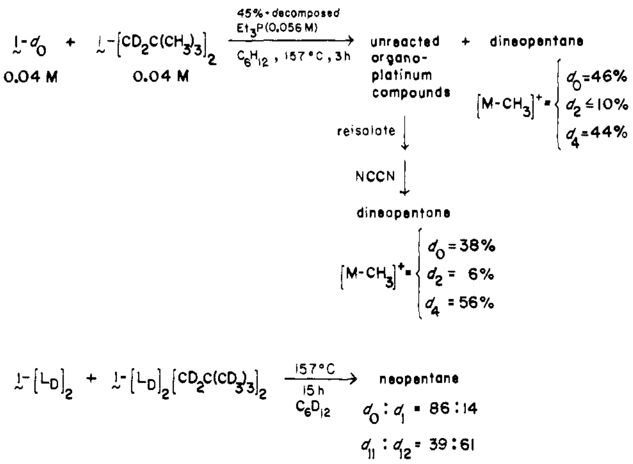
the triethylphosphine, and that little or no hydrogen transfer occurs from the α-position of the neopentyl group or from solvent. Experiments designed to identify the source of hydrogen in a hydrogen-transfer reaction are commonplace in organometallic chemistry and are almost always conducted by substituting deuterium in the position to be tested and examining the products for incorporation of deuterium. While this type of experiment is a necessary one, it may yield ambiguous results. If deuterium *is* transferred in the isotopically labeled system, one can conclude that hydrogen is transferred in the unlabeled system; if deuterium is *not* transferred, one *cannot* conclude that hydrogen is also not transferred, because the partitioning of reactant between paths involving hydrogen abstraction from different sites can be altered by deuterium substitution. That is, deuterium substitution may suppress the reaction of interest through a deuterium isotope effect. This problem is particularly severe because the difficulties associated with the synthesis of isotopically pure organometallic species and with the GC/MS analyses of deuterated compounds produce results with only modest signal-to-background levels and require that a significant fraction of 1 equiv of deuterium/molecule can be transferred before the experimental data can be interpreted with confidence.

Since we knew neither how many reactions were competing in the production of neopentane from **1** nor the isotope effects characterizing the reactions that did occur, it was necessary to proceed by testing the potential sources of hydrogen (deuterium) in two steps. First, a site of interest was labeled with deuterium. If incorporation of this deuterium into the neopentane occurred, then that site was clearly involved in the production of neopentane in unlabeled **1**. If incorporation of deuterium did *not* occur, it was necessary to invert the experiment: that is, to label all the *other* sites with deuterium and to try to detect *hydrogen* transfer from the site of interest. In this type of experiment, of course, a normal kinetic isotope effect would exaggerate the importance of the hydrogen-transfer path being examined, but the amplification would be useful in the qualitative detection of minor pathways.

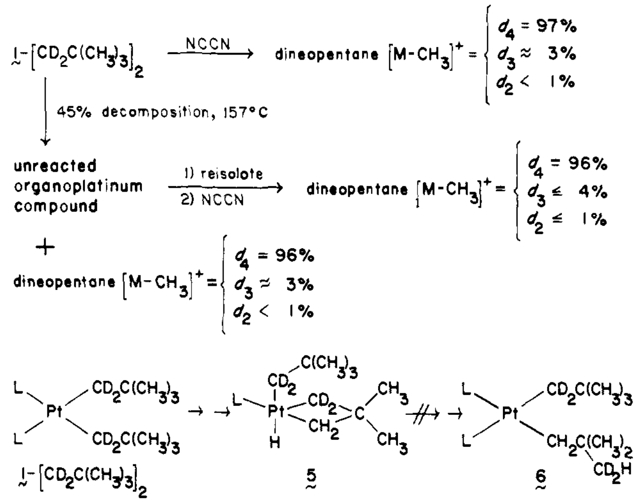
The first two entries in Table I establish that no hydrogen comes from the solvent, since substitution of hydrogen for deuterium in the solvent results in no increase in the hydrogen content of the neopentane. The 11% hydrogen detected in entry 1 is attributable in part to hydrogen impurities in the neopentyl groups of the **1**-$[CD_2C(CD_3)_3]_2$ moieties and possibly also to chemical impurities. Entries 4 and 8 establish the γ-hydrogen of the neopentyl group as the major source of the hydrogen (deuterium) consumed in converting one neopentyl group of **1** to neopentane. Comparison of entries 2 and 5 indicates that the triethylphosphine ligand also donates a small amount of hydrogen in a process which forms neopentane. Comparison of entries 2 and 3 suggests that hydrogen transfer from the α-position, if it occurs at all, is a minor process. The difference in the hydrogen content of the neopentane produced in entries 2 and 3 is close to experimental error. When the experiment is run in the reversed sense—that is, detecting deuterium transfer from the α-position rather than hydrogen (entries 4 and 5 or entries 7 and 9), no detectable transfer occurs. Arguments outlined below indicate that hydrogen abstraction from the methyl groups of the triethylphosphine moieties occurs at ca. 3% the rate of abstraction from the γ-neopentyl groups. Analogous reasoning would indicate that transfer from the α-neopentyl position would be <1% that from the γ-position.

Mixtures of labeled derivatives of **1** were used to explore the molecularity of the thermal decomposition. Decomposition of a 1:1 mixture of undeuterated **1** and **1**-$[CD_2C(CH_3)_3]_2$ to ca. 45% conversion, followed by reisolation of the remaining organoplatinum compounds and treatment with cyanogen, gave the results outlined in Scheme IV. Coupling of neopentyl groups originally located on different platinum atoms is a minor reaction. Thus, intermolecular scrambling of alkyl groups appears to be slow relative to thermal decomposition. Decomposition of a 1:1 mixture of **1**-$[L_D]_2$ and **1**-$[L_D]_2[CD_2C(CD_3)_3]_2$ did, however, suggest significant crossover. The neopentane generated from the former platinum compound contained ca. 14% $(CH_3)_3CCH_2D$ and that from the latter ca. 39% $(CD_3)_3CCD_2H$ (11% would have been expected on the basis of isotopic composition of the starting material). Interpretation of these experiments is complicated by the difference in rate of decomposition of the two platinum complexes (see below). Nonetheless they suggest qualitatively that a significant minority of the reduction events leading to neopentane (10–30%) involve hydride and alkyl groups originally present on different atoms.

Scheme IV. Crossover Experiments Using Mixtures of Nondeuterated and Deuterated Neopentylplatinum Complexes ($L_D = P(C_2D_5)_3$)



Scheme V. Methyl and Methylene Groups of 1 Do Not Interchange during Thermal Decomposition



A separate experiment established that any interchange of the methyl and methylene groups of **1**-$[CD_2C(CH_3)_3]_2$ occurs at a rate less than 10% of the rate of decomposition. Approximately 45% of a sample of this platinum complex was decomposed at 157 °C and the remaining material recovered and converted to dineopentane (Scheme V). GC/MS analysis of dineopentane from the thermal decomposition and from recovered organoplatinum compound showed $[M - \text{methyl}]^+$ had lost less than 4% of the CD_2 groups originally present in the starting organoplatinum complex. Thus, conversion of **5** to **6** is not important.

This observation provides no evidence for the reversible interconversion of **1** and **3** (here, **1**-$[CD_2C(CH_3)_3]_2$ and **5**) but does not rigorously exclude it: in principle, the geometry of **5** might be such that only H–CH_2 bond formation could occur.[25]

Kinetic Studies. These were conducted by using ^1H or ^{31}P NMR spectroscopy or GLC;[26] for ^1H NMR work, **1**-$[P(C_2D_5)_3]_2$ was

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(25) A geometrical requirement for reductive elimination is known for six-coordinate platinum(IV) complexes: Ruddick, J. D.; Shaw, B. L. *J. Chem. Soc. A* **1969**, 2969–2972. Compound **5**, at least as generated initially, should be five-coordinate and might be expected to interconvert stereoisomers rapidly.

Table II. Rate Constants (Eq 6-10) for Decomposition of **1**-d_n and Appearance of Products: $L = P(C_2H_5)_3$, $L_D = P(C_2D_5)_3$

	R_2PtL_2		conc, M			10^6(rate constants)^a				
entry	R	L	R_2PtL_2	L^b	T, °C	k^{obsd}, s^{-1} (method)^c	k_1, $M\ s^{-1}$	$k_{NH(D)}$,^{d,e} $M\ s^{-1}$	$k_{LH(D)}$,^{d,e} $M\ s^{-1}$	k_{NN}, $M\ s^{-1}$
1	$(CD_3)_3CCD_2$-	L_D	0.077	0.054	157	62.2 (G)	3.35	2.94 (D)^f		0.42
2		L	0.082	0.056	157	56.9 (G)	3.19	2.24 (D)^e	0.49 (H)^g	0.45
3	$(CH_3)_3CCH_2$-	L	0.084	0.056	157	167.0 (G)	9.35	8.71 (H)^f		0.64
4		L	0.088	0.022	138	29.7 (N)	0.65	0.063 (H)^f		0.25
5		L_D	0.084	0.022	118	1.23 (N)	0.027	0.024 (H)	0.002 (D)	0.0008
6		L_D	0.081	0.360	157	27.4 (N)	9.86	8.90 (H)	0.55 (D)	0.40
7		L_D	0.081	0.120	157	71.0 (N)	8.52	7.68 (H)	0.48 (D)	0.32
8		L_D	0.084	0.054	157	145.0 (N)	7.83	7.02 (H)	0.43 (D)	0.37
9		L_D	0.081	0.022	157	409.0 (N)	9.00	8.05 (H)	0.50 (D)	0.45
10		L	0.087	0.000	118	15 (N)				

^{a} The experimental accuracy for k^{obsd} is estimated at ±8%. ^{b} The concentration of L added to the solution of L_2PtR_2. ^{c} Method refers to the technique used to determine the rate constants: G = GLC; N = NMR. ^{d} The quantity $k_{NH(D)} + k_{LH(D)}$ was measured experimentally by following the rate of appearance of neopentane. Its separation into component parts followed arguments discussed in the text. ^{e} (H) and (D) refer to the predominant isotope being transferred to neopentane and are included to facilitate comparisons. ^{f} $k_{NH(D)}$ and $k_{LH(D)}$ are not separable; the reported number is their sum. ^{g} This rate constant is inaccurate: the hydrogen content of the $(CD_3)_3CCD_2$- moieties (~10%) makes accurate determination of hydrogen transfer from $P(C_2H_5)_3$ difficult.

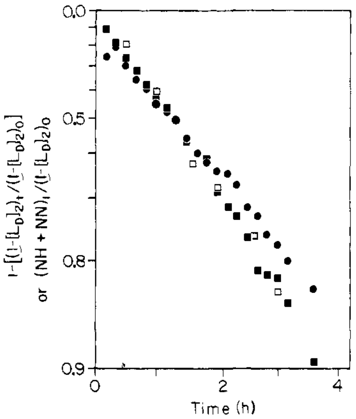

Figure 2. First-order plots for decomposition of **1**-$[L_D]_2$ at 157 °C in cyclohexane solution (0.08 M) containing added L_D (0.055 M): ● = fractional decomposition of **1**-$[L_D]_2$; ■, □ = fractional appearance of neopentane (NH) and dineopentyl (NN) (based on **1**-$[L_D]_2$ originally present). Data indicated with filled symbols were collected by ^{31}P NMR (●) or ^1H NMR (■); open symbols (□) are based on GLC data.

used to minimize interferences between neopentyl and ethyl protons. Most studies were carried out in solutions containing added triethylphosphine to decrease scatter in individual points.

Kinetic data were reduced initially by using eq 5 (P = product:

$$-\frac{d[\mathbf{1}]}{dt} = -\frac{d[P_\infty - P_t]}{dt} = k^{obsd}[\mathbf{1}] \qquad (5)$$

neopentane or dineopentyl).[27] In the presence of added triethylphosphine, the disappearance of **1**, the appearance of neopentane, and the appearance of dineopentyl were all cleanly first order in **1** to greater than 90% decomposition; in the absence of phosphine, the decomposition remained first order for only 1.5–2.0 half-lives, after which the rate of decomposition rapidly increased. Figure 2 summarizes representative data. The presence of dioxygen increased the rate of disappearance of **1**. We believe that addition of triethylphosphine may increase experimental reproducibility by scavenging traces of dioxygen.

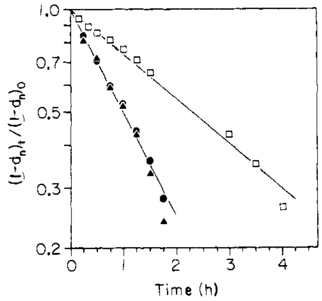

Figure 3. Kinetic plots for thermal decomposition of **1** (●, ▲ = two separate runs) and **1**-$[CD_2C(CD_3)_3]_2$ (□) in cyclohexane solution at 138 °C. The observed uncorrected (see text) value for k_H/k_D is 2.5.

Since we could follow independently the disappearance of **1**-d_n, the appearance of neopentane and dineopentyl, and the isotopic compositions of these hydrocarbons, we were able to estimate kinetic orders, rate constants, and deuterium kinetic isotope effects for several of the three competing processes inferred from the product studies: in solutions containing triethylphosphine, these processes were described accurately by rate equations containing a term in the reciprocal of the phosphine concentration (eq 6–9;

$$-\frac{d[\mathbf{1}]}{dt} = k_1[\mathbf{1}][L]^{-1} \qquad (6)$$

$$-\frac{d([NH]_\infty - [NH]_t)}{dt} = (k_{NH} + k_{LH})[\mathbf{1}][L]^{-1} \qquad (7)$$

$$-\frac{d([N\text{-}N]_\infty - [N\text{-}N]_t)}{dt} = k_{NN}[\mathbf{1}][L]^{-1} \qquad (8)$$

$$k_1 = k_{NH} + k_{LH} + k_{NN} \qquad (9)$$

$L = P(C_2H_5)_3$ or $P(C_2D_5)_3$) (Table II). These rate constants refer, respectively, to the reaction which cleaves the carbon–hydrogen (–deuterium) bond of the neopentyl group and generates **4** ($k_{NH(D)}$), the reaction which transfers hydrogen from the triethylphosphine moiety to the neopentyl group ($k_{LH(D)}$), and the reaction generating dineopentyl (k_{NN}). The quantity ($k_{NH(D)}$ + $k_{LH(D)}$) was estimated experimentally from the rate of appearance of neopentane. The ratio $k_{LH}/k_{ND} = 0.1$ was estimated from the ratio of $(CD_3)_3CCD_2H$ to $(CD_3)_3CCD_3$ generated on thermal decomposition $[(CD_3)_3CCD_2]_2Pt[P(C_2H_5)_3]_2$ (Table I).[28] Comparison of entries 2 and 5 in this table indicates that substitution of $P(C_2H_5)_3$ for $P(C_2D_5)_3$ increases the yield of $(CD_3)_3CCD_2H$ by ~10%. We assume that this increase in yield reflects hydrogen

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(26) An entire kinetic run could be carried out by NMR by using a single tube but was limited to those compounds having distinct, characteristic resonances. GLC required multiple tubes and had greater experimental uncertainty but allowed more compounds to be followed.

(27) When the decomposition of **1**-$[(C_2D_5)_3P]_2$ was followed by ^1H NMR, the appearance of neopentane and dineopentyl could not be separated because the methyl resonances overlapped. Their concentrations at any given time were calculated by using height of methyl/height of Me_4Si = (12[neopentane] + 18[dineopentyl])/12[Me_4Si) and determining the ratio of neopentane to dineopentyl at the termination of the kinetic run by GLC (this ratio was constant throughout the decomposition). Analysis specifically for the appearance of neopentane or dineopentyl was performed by GLC.

(28) The uncertainty in k_{LH} is appreciable, as judged by the variation in the values of this constant in Table II. The value used in estimating k_{NH}/k_{LH} was the one we believed subjectively to be most likely correct.

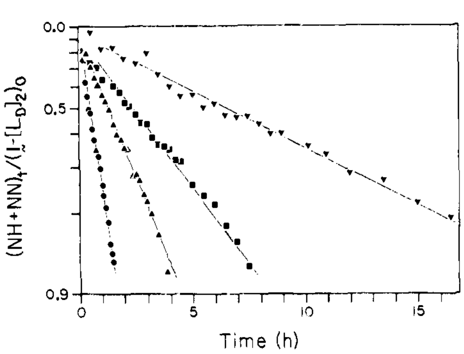

Figure 4. The rate of decomposition of 1-$[P(C_2D_5)_3]_2$ in cyclohexane-d_{12} depends on the concentration of added $P(C_2D_5)_3$ (*M*): ● = 0.022; ▲ = 0.054; ■ = 0.12; ▼ = 0.36; NH = neopentane; NN = dineopentyl.

abstraction from triethylphosphine and solve the statistically corrected eq 10.[29] Comparison of entries 2 and 8 and, less

$$\frac{9k_{LH}}{18k_{ND}} = \frac{\text{yield of neopentane-}d_{11}}{\text{yield of neopentane-}d_{12}} = \frac{10}{90} \qquad (10)$$

accurately, entries 1 and 3 of Table II indicates that the kinetic isotope effect observed on the rate of formation of neopentane when deuterium is substituted for hydrogen in the neopentyl methyl groups is $k_{NH}/k_{ND} \simeq 3$ for decompositions performed in the presence of added triethylphosphine.

In the absence of added triethylphosphine the kinetic isotope effect inferred from the rates of decomposition of 1 and 1-$[CD_2C(CD_3)_3]_2$ (as determined by ^{31}P NMR by following the rate of disappearance of 1) is $(k_H/k_D)^{obsd} = 2.5$ (Figure 3). This *observed* kinetic isotope effect is not corrected for formation of dineopentyl (ca. 5%) from 1 and 1-$[CD_2C(CD_3)_3]_2$ or for transfer of hydrogen from the triethylphosphine to the perdeuterioneopentyl group in 1-$[CD_2C(CD_3)_3]_2$ (ca. 10%).[28] After subtracting the contributions from these side reactions from the rates of decomposition and replotting the data, the corrected kinetic isotope effect in the absence of triethylphosphine becomes $k_{NH}/k_{ND} \simeq 2.9$. This isotope effect is indistinguishable from that observed in the presence of added triethylphosphine *and indicates that the decomposition of* 1 *in the absence of added triethylphosphine does not involve rate-limiting loss of this ligand.*

Figure 4 illustrates the decrease in rate of decomposition of 1-$[P(C_2D_5)_3]_2$ on adding $P(C_2D_5)_3$. The invariance of the rate constants to these changes in phosphine concentration (Table II) justifies the form of eq 6.

Analysis of the temperature dependence of the rate of appearance of neopentane (i.e., $k^{obsd} - k_{NN}$, Table II) at three temperatures in the presence of 0.022 M added triethylphosphine gave a linear Arrhenius plot: E_a = 49 kcal/mol, log A = 20; with no added triethylphosphine, the corresponding values were E_a = 46 kcal/mol, log A = 21 (Figure 5). The close similarity between activation parameters in the presence and absence of added triethylphosphine suggests that the same mechanism describes decompositions in both kinds of solutions.

The rate of decomposition of 1 showed some sensitivity to solvent. Although rates of decomposition of 1 in benzene, diethyl ether, cyclohexane, and decane were all similar, a solution of 1 (0.11 M) in neat triethylphosphine (ca. 6.8 M) decomposed approximately 65 times more rapidly than expected on the basis of eq 6, and a solution of triethylamine decomposed even more rapidly. Dialkylbis(phosphine)platinum(II) complexes are known to have large dipole moments (~7 D),[30] and solvent polarity influences the rate of oxidative addition to platinum.[31] Alternatively, another mechanism or mechanisms may be important at high concentrations of added Lewis bases.[32]

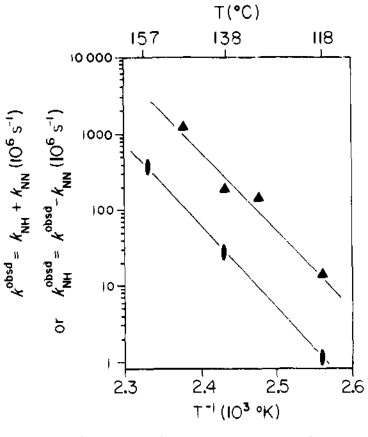

Figure 5. Arrhenius plots for the appearance of neopentane from the decomposition of 1-$[P(C_2D_5)_3]_2$ in cyclohexane-d_{12} containing 0.022 M added $P(C_2D_5)_3$ (●) and for the disappearance of 1 in cyclohexane-d_0 with no added $P(C_2H_5)_3$ (▲).

Phosphine Dissociation. The observation that the rate of decomposition of 1 slows as the concentration of triethylphosphine increases could be rationalized on the basis of either dissociative or associative equilibria involving 1. Evidence based on the ^{31}P NMR spectrum and solubility of 1 in the presence of added triethylphosphine and on an NMR determination of the rate of dissociation of triethylphosphine from 1 both establish $LPtR_2$ as the reactive species. The decomposition of 1 is faster in cyclohexane containing 0.022 M triethylphosphine than in cyclohexane containing 0.3 M triethylphosphine by a factor of ca. 16; its decomposition in cyclohexane containing no added phosphine is faster by a factor of ca. 110.[33] If formation of L_3PtR_2 was responsible for the rate decreases as phosphine was added to solutions of 1, more than 95% of 1 would have to be converted to this species in 0.3 M triethylphosphine to account for the fact that the rate of decomposition is less than 5% that of 1 in 0.02 M triethylphosphine. The ^{31}P NMR spectrum of 1 (0.08 M, in cyclohexane solution containing 0.3 M triethylphosphine at 30 °C) showed only separate resonances due to 1 and triethylphosphine, with no evidence of L_3PtR_2. Integration relative to trimethyl phosphate internal standard established that the intensity of the peak due to 1 quantitatively (±10%) accounted for 1 added to the solution.

Complementary evidence that 1 does not coordinate triethylphosphine to a significant extent comes from the observation that the solubility of 1 is only 1.15 times greater in cyclohexane containing 0.3 M triethylphosphine than in cyclohexane alone. If a species, L_3PtR_2, were formed in a quantity sufficient to rationalize the observed rate differences for 1 in those solutions, the solubility of 1 would be predicted to be greater by more than a factor of 15 in cyclohexane containing 0.3 M triethylphosphine

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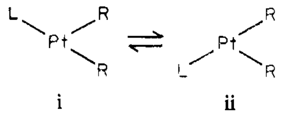
[29] In making this statistical correction, we assume that $LPtR_2$ is the critical intermediate involved and that the three methyl groups of both neopentyl moieties have equal access to the vacant coordination site. Unpublished results indicate processes such as i ⇌ ii (or some equivalent process which renders the R groups equivalent) are fast compared with the rate-limiting step in a β-hydride elimination reaction (McCarthy, T. J.; Nuzzo, R. G., unpublished results.



i ii

[30] Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 4020–4033.

[31] Puddephatt, R. J.; Jawald, J. K. *J. Organomet. Chem.* **1976**, *117*, 297–302.

[32] Evidence for a change in mechanism at high concentrations of added phosphines is clear for the decomposition of diethylbis(triethylphosphine)platinum(II). At sufficiently high concentrations of phosphines, the β-hydride elimination reaction occurs with a rate-limiting transition state having *two* phosphines associated with platinum rather than one. The same explanation is compatible with the kinetic behavior observed in this work for 1, but this kinetic regime has not been explored in any detail. T. J. McCarthy and R. G. Nuzzo, unpublished results.

[33] This latter estimate is derived from comparison of the data at 157 °C for k^{obsd} (entry 6 of Table II) with the rate constant for decomposition in the absence of added triethylphosphine at 157 °C, $k^{calcd} = 3.0 \times 10^{-3}$ s^{-1}, which is obtained from extrapolation of the Arrhenius plot for decomposition of 1 with no added phosphine.

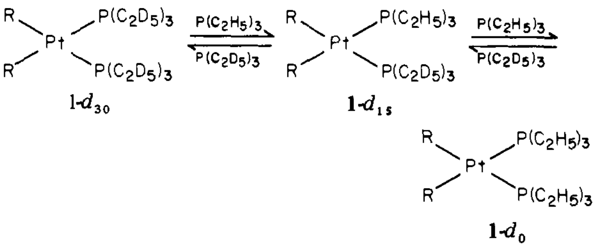
Table III. Photolysis of Dineopentylmercury and 1 in Cyclohexane[a]

MN_2 (conc, M)	phosphine (conc, M)	cyclohexane	% decomp (time, h)[b]	rel product yields[c]				
				NH(D)	N-N	N-S	S-S	others
$[(CH_3)_3CCH_2]_2Hg$ (0.39)	0	C_6D_{12}	19 (48)	1 (69% d_1)	0.80	0.67	0.44	*d*
(0.39)	L_D (0.054)	C_6D_{12}	24 (48)	1 (76% d_1)	0.93	0.71	1.0	*d*
1 (0.080)	L (0.056)	C_6H_{12}	100 (48)	1	0.11	0.12	0.07	*e*
(0.082)	(0.056)	C_6D_{12}	100 (48)	1 (43% d_1)	0.90	0.07	-	*d,f*
1 (0.080) + **1**-$[CD_2C(CH_3)_3]_2$ (0.04)	(0.056)	C_6H_{12}	100 (8)	1	0.13[g]	0.15	0.07	*e*

[a] Photolyses were carried out at 60 °C, using Pyrex tubes and 3500 and 2537-Å lamps. [b] % decomposition was calculated on the basis of the sum of the yields of the observed products. [c] NH(D) = neopentane (D), N-N = dineopentyl, N-S = neopentylcyclohexane, and S-S = dicyclohexyl. [d] Cyclohexene overlapped with cyclohexane in the GLC trace and would not have been detected. [e] Cyclohexene and a trace of ethylene were observed. [f] Ethylene (~0.1 mol/mol of **1**) was observed. [g] d_4 = 26%, d_2 = 51%, and d_0 = 23%.

than in cyclohexane (cf. Experimental Section).

Phosphorus NMR spectroscopy provides additional evidence confirming the compatibility of a dissociative equilibrium generating $LPtR_2$ (eq 11, R = $CH_2C(CH_3)_3$) with the kinetic data.



1-d_{30} **1**-d_{15} **1**-d_0 (11)

Compound **1** and its two isotopically substituted derivatives gave distinct ^{31}P NMR spectra.[34] Kinetic studies over a range of triethylphosphine concentrations from 0.11–1.69 M, although not highly precise, established eq 12[35] as the empirical rate equation

$$-\frac{d[\mathbf{1}\text{-}[P(C_2D_5)_3]_2]}{dt} = 2(7.7 \times 10^{-5}\ s^{-1})[\mathbf{1}\text{-}[P(C_2D_5)_3]_2][P(C_2D_5)_3]^{0.0\pm0.3} \quad (12)$$

describing the disappearance of **1**-d_{30} at 30 °C (representative spectra and individual rate constants are given in the Experimental Section). Although the error in the exponent of the term in the concentration of $P(C_2D_5)_3$ is large, this rate law indicates that the interchange of phosphines on **1** occurs by an S_N1 process: rate-limiting dissociation of phosphine from **1**, followed by recombination of a new phosphine with the resulting $LPtR_2$ intermediate. Thus, ^{31}P NMR spectroscopy provides direct evidence for dissociation of phosphine ligands from **1** at a rate significantly faster than the rate of decomposition of **1**.

Analysis of the dependence of k_{NH} on triethylphosphine concentration indicated qualitatively that the rate of phosphine dissociation inferred from this dependence is compatible with the rate determined by ^{31}P NMR. Substitution of eq 5 into eq 1 and inversion generates eq 13; similar manipulation converts eq 2 into eq 14. In either event, a plot of $(k^{obsd})^{-1}$ vs. [L] should generate

$$\frac{1}{k^{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1}\left(\frac{1}{k_2}\right)[L] \quad (13)$$

$$\frac{1}{k^{obsd}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1}\left(\frac{k_{-2} + k_3}{k_2 k_3}\right)[L] \quad (14)$$

a straight line, with the intercept [L] = 0 being the reciprocal of the phosphine-dissociation rate $(k_1)^{-1}$. This plot (from entries 6–9 of Table II) is shown in Figure 6. The intercept is not accurately defined from the plot, and only a lower limit for k_1 can be extracted: $k_1 \geq 1.3 \times 10^{-3}\ s^{-1}$.

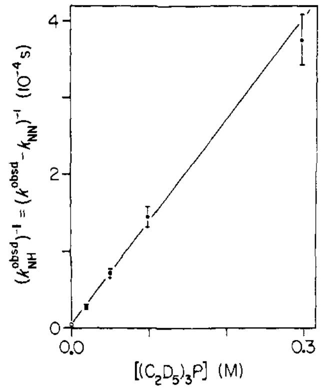


Figure 6. Plot of $(k_{NH}^{obsd})^{-1} = (k^{obsd} - k_{NN})^{-1}$ vs. the concentration of added $P(C_2D_5)_3$. Rate constants were obtained at 157 °C in cyclohexane solution by ^{31}P NMR spectroscopy.

This rate constant is estimated from data collected at 157 °C and cannot be compared directly with that from the ^{31}P NMR observations at 30 °C. The latter rate can, however, be extrapolated approximately to 157 °C by first assuming reasonable values of the Arrhenius preexponential factor and calculating values of the activation energy for phosphine dissociation: for $A = 10^{16}$ (assumed),[36] E_a = 27 kcal mol^{-1} [33] and k_1(extrapolated) = 10^2 s^{-1}; for $A = 10^{20}$ (assumed),[36] E_a = 33 kcal mol^{-1} [37] and k_1(extrapolated) = 10^3 s^{-1}. These estimates of rates are compatible with that estimated by extrapolating the line in Figure 6 to [L] = 0 but are much more reliable quantitatively. Because the quality of the latter data are such that they lead only to a lower limit for k_1, we will use the estimate from ^{31}P NMR as the basis for further discussion. The exchange of $(C_2H_5)_3P$ into 4-$[(C_2D_5)_3P]_2$ was measured by ^{31}P NMR and was calculated to have a half-life of ca. 15 min ($k \simeq 10^{-3}\ s^{-1}$, 30 °C, cyclohexane, assuming an S_N1 mechanism). With the assumption that **1** and **4** follow the same mechanisms for phosphine exchange, compound **4** exchanges ~10 times faster than **1**.

Radical Mechanisms. A comparison of the products of thermal decomposition of **1** with those of a reaction which generates authentic neopentyl radicals—photolysis of dineopentylmercury—indicates that it is very unlikely that the former reaction involves neopentyl radical intermediates. Table III lists products of photolysis of dineopentylmercury and **1** in cyclohexane and in cyclohexane containing triethylphosphine. The array of products observed on photolysis is that expected for a radical reaction. In particular, the products are derived in major part from attack on the cyclohexane solvent. This distribution is clearly very different from that observed in thermal decomposition of **1**.

Compound **1** was itself photolyzed to establish that this difference does not reflect very high reactivity of **1** toward neopentyl radicals. The mechanism of photolytic decomposition of orga-

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(34) The ^{31}P NMR (C_6H_{12}) chemical shift for $(C_2D_5)_3P$ is 2.4 ppm upfield from $(C_2H_5)_3P$ (−19.9 ppm). When they are complexed, as in **1**-$[(C_2D_5)_3P]_2$ and **1**, they differ by 1.6 ppm in the same sense. The mixed complex **1**-$[(C_2D_5)_3P]$-$[(C_2H_5)_3P]$ shows half of an AB pattern (only ^1H was decoupled; phosphines coupled to deuterium are broadened) with $J_{P,P}$ = 12 Hz.

(35) This equation assumes that the exchange is first order in **1**-$[(C_2D_5)_3P]_2$. Duffield, R. B.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 557–561. Frost, A. A.; Pearson, R. G. "Kinetics and Mechanism", 2nd ed.; Wiley: New York, 1961; p 192.

(36) $A = 10^{16}$ was chosen as typical of a unimolecular dissociation; $A = 10^{20}$ is the value estimated from Figure 4.

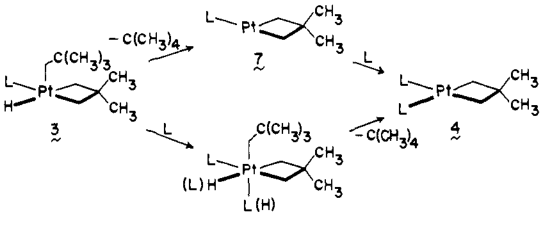
(37) This activation energy is comparable to values obtained for $(F_3P)_3Pt^0$ (24 kcal/mol) which also exchanges phosphines by an S_N1 mechanism. Johnston, R. D.; Basolo, F.; Pearson, R. G. *Inorg. Chem.* **1971**, *10*, 247–251.

noplatinum complexes has not been established, but the products of this reaction can plausibly be derived, at least in part, from neopentyl radicals. The distribution of a 1:2:1 mixture of dineopentyls-d_0, -d_2, and -d_4 from photolysis of a mixture of **1** and **1**-$[CD_2C(CH_3)_3]_2$ is compatible with this path. The relatively low incorporation of deuterium into neopentane in C_6D_{12} suggests, however, that another, more selective, nonradical path may also be important. In any event, these product distributions are so different from those observed in thermal decomposition of **1** as to exclude radical paths for the thermal decompositions, even though the reaction conditions in the thermolysis and photolyses are quite different.

Discussion

Six lines of evidence support the mechanism outlined in Scheme I for the thermal decomposition of **1**: (1) the platinacyclobutane **4** and neopentane are the major products; (2) the decomposition involves an intramolecular transfer of hydrogen from a methyl group of one neopentyl moiety to the methylene group of a second; (3) a kinetic isotope effect of $k_H/k_D \simeq 3.0$ is observed for the transferred hydrogen; (4) dissociation of triethylphosphine and formation of a three-coordinate intermediate $LPtR_2$ is required for the reaction; (5) neopentyl radicals are not intermediates; (6) the methyl and methylene groups of the neopentyl moieties do not interchange during the reaction.

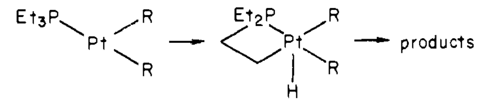
The most important question unresolved by these data is the overall rate-limiting step: carbon-hydrogen bond breaking (**2** → **3**) and carbon-hydrogen bond making (**3** → **4**) are both compatible with the kinetic isotope effect and the observation that the methyl and methylene groups of **1** do not equilibrate during decomposition does not exclude reversible formation of **3**. A second question is that of the timing of neopentane loss and triethylphosphine addition involving **3** (eq 15). The large Arrhenius preexponential factor (log $A \simeq 20$) is most compatible with a mechanism in which reductive elimination (**3** → **7**) is overall rate limiting. This mechanism would involved a transition state in which three particles (L, **7**, and neopentane) are generated in the transition state from one particle (**1**) in the ground state and would be expected to be characterized by a large, favorable, entropy of activation.[38] In the absence of clear models for such a process and with the fact that relief of steric crowding (see below) may be accompanied by an increase in entropy of unpredictable magnitude, this mechanistic proposal should be considered tentative. We note that the observed isotope effect ($k_H/k_D \simeq 3$) is similar to that observed for reductive elimination of methane from bis(triphenylphosphine)hydridomethylplatinum(II) ($k_H/k_D = 3.5$).[39] On the assumption that neopentane loss is rate limiting, phosphine association must follow neopentane loss: that is, the reaction path must be **3** → **7** → **4**.



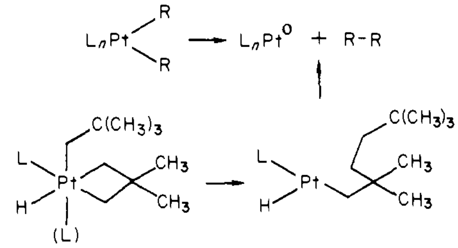
(15)

Comparison of the results of this study with that for *cis*-di-*n*-butylbis(triphenylphosphine)platinum(II) and *cis*-diethylbis(triethylphosphine)platinum(II)[32] suggests the parallel that a three-coordinate complex $LPtR_2$ is an important reactive species in each case. These studies indicate that the relative rates of intramolecular loss of different types of hydrogen by processes involving additions to platinum are β-CH (β-hydride elimination) > γ-CH (cyclometallation) > α-CH (carbene formation). Note, however, that this order is not necessarily the same as the order of the addition reactions themselves since C–H bond cleavage is rate limiting in none of these reactions. The requirement for phosphine dissociation in these reactions rationalizes the observation that organoplatinum compounds are more stable as solids than in solution and that solution stability is increased by adding phosphines.

The side-reactions accompanying the transformation of **1** to **4**—that is, neopentane production by abstraction of hydrogen from triethylphosphine and dineopentane production—are interesting in that they seem similar in kinetic behavior. The first of these reactions is probably a competitive cyclometallation, and the kinetic similarity is not surprising (eq 16). The second reaction forms a carbon–carbon bond and is a different type of process. The reaction proceeds in this system in a yield which is too low to make detailed mechanistic study practical (although it is approximately 40% for dineopentylbis(triphenylphosphine)platinum(II) in some conditions). We note, nonetheless, that the reaction need not proceed by reductive elimination from a dineopentylplatinum(II) species (eq 17a) but may reflect an alternative mode of decomposition of the platinum(IV) species **3** (or some derivative) (eq 17b). Reductive elimination with carbon–carbon bond formation and platinacyclopentane ring opening has been observed.[40] There is, to date, no well-established example of carbon–carbon bond formation by reductive elimination from a dialkylplatinum(II) group.



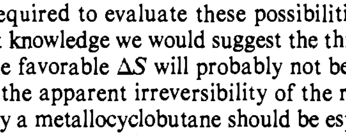
(16)



(17a)

(17b)

The mechanism of decomposition of **1** suggests hypotheses (although not yet firm answers) for two general questions. First, why does the reaction **1** → **4** + neopentane occur? Second, if addition of C–H bonds from neopentyl moieties and from triethylphosphine occurs readily, why is solvent not attacked? The simplest thermodynamic analysis of the overall reaction identifies no obvious driving force for the reaction (eq 18): it simply interchanges Pt–C and C–H bonds. Three factors seem capable, in principle, of making the reaction exergonic: first, since two particles are produced from one, ΔS for the reaction should be positive; second, there may be some special stability associated with a platinacyclobutane ring; third, the reaction may relieve unfavorable steric interactions in the starting material. Further work will be required to evaluate these possibilities, but on the basis of current knowledge we would suggest the third as the most important. The favorable ΔS will probably not be large enough to account for the apparent irreversibility of the reaction;[41] it is not obvious why a metallocyclobutane should be especially stable; **1** is, however, probably significantly more strained by interaction of the bulky ligands than is **4**. If this analysis is correct, then, in principle, it should be possible to find instances in which solvent C–H bonds add to platinum.[42] In the particular case of **1**, it



(18)

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[38] A related mechanism with a similar value for *A* has been inferred for the decomposition of diethylbis(triethylphosphine)platinum(II).[32]

[39] Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* **1978**, *100*, 2915–2916.

[40] Young, G. B.; Whitesides, G. M. *J. Am. Chem. Soc.* **1978**, *100*, 5808–5815.

[41] The entropy changes for radical recombination reaction in nonpolar solvents are generally small, ca. 5–10 eu: Moelwyn-Huges, E. A. "The Chemical Statics and Kinetics of Solutions"; Academic Press: New York, 1971; p 69.

appears that the second most reactive C–H bonds in the system are those of the triethylphosphine moieties: this reactivity certainly reflects the favorable influence of high local concentration and may reflect electronic factors as well. Further, if the cyclohexane solvent was to add, it would probably *increase* rather than decrease the unfavorable steric interactions around the metal: the solvent molecule added should, at minimum, be smaller than the alkyl group it replaces to encourage addition.

Experimental Section

General Data. Organometallic reactions were carried out under argon or prepurified dinitrogen by using standard anaerobic techniques. Melting points were obtained in open tubes and are uncorrected. Mass spectra were obtained by using a Hewlett-Packard 5990A GC/MS, with a 70-eV ionizing voltage. ^{31}P NMR spectra were taken by using a JEOL FX 90 Q spectrometer and a modified Bruker HFX-90 spectrometer and are referenced to 85% H_3PO_4 (external). Grignard reagents were titrated by using the procedure of Eastham.[43] Ethereal solvents were dried by distillation from disodium benzophenone dianion. Bulb-to-bulb distillations and gas transfers were carried out by using a calibrated volume vacuum line equipped with a mechanical pump to maintain a 0.002 torr vacuum. Sealed tubes for kinetic studies were prepared by using this same line. Photolyses were carried out in Pyrex tubes by using a Rayonet reactor containing eight 350-nm and eight 253.7-nm mercury lamps.

Cycloocta-1,5-diene (Tech., Aldrich) and cyanogen (Matheson, tech) were used without purification. Acetone-d_6 (99.5%, Stohler Isotope Chemicals), $LiAlD_4$ (99% D, Stohler Isotope Chemicals), D_2O (99.7% D, Merck), and DCl (38% in D_2O, 99% D, Stohler Isotope Chemicals) were used as received; cyclohexane-d_{12} was purified by distillation from P_2O_5. $TiCl_4$ (Alfa) was distilled before use.

Neopentylmagnesium bromide was prepared in 80% yield by reaction of neopentyl bromide with Rieke magnesium[44] in ether, followed by centrifugation to remove precipitated magnesium salts. *cis*-Dichloro-1,5-cyclooctadieneplatinum(II) (without melting 255–280 °C dec) was obtained in 96% yield by reaction of K_2PtCl_6 with 1,5-cyclooctadiene in acetic acid–water.[45]

Dineopentylmercury was prepared from mercuric chloride and neopentylmagnesium bromide by following a literature[46] procedure. It had mp 38–39 °C (lit.[46] 31–33 °C) and bp 58 °C (0.01 torr): ^1H NMR ($CDCl_3$) δ 1.0 (t, 9 H, $J_{Hg-H} = 5$ Hz, $C(CH_3)_3$), 1.1 (t, 2 H $J_{Hg-H} = 94$ Hz, $HgCH_2$–).

Pinacol-d_{12} $[(CD_3)_2COH]_2$.[47] To a 3-L Erlenmeyer flask equipped with a stopper and thermometer was added $HgCl_2$ (13.2 g, 0.05 mol), dry tetrahydrofuran (THF, 300 mL), and magnesium powder (45.6 g, 1.87 g/atom, 40 mesh). The reaction mixture was allowed to stir for 2 h, and the supernatant solution was removed from the dark magnesium amalgam by cannula. Dry THF (1.8 L) was added, and the mixture was cooled to <−30 °C in a dry ice–acetone bath. Titanium tetrachloride (178 g, 104 mL, 0.94 mol) was added slowly while this temperature was maintained. After the addition had been completed, the yellow-green slurry was warmed to −10 °C in an ice–acetone bath and swirled for 1 h. To the mixture was added 40 g (0.63 mol) of acetone-d_6 in 5-g aliquots while keeping the temperature below 0 °C (this reaction is extremely exothermic, with variable induction periods). A blue-black mixture resulted which was allowed to stand for 8 h and was quenched with a saturated solution of K_2CO_3 in water. The solution was separated from solids by centrifugation, acidified (pH 6) with 0.1 M H_2SO_4, and extracted with four 100-mL portions of ether. The ether was removed on a rotary evaporator at room temperature, and the residual oil was dried by addition of benzene (~30 mL) and azeotropic distillation. The remaining oil (32.5 g) was distilled to yield 26.4 g (65%) of pinacol-(OH)-d_{12} with bp 172 °C. This material had significant NMR adsorption only at δ 3.37 (s, OH). (We note that although this procedure provided the desired material, it was poorly reproducible.) Pinacol-d_{14} was prepared by exchanging the OH proton against D_2O, followed by azeotropic drying. This exchange had no influence on the isotopic purity of the pinacolone into which it was converted.

Pinacolone-d_{12}. B_2O_3 (6.0 g, 86 mmol, dried by flaming under vacuum) and 11.0 g (83 mmol) of pinacol-d_{14} were mixed in a round-bottomed flask equipped with a short-path distillation head. The reaction mixture was gradually heated over a period of 1 h to 180 °C. At 125 °C the heterogeneous mixture turned to a viscous clear solution and slowly darkened as the temperature approached 185 °C. A mixture distilled from the syrup which was initially predominately water and subsequently pinacolone. The last traces of product were obtained by heating the flask with a torch until a solid mass of discolored B_2O_3 remained. Pentane (15 mL) was added to the crude distillate, and the organic layer was separated from the water layer, dried (Na_2SO_4), and distilled: Pinacolone-d_{12} (8.1 g, 87%) had bp 99–102 °C. GC/MS: m/e (%) 18 (3.7), 30 (5.7), 34 (21.1), 42 (15.2), 44 (4.0), 45 (5.6), 46 (85.5), 47 (2.9), 62 (2.4), 64 (5.5), 65 (5.0), 66 (100), 67 (4.6), 110 (0.9), 111 (7.0), 112 (26.1), 113 (1.7). This analysis corresponds to no greater than 5% H in the *tert*-butyl portion and a methyl ketone portion having 77% d_4, 21% d_2, and 2% d_1.

Pivalic Acid-d_9, $(CD_3)_3CCO_2H$ (bp 162–164 °C), was prepared in 82% yield on a 19-g scale by using the procedure of Vogel.[48] Methyl pivalate-d_9 (bp 98–101 °C) was obtained from this pivalic acid in 95% yield by treatment with diazomethane.[49] **$(CD_3)_3CCD_2OH$** (bp 110–112 °C) and **$(CD_3)_3CCH_2OH$** (bp 110–113 °C) were isolated in 80–85% yield after treatment of methyl pivalate-d_0 with $LiAlD_4$ and $LiAlH_4$, respectively, in THF. **$(CH_3)_3CCD_2OH$** (bp 110–113 °C) was prepared in 70% yield by reduction of pivalyl chloride with $LiAlD_4$ in THF. **$(CD_3)_3CCD_2Br$** (bp 109 °C) and **$(CD_3)_3CCH_2Br$** were prepared in 75% yields from the respective alcohols and tri-*n*-butylphosphine dibromide in DMF.[50] **$(CH_3)_3CCD_2Br$** (104–106 °C) was prepared from neopentyl-d_2 tosylate by reaction with lithium bromide in HMPA.[51]

CD_3CD_2Br was prepared in 78% yield by the procedure of Gilman[52] from C_2D_5OH. Reaction with magnesium in diethyl ether at 0 °C yielded CD_3CD_2MgBr.

$(CD_3CD_2)_3P$. Triphenyl phosphite (17.3 g, 56 mmol) and 250 mL of ether were placed in a flame-dried, 1-L, one-necked flask and cooled to −80 °C.[53] A 1.3 M solution (180 mL, 0.19 mol) of perdeuterioethylmagnesium bromide in ether was slowly added over a period of 1 h by cannula. The mixture was allowed to warm to room temperature over a period of 8 h. The ether was carefully distilled directly from the crude reaction mixture until ca. 50 mL of liquid remained. The remaining ether and triethylphosphine were removed from the magnesium salts in vacuum by slowly heating the flask with a glass blower's torch and condensing the evolved vapors in a −196 °C trap. The condensed material was distilled under argon: $(C_2D_5)_3P$ (3.4 g, 46%, bp 126–127 °C) had: ^{31}P NMR (C_6H_{12}, external H_3PO_4) δ −21.9 (s, br).

$(CH_3)_3CCH_2D$ and $(CH_3)_2C(CH_2D)_2$ were prepared by reduction with *n*-Bu_3SnD.[54] Into a 25-mL flask was placed $LiAlD_4$ (0.5 g, 11.9 mmol, 99% *d*) with 10 mL of deolefinated decane and 3.9 g (11.9 mmol) of tri-*n*-butyltin chloride. The contents of the flask were periodically warmed with a heat gun and stirred for 15 min. After the solution was cooled to room temperature, 2.4 g (11.9 mmol) of neopentyl iodide was added and the contents of the flask were stirred overnight. The neopentane produced, 86% yield, was analyzed by GC/MS: m/e (%) 15 (5.4), 27 (6.6), 28 (4.4), 29 (8.3), 30 (5.3), 39 (15.6), 40 (7.3), 41 (32.0), 42 (25.5), 55 (1.8), 56 (4.6), 57 (35.3), 58 (100), 59 (4.7). Similarly 1,3-dideuterioneopentane was produced from 1 g (24 mmol) of $LiAlD_4$, 7.8 g (24 mmol) of *n*-Bu_3SnCl, and 3.9 g (11.9 mmol) of 1,3-diiodoneopentane. The GC/MS of the neopentane formed showed: m/e (%) 15 (3.6), 27 (5.0), 29 (7.1), 30 (10.3), 31 (3.0), 39 (13.8), 40 (13.0), 41 (25.7), 42 (44.4), 43 (15.0), 55 (1.5), 56 (3.9), 57 (8.8), 58 (99.7), 59 (99.1), 60 (4.8). Both neopentanes were isolated from the decane solution by bulb-to-bulb distillation under vacuum into a −196 °C trap. They

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(42) It is not necessarily the case that solvent addition, even if it were to occur, would result in formation of stable adducts. Halpern and co-workers argue convincingly that the conversion of a bis(phosphine)hydridoalkylplatinum(II) species to bis(phosphine)platinum(0) and alkane should normally be exergonic,[39] although systems incorporating chelating phosphines may provide counter examples: Yoshida, R.; Yamaguchi, R.; Tulip, T.; Ibers, J. A.; Otsuka, S. *J. Am. Chem. Soc.* **1978**, *100*, 2063–2073.

(43) Watson, S. C.; Eastham, J. F. *J. Organomet. Chem.* **1967**, *9*, 165–168.

(44) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775–1781.

(45) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521–6528.

(46) Whitmore, F. C.; Rohrmann, E. *J. Am. Chem. Soc.* **1939**, *61*, 1591. Singh, G.; Reddy, G. S. *J. Organomet. Chem.* **1972**, *42*, 267–275.

(47) The synthesis was adapted from the work: Corey, E. J.; Danheiser, R. L.; Chandrasekaran, S. *J. Org. Chem.* **1976**, *41*, 260–265. For information on the actual reducing species see: Sobota, P.; Jezowska-Trzebiatowski, B. *Coord. Chem. Rev.* **1978**, *26*, 71–84.

(48) Vogel, A. L. "Practical Organic Chemistry". 3rd ed.; Longman: London, 1972; p 351.

(49) Fiser, L. F.; Fieser, M. "Reagents for Organic Synthesis"; Wiley: New York, 1967; Vol. 1, pp 191–192.

(50) Wiley, G. A.; Hershkowitz, R. L.; Rein, B. M.; Chung, B. C. *J. Am. Chem. Soc.* **1964**, *86*, 964–965.

(51) Mosher, H. S.; Stephenson, B.; Solladie, G. *J. Am. Chem. Soc.* **1972**, *94*, 4184–4188. See also: Sowinski, A.; Whitesides, G. M. *J. Org. Chem.* **1979**, *44*, 2369–2376.

(52) Gilman, H.; Blatt, A. H. "Organic Synthesis"; Wiley: New York, 1941; Collect. Vol. 1, p 31.

(53) Markham, R. T.; Dietz, E. A., Jr.; Martin, D. R. *J. Inorg. Nucl. Chem.* **1973**, *35*, 2659–2660. Wolfsberger, W.; Schmidbauer, H. *Synth. React. Inorg. Met.-Org. Chem.* **1974**, *4*, 149–156.

(54) Kuivila, H. G.; Menapace, L. W. *J. Org. Chem.* **1963**, *28*, 2165–2167.

were purified by three trap-to-trap fractionations through a 0 °C trap.

***cis*-Dineopentyl-1,5-cyclooctadieneplatinum(II).** To a stirred suspension of 3.5 g (9.4 mmol) of *cis*-dichloro-1,5-cyclooctadieneplatinum(II) in 200 mL of dry ether at −80 °C was added, over a period of 2 h, 270 mL (20 mmol) of 0.075 M solution of neopentylmagnesium bromide in tetrahydrofuran. The mixture was allowed to stir for 8 h while slowly being warmed to room temperature, quenched with 100 mL of NaCl–H_2O (50% saturated), and diluted with 150 mL of pentane. The aqueous portion (sometimes black) was extracted with two 150-mL portions of pentane and combined with the organic layer. The organic portion was dried over Na_2SO_4, filtered, and concentrated at room temperature by using a rotary evaporator. The product was an oily solid, which was recrystallized by dissolving in 25 mL of acetone and cooling to −15 °C. A light yellow crystalline product (1.4 g) was obtained; an additional 1.3 g was obtained from the mother liquor by adding 1 mL of water and cooling (total 2.7 g, 65%, mp 109 °C). ^1H NMR (C_6D_6): δ 1.31 (t, 18 H, J = 4 Hz, $-C(CH_3)_3$), 1.81–1.92 (br m, 8 H, $-CH_2CH_2-$), 2.16 (t, 1:4:1, 4 H, J_{Pt-H} = 92 Hz, $PtCH_2-$), 4.74 (t br, 1:4:1, 4 H, J_{Pt-H} = 38 Hz, $CH{=}CH$). IR (KBr pellet): 2900 (vs), 2795 (s), 1470 (s), 1455 (s), 1425 (s), 1370 (s), 1350 (vs), 1335 (m), 1230 (s), 1140 (s) cm^{-1}.

Anal. Calcd for $C_{18}H_{34}Pt$: C, 48.54; H, 7.64. Found: C, 48.65, H, 7.82.

Deuterated analogues of $CODPt[CH_2C(CH_3)_3]_2$ were prepared by using the same procedure: all had mp 107 °C and ^1H NMR spectra consistent with the assigned structures.

***cis*-Dineopentylbis(triethylphosphine)platinum(II) (1).** To a 10-mL solution of 1.1 M *cis*-dineopentyl-1,5-cyclooctadieneplatinum(II) in ether was added triethylphosphine-d_0 (0.27 g, 0.34 mL, 2.3 mmol). The reaction was allowed to stand for 10 h. The solution was passed through a column of activity I alumina (3 cm × 1 cm) and eluted with additional ether to remove any unreacted triethylphosphine and phosphine oxide. The solvent was removed under vacuum to leave an off-white crystalline solid. The solid was dissolved in a minimum of pentane (~20 mL) by gently warming and cooled to −10 °C to yield 0.4 g (79%) of **1**. Material used in kinetic studies was recrystallized again from pentane: mp 130–132 °C dec; ^{31}P NMR (C_6H_6, H_3PO_4 external reference) δ −2.1 (t, 1:4:1, J_{Pt-P} = 1638 Hz); ^1H NMR (CD_2Cl_2) δ 0.25–0.76 (6 line m, 36 H), 0.76–1.64 (7 line m, 16 H); IR (KBr pellet) 2880 (vs), 1450 (br s), 1430 (s), 1370 (s), 1345 (s), 1230 (s), 1025 (s), 750 (s), 710 (s) cm^{-1}.

Anal. Calcd for $C_{22}H_{52}P_2Pt$: C, 46.10; H, 9.07. Found: C, 45.96; H, 9.16.

Deuterated analogues of **1** were prepared by analogous procedures. All had melting points with decomposition in the range 127–133 °C.

Quantitative Protolysis of 1. Into a 1-mL centrifuge tube was weighed 12.8 mg (0.022 mmol) of **1**. A No-Air stopper was fitted to the tube, and the solid was dissolved in 0.3 mL of a standard solution of 0.1 M cyclopentane (as a GLC internal standard) in cyclohexane. The solution was treated with 0.1 mL of HCl (38% in H_2O), HCl (concentrated), or trifluoromethanesulfonic acid and was shaken for 2 min. The organic layer was analyzed by GLC with the use of a cold clean injection port (50 °C) to obtain 100% of the theoretical 2 equiv of neopentane. This procedure was not used for deuterium incorporation experiments.

DCl Quenches of Alkylplatinum(II) Complexes. Into a flame-dried 1-mL centrifuge tube was weighed ca. 15 mg of an alkylplatinum(II) complex. A No-Air stopper was fitted to the tube, and the solid was dissolved in the appropriate solvent (0.2 mL), depending on solubility (usually benzene, cyclohexane, or methylene chloride was used). A syringe which had been rinsed three times with D_2O (99% D) was used to add 0.1 mL of D_2O (99% D) to the tube. The tube was shaken and centrifuged, and the D_2O layer was removed by syringe; this rinsing was repeated three times. Another syringe which was rinsed four times with D_2O (99.7% D) was used to add 0.1 mL of fresh DCl (38% in D_2O, 99% D) to the alkylplatinum solution. The tube was shaken for 0.5 h and analyzed by GC/MS. The injection port of the GC/MS was kept at 60 °C and cleaned with 20 μL of D_2O (99% D) before a sample was analyzed. Mass spectra were accumulated over the width of the GLC peak width. Reported ion intensities typically represent an average of ca. 50 mass spectra.[55] Results of mass spectral analysis of **1** and derivatives are summarized in Table I.

Protolysis of *n*-BuMgBr in THF. In a one-necked 25-mL flask equipped with a stopcock was made a solution of *n*-BuMgBr in THF by using established procedures. The radical disproportionation products, butane and butene, were removed by distilling 50% of the THF from the solution under vacuum. The flask was brought to 1 atm with argon, and the reaction was quenched with D_2O or DCl with a syringe that had been rinsed three times with D_2O.

Reaction of 1 with Cyanogen. In a 1-mL centrifuge tube was placed 11.4 mg (0.02 mmol) of **1**-d_0. After the tube was fitted with a No-Air stopper, 0.6 mL of a solution containing nonane (7.58 mM, GLC internal standard) in methylene chloride was added, followed by 0.1 mL of a saturated solution of cyanogen in methylene chloride. The tube was shaken and gently heated on a steam bath for 5 min. The yield of dineopentyl (typically ~30%) was determined by GLC with a 50 °C injection port. The same procedure was used with deuterated analogues of **1**.

Isolation of Bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (4). In each of eight flame-dried, argon-filled 20-mL Pyrex tubes was placed 0.50 g (0.88 mmol) of **1**, 0.033 mL (23 mg, 0.19 mmol) of triethylphosphine, and 10 mL of cyclohexane. The contents of the tubes were degassed and the tubes sealed and heated at 157 °C for 2.25 h and cooled quickly at −196 °C. The tubes were opened and the contents flushed with argon while still frozen. After being warmed to 25 °C, the contents of the tubes were transferred by Teflon cannula to a 250-mL round-bottomed flask. The solvent was removed at reduced pressure (80 torr) and the residual oil taken up in 30 mL of degassed acetonitrile to precipitate unreacted **1**. The acetonitrile solution was separated, the acetonitrile removed under vacuum and then the residual brown oil dissolved in a minimal volume (ca. 15 mL) of degassed ether. An equivalent volume of degassed methanol was added, the solution cooled to −78 °C, and the volume reduced by rapidly flowing argon over the solution as fine, white crystals precipitated. The supernatant was transferred by cannula to a clean flask and further reduced in volume as before, and the precipitates were combined and recrystallized in the same manner from fresh methanol–ether to give 2.50 g (71% yield) of **4** as a white, crystalline solid: mp 41.3–42.5 °C; ^{31}P NMR (C_6D_6, H_3PO_4 external reference) δ +8.8 (t, 1:4:1, J_{Pt-P} = 1868 Hz); ^1H NMR (C_6D_6) δ 0.88–1.59 (multiplet); mass spectrum, m/e (%) 468 (5), 431 (49), 403 (42), 375 (45), 347 (21), 313 (13), 118 (46).

Anal. Calcd for $C_{17}H_{40}P_2Pt$: C, 40.71; H, 8.04. Found: C, 40.54; H, 8.01.

Cryoscopic Molecular Weight Determination of 4. Using a modification of a standard procedure,[57] 0.0150 g (0.030 mmol) of **4** was weighed into a flame-dried 6 × 50 mm disposable culture tube. The tube was capped with a rubber septum and 0.511 g (6.55 mmol) of distilled benzene added by syringe. The contents of the tube were mixed thoroughly and then frozen at −78 °C, and the tube was attached to a Beckmann thermometer and suspended in a Dewar of ice-water being stirred slowly at 0 °C. The temperature of the bath was allowed to increase at ~0.05 °C/min, and the temperature at which the solution first began to melt was recorded. A second determination was performed, and then predetermined additional amounts of benzene were added to the tube and the melting points determined with respect to a tube of pure benzene. Workup of the data in the usual manner yielded a molecular weight for **4** of 515 (calculated 501).

Reactions of 4 with DCl, Br_2, and I_2. Into a flame-dried 1.0-mL centrifuge tube was weighed 15 mg (0.030 mmol) of **4**. The tube was capped with a rubber septum and flushed with argon. To the tube was added 0.25 mL of a 0.1 M solution of cyclopentane (GLC internal standard) in cyclohexane followed by 0.05 mL of DCl (38% in D_2O, 99% D), and the tube was shaken for 0.5 h. GLC analysis showed a 98% yield of neopentane which was determined to be 99% $(CH_3)_2C(CH_2D)_2$ and 1% $(CH_3)_3CCH_2D$ by GC/MS.

With use of a similar procedure, reaction of **4** with 1 equiv of I_2 dissolved in cyclohexane at 25 °C yielded 98% 1,1-dimethylcyclopropane and 2% 1,3-diiodo-2,2-dimethylpropane. Reaction with 2 equiv of Br_2 was carried out in a similar manner.

Isolation of 4-$[P(C_2D_5)_3]_2$. In a Pyrex tube was placed 0.28 g (0.6 mmol) of **1**-$[P(C_2D_5)_3]$ and 7 mL of a 0.051 M solution of cyclopentane in cyclohexane. The contents of the tube were degassed, and the tube was sealed and heated at 150 °C for 24 min, quenched thermally at −196 °C, and analyzed for neopentane by GLC and GC/MS. The analysis showed that the thermolysis was 97% complete with 98% neopentane-d_0 produced. A ^{31}P NMR spectrum (C_6H_{12}, external H_3PO_4 reference) of the decomposition solution showed only one major phosphine-containing product: δ +10 (t, 1:4:1, J_{Pt-P} = 1862 Hz). The solvent was removed

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[55] The Hewlett-Packard 5990A GC/MS can be set to accumulate and average eight consecutive spectra automatically and to store the resulting average. Another series of scans was initiated manually as soon as the previous one was completed. In the completion of a peak, the series of these eight-scan averages (typically 48 spectra) was averaged manually.

[56] These spectra of the CH_2 protons are properly considered as part of a $AMM'X_2X_2'$ spin system. The approximately triplet splitting due to coupling between ^1H and ^{31}P does not reflect J_{P-H} accurately and should be considered only as an empirical parameter. The reported "J" values are the separation between the outer lines of these triplets. Shaw, F. C., III; Lundeen, J. W.; Tobias, R. S. *J. Organomet. Chem.* **1973**, *51*, 365–374.

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in a stream of argon, and the residual oil was taken up in 2 mL of acetonitrile to precipitate unreacted **1**-$[P(C_2D_5)_3]_2$. The acetonitrile solution was separated and acetonitrile removed under vacuum, leaving an oil which could not be made to crystallize. Volatile proton-containing materials were removed from the oil by adding and evaporating several 2-mL portions of C_6D_6. The ^1H NMR spectrum (see the text) indicated the presence of ca. 10% impurity resonance δ 1.35 (s). The ^{31}P NMR spectrum was identical with that of the crude reaction solution, with the addition of a small new resonance at δ 8.8. The complex was very soluble in all organic solvents but insoluble in water. It decomposed on a silica gel column when eluted with ether; further attempts to purify the air-stable oil were not made. The ^1H NMR spectrum of **4**-$[(C_2D_5)_3P]_2$ showed two types of protons: δ (C_6D_6) 0.73 (t of t, 1:4:1, 4 H, J_{Pt-H} = 74 Hz, "J" = 12 Hz, $PtCH_2$) and 1.57 (t, 6H, "J" = 3 Hz, $C(CH_3)_2$).[56] The proton-decoupled ^{31}P spectrum showed one type of phosphorus: δ (C_6H_{12}, 85% H_3PO_4 external reference) +9.0 (t, 1:4:1, J_{Pt-P} = 1862 Hz).

Reactions of 4-$[P(C_2D_5)_3]_2$ and 4-d_{10} with DCl, HCl, and NCCN. Compound **1**-$[P(C_2D_5)_3]_2$ (29.4 mg, 0.048 mmol) was placed in an NMR tube containing 10 μL of tetramethylsilane, 2 μL of $(C_2D_5)_3P$, and 0.6 mL of C_6D_{12}. The tube was degassed, sealed, and heated at 157 °C until neopentane production stopped (ca. 3 h). The tube was opened and fitted with a No-Air stopper, and 0.5 mL of a 0.093 M solution of cyclopentane (GLC standard) in cyclohexane was added. GLC analysis showed 105% yield of neopentane and 7% yield of dineopentyl based on initial **1**-d_{30}. The solvents were removed in a stream of argon, and the residual oil was dissolved in 0.5 mL of a 0.093 M solution of cyclopentane in cyclohexane. This solution was treated with 0.05 mL of DCl (38% in D_2O, 99% D) to yield neopentane (85% based on initial **1**-d_{30}) which gave a GC/MS analysis with fragmentation pattern: m/e (%) 56 (4.8), 57 (15.9), 58 (100), 59 (81.5), 60 (4.0). A 100% mass balance of neopentyl groups was obtained based on **1**-d_{30}. Reactions with HCl and cyanogen were carried out by using similar procedures.

Sealed-Tube Reactions. General Methods. Reaction vessels used for thermolysis reactions were made from 6-mm o.d. medium-walled Pyrex tubing with a length of 15 cm. A constriction was placed 6.5 cm from a sealed end. These tubes were washed with acetone, distilled water, acetone (reagent), and cyclohexane reagent, stored at 125 °C, and flame dried under vacuum just before use. Hydrocarbons used as solvents (cyclohexane, cyclohexane-d_{12}, decane) were stirred over concentrated H_2SO_4 for 1 week, decanted, dried over P_2O_5 for 3 days, and distilled under argon. GLC showed no detectable impurities. In general, it is important to keep reagents as dry as possible in these experiments. Into a tube cooled to room temperature was weighed the platinum complex. The tube was fitted with a No-Air stopper, and the powder was tapped to the bottom. The tube was flushed with argon by inserting a 2-in., 16-gauge syringe needle (to act as vent) and a 20-gauge (8-in.) syringe needle attached to an argon line through the 16-guage syringe needle down into the tube as far as possible. Care was taken not to disturb the solid. After flushing for 5 min, the needles were removed and 0.3 mL of a standard solution of triethylphosphine in cyclohexane was added by syringe. The tube was attached to a vacuum line by means of 5-cm, 0.25-in. i.d. rubber vacuum tubing by removing the No-Air stopper under a stream of nitrogen emerging from the piece of rubber tubing (the rubber tube was washed with cyclohexane and pumped on for 3 days before use). The tubing was wired firmly to the sample tube. The contents of the tube were isolated from the vacuum system by pinching the rubber tube with a hemostat, degassed three times to 0.005 torr, and sealed. It is important that the platinum complex was not deposited at the constriction and pyrolyzed during sealing. The pyrolyses were performed in a constant-temperature bath (made from a Dry Ice condenser whose well was filled with oil) heated by refluxing solvent: water (100 °C), acetic acid (118 °C), *p*-xylene (138 °C), and bromobenzene (157 °C). The tubes were quenched in liquid nitrogen, cracked open, and fitted with a No-Air stopper. A standard solution (0.3 mL) of ca. 0.1 M cyclopentane in cyclohexane was added for GLC analysis. A 1-μL sample of the thermolysis solution was injected into a 50 °C injection port for GLC or GC/MS analysis. (Decomposition of **1** was not observed in a clean injection port at 70 °C.)

Kinetic studies by NMR were performed in 5-mm NMR tubes cleaned, filled, sealed, and heated as described for sealed-tube pyrolysis. The NMR tubes were typically charged with ca. 30 mg of **1**-$[(C_2D_5)_3P]_2$, 0.6 mL of C_6D_{12} (distilled from P_2O_5 under argon), 2 to 200 μL of $(C_2D_5)_3P$, and 10 μL of $(CH_3O)_3PO$ (for phosphorus analyses) or 10 μL of tetramethylsilane (for neopentane analyses). Decomposition or product appearance was followed by taking duplicate NMR spectra and measuring the peak height of the desired peak relative to the internal standard. The reproducibility and accuracy of using peak heights for ^1H NMR analysis was shown to be ±5% and for ^{31}P NMR analysis ±8%. At the termination of a kinetic run, the tubes were opened at −196 °C and fitted with a No-Air stopper. A standard 0.1 M solution of cyclopentane in cyclohexane (0.5 mL) was added to standardize the ^1H NMR internal standard (tetramethylsilane) and determine the hydrocarbon products at the end of the thermolysis. An appropriate quench of the remaining platinum complex, **4**-$(L_D)_2$, or GC/MS analysis of the hydrocarbon products was performed at this point.

Partial Thermolysis of 1-$[CD_2C(CH_3)_3]_2$. In a Pyrex tube was placed 14.6 mg (0.025 mmol) of **1**-$[CD_2C(CH_3)_3]_2$ and 0.3 mL of a 0.056 M solution of triethylphosphine in cyclohexane. The tube was degassed, sealed, heated at 157 °C for 1.4 h, cooled to −196 °C, cracked open, and fitted with a No-Air stopper. The unreacted platinum complex precipitated upon cooling and was centrifuged to the bottom of the tube. The solution was separated by syringe and analyzed by GLC for neopentane (43% of one equivalent). The remaining solid was dried in a stream of argon and treated with a saturated solution of cyanogen in methylene chloride. The dineopentyl produced was analyzed by GC/MS to give fragmentation pattern: m/e (%) 126 (0.6), 127 (1.8), 128 (2.8), 129 (1.7), 130 (8.3), 131 (100), 132 (11.7), 133 (3.0).

Thermal Decomposition of 1-$[P(C_2D_5)_3]_2$ in the Presence of Added Triethylphosphine-d_{15}. The thermolyses of four 0.081 M solutions of **1**-d_{30} in the presence of added $(C_2D_5)_3P$ (concentrations 0.022, 0.054, 0.12, and 0.36 M) at 157 °C were followed by the ^1H NMR method. The observed rate constants, k^{obsd} = 40.9, 14.5, 7.1, and 2.7 × 10^{-5} s^{-1}, respectively, were derived from data that extended through 3 half-lives. The ratios of neopentane to dineopentyl observed at the termination of the thermolysis were 18.7, 20.1, 25.1, and 24.7, respectively, and the yields of neopentane-d_1 were 4.8, 5.3, 7.1, and 13.5%, respectively.

Thermolysis of 1-$[P(C_2D_5)_3]_2$ at Several Temperatures. In three ^1H NMR tubes was placed 0.6 mL of a solution of **1**-d_{30} (0.086 M) and $(C_2D_5)_3P$ (0.022 M) in C_6D_{12}. The thermolyses were run at 118, 138, and 157 °C, and followed by ^1H NMR: k^{obsd} = 0.123, 2.98, and 40.8 × 10^{-5} s^{-1}, respectively, for data that extended through 2 half-lives. The ratios of neopentane to dineopentyl observed at the termination of the thermolysis were 36.6, 25.4, and 18.7, respectively. The yields of neopentane-d_1 at 118 and 157 °C were 13.9% and 4.8%, respectively.

Thermal Decompositions of 1 and 1-$[CD_2C(CD_3)_3]_2$ in the Absence of Added Triethylphosphine. In a typical procedure, 30 mg (0.052 mmol) of **1**, 0.50 mL of a 0.237 M solution of triethyl phosphate (internal standard) in cyclohexane, and 0.10 mL of cyclohexane-d_{12} were placed in a 5-mm NMR tube, the contents were degassed and sealed, and the thermolysis was followed by ^{31}P NMR through 1.5–2.0 half-lives. The observed rate constants (averages of two runs) for thermolysis of **1** at 118, 131, 138, and 149 °C were k^{obsd} = 1.40, 16.1, 19.0 and 125 × 10^{-5} s^{-1}, respectively. The thermolysis of **1**-$[CD_2C(CD_3)_3]_2$ at 138 °C yielded k^{obsd} = 7.7 × 10^{-5} s^{-1}.

Thermolysis of 1 in Various Solvents. In each of four Pyrex tubes was placed 16.0 mg of **1**-d_0 and 10 μL of triethylphosphine. The tubes were filled with 0.3 mL of triethylphosphine, triethylamine, C_6D_6, or C_6D_{12}, degassed, sealed, and heated at 157 °C for 2.25 h. The reactions were quenched thermally at −196 °C, the tubes opened and fitted with a No-Air stopper, and the mixtures treated with a solution containing a GLC internal standard and analyzed for neopentane. The yields of neopentane observed were 70%, 100%, 49%, and 50%, respectively, on the basis of 1 equiv of **1**-d_0. The neopentane from the tube containing C_6D_6 was analyzed by GC/MS as neopentane-d_0 (98%) and neopentane-d_1 (2%). The quantity of dineopentyl could not be determined since the solvent peaks interfered.

The solubility of 1-d_0 in cyclohexane was determined with and without 0.34 M triethylphosphine present. A mixture of excess solid **1**-d_0 and cyclohexane or of excess **1**-d_0 and a 0.34 M solution of triethylphosphine in cyclohexane (both containing cyclopentane as a GLPC internal standard) was frozen, evacuated and sealed in Pyrex tubes, and shaken at 22 °C for 24 h. The tubes were cracked open at 22 °C, and ca 0.2 mL of the solution was removed by syringe, taking care not to disturb the solid **1**-d_0 at the bottom of the tube. The solutions were treated with 0.1 mL of trifluoromethanesulfonic acid and analyzed for neopentane. A saturated solution of **1**-d_0 in cyclohexane at 22 °C is 0.051 M and in cyclohexane containing 0.34 M Et_3P, 0.059 M.[58]

Measurement of k_1 by ^{31}P NMR Sepctroscopy. Into each of four NMR tubes was weighed 32.8 mg (0.054 mmol) of **1**-$[P(C_2D_5)_3]_2$. The tubes were fitted with No-Air stoppers and flushed with argon, and 10-μL aliquots of $(CH_3O)_3PO$ (12.5 mg, 0.089 mmol) and 0.6-mL aliquots of C_6H_{12} were added. At t = 0 s, a 200-, 100-, 20-, or 10-μL quantity of $(C_2H_5)_3P$ was added to a tube. The No-Air stopper was sealed with wax, and a ^{31}P NMR spectrum was immediately taken. The probe temperature was regulated to 303 ± 0.5 K. Proton-decoupled spectra were recorded over intervals of 30 min until no change in peak heights was

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[58] The use of solubility measurements of this type to differentiate between associate and dissociative equilibria is discussed in: Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 5258–5270.

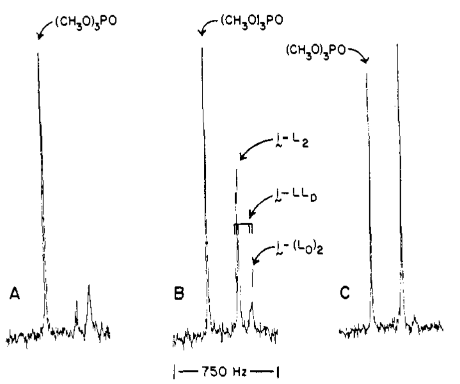

Figure 7. Representative $\{^1H\}$-^{31}P NMR spectra used to follow the conversion of 1-$[P(C_2D_5)_3]_2$ to 1-$[P(C_2H_5)_3]_2$ by exchange with added triethylphosphine.

observed. Typical spectra are shown in Figure 7. When the appearance of $(C_2H_5)_3P$-Pt was observed, the first-order rate constants obtained for 200, 100, and 20 μL of added $(C_2H_5)_3P$ were 6.3, 8.3, and 1.2 × 10^{-4} s^{-1}, respectively. For the exchange reaction with 10 μL of added $(C_2H_5)_3P$, the exchange was followed by observing the decrease of free $(C_2H_5)_3P$ and yields a first-order rate constant of 1.0 × 10^{-4} s^{-1}. With the assumption that the exchange was first-order in $(C_2H_5)_3P$, the calculated second-order rate constants would be 0.4, 0.9, 5.6, and 9.1 × 10^{-4} M^{-1} s^{-1}.

Photolyses of dineopentylmercury and 1 were carried out at ambient temperature by using cyclohexane as solvent. The progress of the photolysis of 1 was monitored by ^{31}P NMR spectroscopy. During the reaction, the resonance of 1 and free triethylphosphine disappeared and were replaced by a 1:4:1 triplet at δ +41 ($(Et_3P_3)Pt^0$, J_{Pt-P} = 4226 Hz).

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Supplementary Material Available: Table IA of mass spectral data used in analyzing isotopic compositions (3 pages). Ordering information is given on any current masthead page.

Complexation of Metal Ions by Monensin. Crystal and Molecular Structure of Hydrated and Anhydrous Crystal Forms of Sodium Monensin

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Abstract: The conformations of the sodium–monensin complex observed in anhydrous and dihydrate crystal forms are nearly identical with one another, with the previously reported Ag^+ complex, and with a complex with sodium bromide. The dihydrate crystallizes in the orthorhombic space group $P2_12_12_1$ (a = 16.387 (4) Å, b = 18.684 (4) Å, c = 12.792 (3) Å, Z = 4) and the anhydrous complex crystallizes in the monoclinic space group $P2_1$ (a = 9.218 (5) Å, b = 12.702 (1) Å, c = 16.274 (7) Å, β = 101.02 (1)°, Z = 2). The conformations of all of the metal complexes differ from that of the free acid in the carboxylic acid conformation, the heat-to-tail hydrogen bonding, and the conformation of one of the five-membered rings. Although individual torsion angle differences between uncomplexed and complexed monensin seldom exceed 15°, the positions of three of the coordinating oxygens are shifted by 1.0, 1.9, and 2.1 Å relative to the oxygens in the invariant part of the molecule. A comparison of the complexed and uncomplexed structures suggests that complexation could easily be initiated by association of a metal ion with an ether oxygen, O(7), which is near the surface of the free acid. Two other oxygen atoms, O(6) and O(4), in the invariant part of the molecule are then positioned to displace additional water of hydration from the ion. No change in the monesin conformation is necessary during this step, but a minor rearrangement of the intramolecular hydrogen bonds must take place. This rearrangement initiates a change in head-to-tail hydrogen bonding and the repositioning of the O(8), O(9), and O(11) atoms so that the remaining solvent is displaced from the metal ion completing the coordination. If the ability of monensin to complex metal ions is in part attributable to the flexibility of the five-membered C ring it may be possible to modify monensin by methyl substitutions on this ring, stabilizing a particular conformation.

Ionophores are natural or synthetic compounds that facilitate transport of ions across membranes. Comparison of the crystal structures of complexed and uncomplexed ionophores provides information concerning the flexibility of these molecules and the coordination of the complex ions. These data may provide an explanation for the ion specificity of a particular compound and the mechanism of ion capture and release.[1]

Monensin (Figure 1) is a monocarboxylic acid that has specificity for Na^+ ions.[2] The crystal structures of the silver monensin complex[3] revealed that the molecule adopts a cyclic conformation with the carboxylic oxygens [O(1) and O(2)] on one end hydrogen bonded to the hydroxyls at the other end [O(10) and O(11)]. The molecule surrounds the silver ion and provides it with irregular sixfold coordination. The crystal structure of the hydrated free acid of monensin also possesses head-to-tail hydrogen bonding, but two different hydrogen bonds link the ends of the molecule together [O(2) → O(11) and O(10) → O(4)].[4] Steinrauf has noted that the substituents on carbon atoms C(3) and C(4) are

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