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

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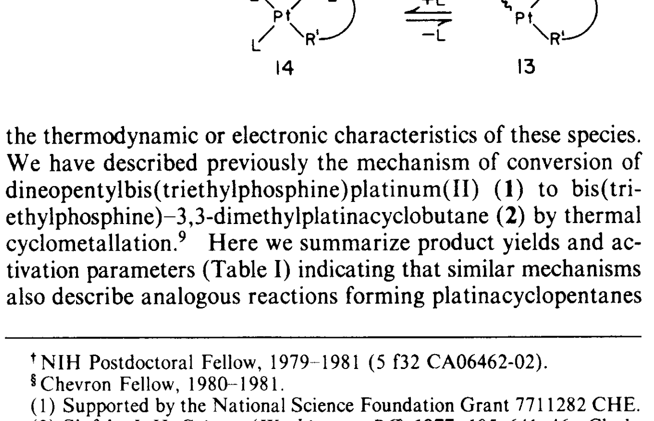
Metallacycloalkanes have been identified as intermediates in a variety of metal-catalyzed reactions,[2-8] but little is known about

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 $\lesssim 5$ 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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(8) The relative rates of exchange of hydrogen for deuterium at C–H bonds of trialkylphosphines coordinated to platinum(II) suggest that the ease of cyclometallation decreases in the order 5-membered > 6-membered > 4-membered rings. Kiffen, A. A.; Masters, C.; Raynand, L. *J. Chem. Soc., Dalton Trans.* **1975**, 853–57.

(9) Foley, P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1979**, *101*, 2732–3. Foley, P.; DiCosimo, R.; Whitesides, G. M. *Ibid.* **1980**, *102*, 6713–25.

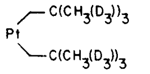
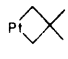
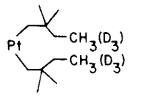
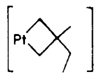
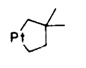
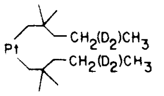
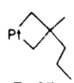
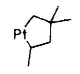
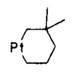
(10) Benson, S. W. "Thermochemical Kinetics"; 2nd ed.; Wiley: New York, 1976; p 273. Strain energies are (kcal mol^{-1}): C_3H_6, 27.6; C_4H_8, 26.2; C_5H_{10}, 6.3; C_6H_{12}, 0.2.

(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, *100* [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 $^{31}P\{^1H\}$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 metallacylic 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 metallacylic 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 $k_{3\to5}/k_{3\to4}$ = 160. After accounting for the numbers of equivalent C–H bonds, the corresponding statistically corrected ratio of rate constants is $k_{3\to5}/k_{3\to4}$ = 320, and correponds to $\Delta G^{\ddagger}_{3\to4} - \Delta G^{\ddagger}_{3\to5} \simeq 4.6$ kcal mol^{-1}. Similiar comparison of statistically corrected rate constants based on the yields of products from **6** indicates that $\Delta G^{\ddagger}_{6\to7} - \Delta G^{\ddagger}_{6\to9} = -0.24$ kcal mol^{-1} and $\Delta G^{\ddagger}_{6\to7} - \Delta G^{\ddagger}_{6\to8} = 1.8$ 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]

(14) The assignment of the rate-limiting step to reductive elimination (**11** → **12**) rather than oxidative addition (**10** → **11**) is based on the large value of log *A*. For comparison, log *A* = 14 for an analogous reaction involving dissociation of a phosphine [$(Et_3P)_2PtEt_2 \to Et_3P + Et_3PPtEt_2$: McCarthy, T. J.; Nuzzo, R. N.; Whitesides, G. M. *J. Am. Chem. Soc.*, in press].

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