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

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Metallacycloalkanes have been identified as intermediates in a variety of metal-catalyzed reactions, but little is known about the thermodynamic or electronic characteristics of these species. We have described previously the mechanism of conversion of dicyclopentylbis(triethylphosphine)platinum(II) (1) to bis(triethylphosphine)-3,3-dimethylplatinacyclobutane (2) by thermal cyclometallation. Here we summarize product yields and activation parameters (Table I) indicating that similar mechanisms followed rate eq 1 (L = Et_3P). The activation parameters summarized in Table I were obtained by following the disappearance of 1, 3, and 6 from cyclohexane solutions containing added triethylphosphine; similar numbers were obtained in the absence of added phosphine. Isotope effects are those observed or inferred 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 I → 2 is followed, we propose that the rate-limiting step for each of the transformations 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).

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

\[ \frac{d[L_2PtR_2]}{dt} = k[L_2PtR_2][L]^{-1} \]
Table I. Conversion of Dialkylbis(triethylphosphine)platinum(II) Complexes to Bis(triethylphosphine)-Platinacycloalkanes

<table>
<thead>
<tr>
<th>PhR2</th>
<th>Platinytcycloalkane, %Yield</th>
<th>Ea</th>
<th>log A</th>
<th>ΔHf</th>
<th>ΔSf</th>
<th>kH/kD</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>2.6</td>
<td>5.7</td>
<td>-0.5</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>3.5</td>
<td>4.5</td>
<td>0.5</td>
<td>0.7</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>4.0</td>
<td>5.0</td>
<td>0.3</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>4.5</td>
<td>5.5</td>
<td>0.3</td>
<td>0.6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

*Product yields, ΔHf, and ΔSf for cyclometallations of 1, 3, and 6 are reported for reactions at 157, 126, and 146 °C, respectively. Yields are based on 31P{1H}NMR spectroscopy and refer to the undeuterated compounds. Compounds 2 and 5 were isolated in 71% and 78% yields, respectively. b Ea and ΔHf are expressed in kcal mol⁻¹. c Estimated from the yield of the deuterated species: see the text. From ref 9. * 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). 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-d6 yields 5-d3 and 4-d2 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-d2 by the observed kinetic isotope effect (3.2, Table I): this division yields k5-d3/k4-d2 = 160. After accounting for the numbers of equivalent C–H bonds, the corresponding statistically corrected ratio of rate constants is k5-d3/k3-d4 = 320, and corresponds to ΔGf°-4-d2 = 4.6 kcal mol⁻¹. Similar comparison of statistically corrected rate constants based on the yields of products from 6 indicates that ΔGf°-6-d7 - ΔGf°-6-d4 = 0.24 kcal mol⁻¹ and ΔGf°-6-d7 - ΔGf°-6-d4 = 1.8 kcal mol⁻¹.

These values of ΔΔGf° obviously do not correspond exactly to the differences in strain energies between four- and five-, and four- and six-membered metallacyclic rings. Contributions to ΔΔHf° 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 ΔΔSf° are significant in many reactions which form rings from linear precursors. 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 ΔΔGf° 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 appears to be more facile than the corresponding reactions in all-carbon systems.