cation with solvent, to form substitution product, is not the rate-limiting step.[20] The rate of bonding of the cation to solvent is indicated to be controlled in some other kind of process, such as separation of the intimate ion pair.[21]

These results call for reinterpretation of correlations with the solvent parameter, $Y_{2\text{-AdOTs}}$. As originally advocated,[4,5,16] they were predicated on the rate-limiting step in 2-adamantyl *p*-toluenesulfonate solvolysis being formation of the intimate ion pair.

As for pinacolyl benzenesulfonate, the backside of C-2 is considerably hindered;[22] accordingly S_N2 attack by the weakly nucleophilic CF_3COOH is extremely improbable, and even backside attack on the intimate ion pair is likely to be impeded. These are features shared by the 2-adamantyl system, and one might naively anticipate much internal return in the pinacolyl series. However, oxygen scrambling does not occur during solvolysis. This is compatible with either of two models recently advocated. In one, proposed on the basis of the nearly total incidence of carbon skeleton rearrangement and the high solvolytic reactivity of pinacolyl arenesulfonates in solvents of low nucleophilicity, rapid methyl shift occurs in the carbocation immediately after its formation.[23] The other, which accommodates the foregoing evidence as well as the substantial γ carbon-14 isotope effect reported by Ando and Morisaki,[24] is one of methyl shift concerted with ionization.

Our results greatly clarify the role of ion-pair return in solvolyses of *sec*-alkyl arenesulfonates. Judgments on controversial questions can now be made on the basis of straightforward fact with reduced reliance on indirect arguments and unverified hypotheses. The technique that we have employed should be attractive to other investigators.

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(20) Some caution must be observed in interpreting the solvent dependence of the minimum fraction of internal return for the 2-adamantyl ester in Table I solely in terms of solvent nucleophilicity. The experiments in CF_3COOH were conducted at a much lower temperature (25 °C) than were those in acetic acid or 80% ethanol (80 °C). One does not know to what extent the fraction of internal return depends on temperature.

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Ring Strain in Bis(triethylphosphine)–3,3-Dimethylplatinacyclobutane Is Small[1]

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Metallacycloalkanes have been identified as intermediates in a variety of metal-catalyzed reactions,[2–8] but little is known about

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Scheme I. Mechanism of Cyclometallation Reactions Generating Platinacycloalkanes (L = Et_3P; R = CH_3, CH_2CH_3, $CH_2CH_2CH_3$)
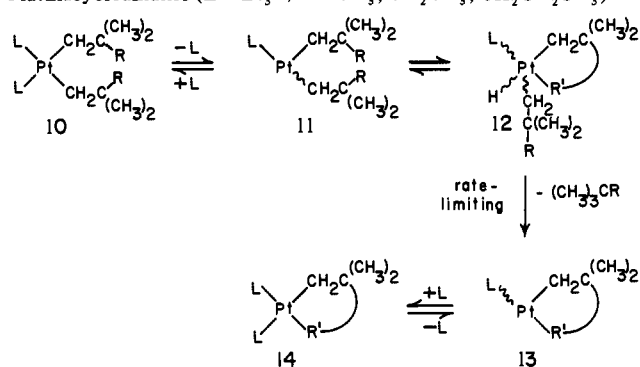
the thermodynamic or electronic characteristics of these species. We have described previously the mechanism of conversion of dineopentylbis(triethylphosphine)platinum(II) (**1**) to bis(triethylphosphine)–3,3-dimethylplatinacyclobutane (**2**) by thermal cyclometallation.[9] Here we summarize product yields and activation parameters (Table I) indicating that similar mechanisms also describe analogous reactions forming platinacyclopentanes and platinacyclohexanes and interpret these data as evidence that the platinacyclobutanes are much less strained (ring strain ≲5 kcal mol^{-1} greater than that of an analogous platinacyclopentane) than cyclobutane itself (ring strain = 26 kcal mol^{-1}).[10]

Compounds **1**, **3**, and **6** and their deuterated analogues were prepared, characterized, and decomposed thermally following techniques described previously.[9,11] Kinetics of decomposition followed rate eq 1 (L = Et_3P). The activation parameters sum-

$$-d[L_2PtR_2]/dt = k[L_2PtR_2][L]^{-1} \qquad (1)$$

marized in Table I were obtained by following the disappearance of **1**, **3**, and **6** from cyclohexane solutions containing added triethylphosphine;[12] similar numbers were obtained in the absence of added phosphine. Isotope effects are those observed or inferred[13] for deuterium substitution at the positions indicated in Table I. The similarity in products and activation parameters and the magnitudes of the kinetic isotope effects indicate that the same mechanism is followed in all of these cyclometallations.

If the reasoning described in detail for **1** → **2** is followed,[9] we propose that the rate-limiting step for each of the transformations

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(11) Kinetic studies were carried out at temperatures between 69 and 157 °C (depending on the compound) by using cyclohexane solutions originally 0.08 M in organoplatinum compound, 0.02 M in triethylphosphine, and 0.16 M in triethylphosphate as internal standard. The rate of disappearance of starting material was determined by following the change in its concentration relative to internal standard by $^{31}P\{^1H\}NMR$ and was equivalent to the rate of production of alkane monitored by gas chromatography. Metallacyclic products were identified either by comparison with independently synthesized samples or by a combination of ^1H and $^{31}P\{^1H\}NMR$ spectroscopy, elemental analysis, and chemical reactions.

(12) Reactions in the presence of added triethylphosphine were more reproducible than those in its absence.

(13) The kinetic isotope effect for **6** → **8** was determined by setting the rate of formation of **8** equal to 68% of the rate of disappearance of **6** (the relative yield of **8** from the reaction is 68%). A similar treatment of the rate of decomposition of deuterated **6** (for which the yield of **8** is 43%) yielded the rate of formation of deuterated **8**. These calculated rates were used to determine k_H/k_D. The relative yields of **7**, **8**, and **9** did not change over the course of the reaction.

Table I. Conversion of Dialkylbis(triethylphosphine)platinum(II) Complexes to Bis(triethylphosphine)–Platinacycloalkanes[a]

PtR$_2$	Platinacycloalkane, % Yield	E_a[b]	log A	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[b]	k_H/k_D[c]
1	**2,**/00[d]	49±4[d]	20±2[d]	48±4[d]	30±9[d]	3.0[d]
3	**4,**0.5[e] **5,**99.5[e]	42±2	20±1	41±2	30±5	3.2±0.1
6	**7,**23 **8,**68 **9,**9	43±2	20±2	42±2	30±9	2.8±0.2[f]

[a] Product yields, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for cyclometallations of **1**, **3**, and **6** are reported for reactions at 157, 126, and 146 °C, respectively. Yields are based on ^{31}P{^{1}H}NMR spectroscopy and refer to the undeuterated compounds. Compounds **2** and **5** were isolated in 71% and 78% yields, respectively.[11] [b] E_a and $\Delta H^{\ddagger}$ are expressed in kcal mol^{-1}, $\Delta S^{\ddagger}$ in eu. [c] Isotope effects are those observed for the deuterium substitution indicated in PtR$_2$. [d] From ref 9. [e] Estimated from the yield of the deuterated species: see the text. [f] See ref 13.

in Table I is loss of alkane by reductive elimination from an intermediate which already contains a metallacyclic ring (**12** → **13**, Scheme I).[14] The *relative* yields of metallacycles of different sizes but comparable structures formed during decomposition of a common starting material should therefore reflect in major part differences in the energies of the metallacyclic rings present in the transition states. The compounds in Table I afforded two comparable pairs: **4** and **5** and **7** and **9**. (Both require formation of metallacyclic rings by oxidative addition of methyl C–H bonds to platinum.) Decomposition of undeuterated **3** (126 °C) yields **5** as the only observed product, but decomposition of **3**-d_6 yields **5**-d_3 and **4**-d_2 in relative yields of 50:1. We estimate the relative rates of formation of undeuterated **5** and **4** by dividing the relative yield of **4**-d_2 by the observed kinetic isotope effect (3.2, Table I): this division yields $k_{3\rightarrow5}/k_{3\rightarrow4} = 160$. After accounting for the numbers of equivalent C–H bonds, the corresponding statistically corrected ratio of rate constants is $k_{3\rightarrow5}/k_{3\rightarrow4} = 320$, and corresponds to $\Delta G^{\ddagger}_{3\rightarrow4} - \Delta G^{\ddagger}_{3\rightarrow5} \simeq 4.6$ kcal mol^{-1}. Similiar comparison of statistically corrected rate constants based on the yields of products from **6** indicates that $\Delta G^{\ddagger}_{6\rightarrow7} - \Delta G^{\ddagger}_{6\rightarrow9} = -0.24$ kcal mol^{-1} and $\Delta G^{\ddagger}_{6\rightarrow7} - \Delta G^{\ddagger}_{6\rightarrow8} = 1.8$ kcal mol^{-1}.

These values of $\Delta\Delta G^{\ddagger}$ obviously do not correspond exactly to the differences in strain energies between four- and five-, and four- and six-membered platinacyclic rings. Contributions to $\Delta\Delta H^{\ddagger}$ could arise from differences in steric or electronic interactions in transition states, having nothing to do with ring strain, or differences in the extent of bond breaking or bond forming in these transition states; differences in $\Delta\Delta S^{\ddagger}$ are significant in many reactions which form rings from linear precursors.[15] Although we have no way of estimating these effects, we believe that the differences in structure characterizing the two pairs of metallacycles **4** and **5** and **7** and **9** are sufficiently small that most of the possible contributions to $\Delta\Delta G^{\ddagger}$ unrelated to metallacyclic ring strain should be small.

Although this work does not provide accurate numerical estimates of ring strain in this series of platinacyclic rings, it strongly suggests that the strain in a platinacyclobutane is much smaller than that in cyclobutane itself. This suggestion is significant in rationalizing why metallacyclobutanes seem to be more important as intermediates in organometallic reactions than cyclobutanes

are in organic reactions and explaining why isomerization of five-membered to four-membered metallacycles[4] appears to be more facile than the corresponding reactions in all-carbon systems.[16]

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Conformational Control of Reactivity and Regioselectivity in Singlet Oxygen Ene Reactions: Relationship to the Rotational Barriers of Acyclic Alkylethylenes

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A puzzling aspect of the singlet oxygen ene reaction,[1] shown below, is the "cis effect" in acyclic trisubstituted alkenes: allylic hydrogens on the disubstituted side of the alkene linkage are abstracted more readily than those on the monosubstituted side.[2–5] We wish to point out that the "cis effect" for singlet oxygen ene reactions of acyclic alkenes, as well as subtle regiochemical and

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