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Olefin Formation from Platinacyclobutanes

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Abstract: Deuterium-labeled cyclopropanes **6a–c** were synthesized and reacted with Zeise's dimer to give the platinacyclobutanes **7a–c**. Decomposition of these platinacyclobutanes gave deuterium-labeled 2,3-dimethylbut-1-enes **8–13**. The results indicated that the olefins were formed from what is formally a β-hydrogen abstraction followed by a reductive elimination. The results also indicated that an α-hydrogen abstraction process was not operative. Two types of β-hydrogen abstraction processes were possible and both occurred, although β-hydrogen abstraction from the ring of the platinacylobutane was favored over β-hydrogen abstraction from a methyl substituent. The dissociated pyridine did not participate in the hydrogen-abstraction process. Additionally, the rearrangement of 4 to 1 was shown not to occur by a 1,2-methyl migration which had been previously suggested as a possible rearrangement route.

Zeise's dimer[1] reacts with cyclopropanes to form platinacyclobutanes.[2,3] Phenylcyclopropane forms a platinacyclobutane which undergoes interesting rearrangement reactions[4] and has been the subject of mechanistic inquiries.[5] Conversely, the chemistry of platinacyclobutanes formed from alkyl-substituted cyclopropanes is dominated by olefin formation.[3] Olefin formation has also been reported to be a dominant pathway in the decomposition of platinacyclopentanes.[6] Both aryl- and alkyl-substituted platinacyclobutanes will give cyclopropanes upon treatment with phosphines or aqueous KCN[2,3] and there has been a rearrangement observed for one alkyl-substituted platinacyclobutane.[7] In this paper we report upon a study of olefin formation from dichlorobis(pyridine)-(1,1,2-trimethylpropane-1,3-diyl)platinum(IV) (**1**).

Results

Complex **1** was prepared according to the method of Brown[7] and was decomposed in CHCl$_3$ at 25 ± 2 °C to give 2,3-dimethylbut-1-ene as the major product (>95%). The olefin **2**
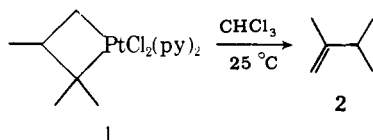
could in theory arise by at least three independent routes from **1** as illustrated in Scheme I.

The three routes all require prior dissociation of a pyridine ligand, a process which has been established in platinacyclobutane chemistry.[4,5] Olefin formation routes (b) and (c) require the well-known β-hydrogen abstraction (β-hydride elimination) reaction followed by the equally well-known reductive elimination process.[8] Route (a) requires an α-hydrogen abstraction prior to reductive elimination.[8] Whitesides found that methyl-substituted platinacyclopentanes failed to form olefins significantly faster than their unsubstituted analogues.[6]

Scheme I
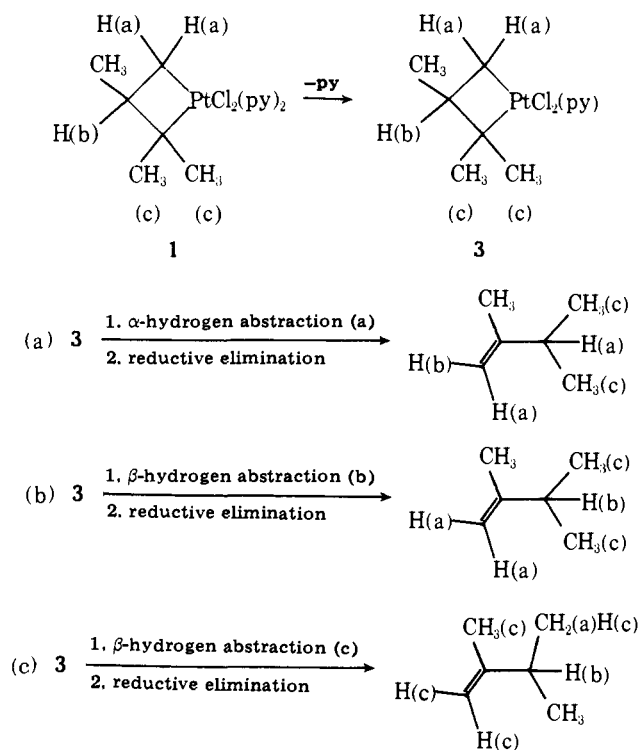
By the preparation of deuterium-labeled cyclopropanes we hoped to differentiate between the three possible modes of olefin formation and to gain some insight into reactivity differences between a ring-substituted β hydrogen vs. the β hydrogen of a methyl substituent.

Additionally, Brown has shown that **1** is the rearranged product of dichlorobis(pyridine)(1,2,2-trimethylpropane-

Scheme II

$$Me_2CHCO_2Me \xrightarrow[\text{2. CD}_3\text{COCl}]{\text{1. LiN(}i\text{-Pr)}_2} CD_3COCMe_2CO_2Me$$

5a
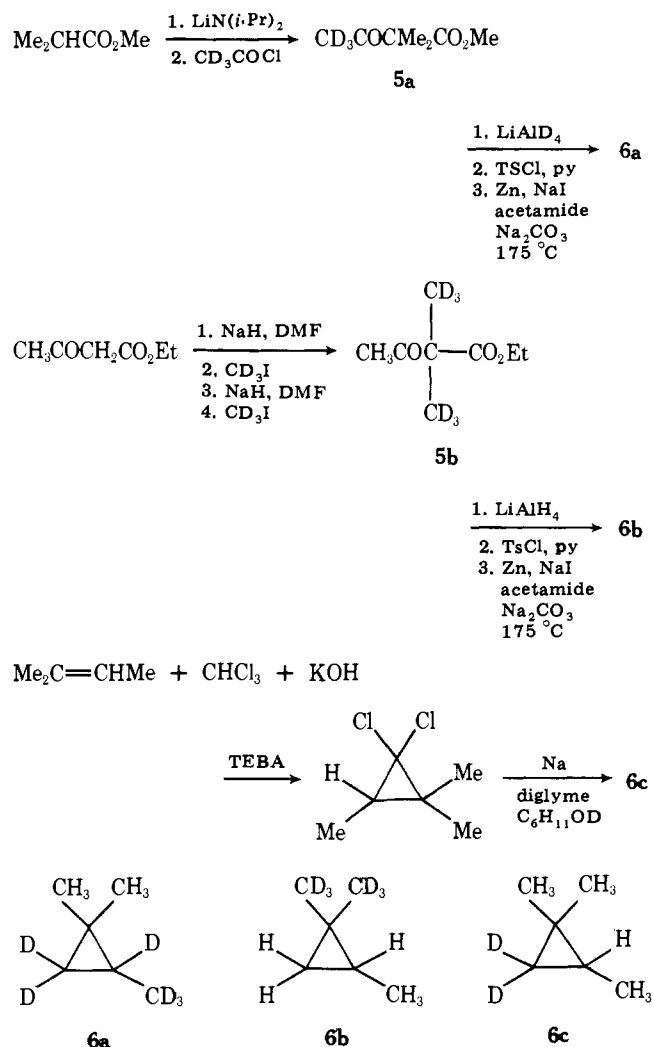
Table I. Chemical Shifts for Carbons and Protons for 2,3-Dimethylbut-1-ene[a]

proton[b]	shift,[a] ppm	carbon[b]	shift,[a] ppm
a	4.71[c]	α	151.07
b	2.35[d]	β	107.47
c	1.78[c]	γ	20.02
d	1.09[e]	δ	35.13
		ε	21.35

[a] Downfield from Me$_4$Si in CDCl$_3$. [b] The proton and carbon designations are shown in Figure 1. [c] Singlet. [d] Septuplet. [e] Doublet, J = 6.5 Hz.

Scheme III
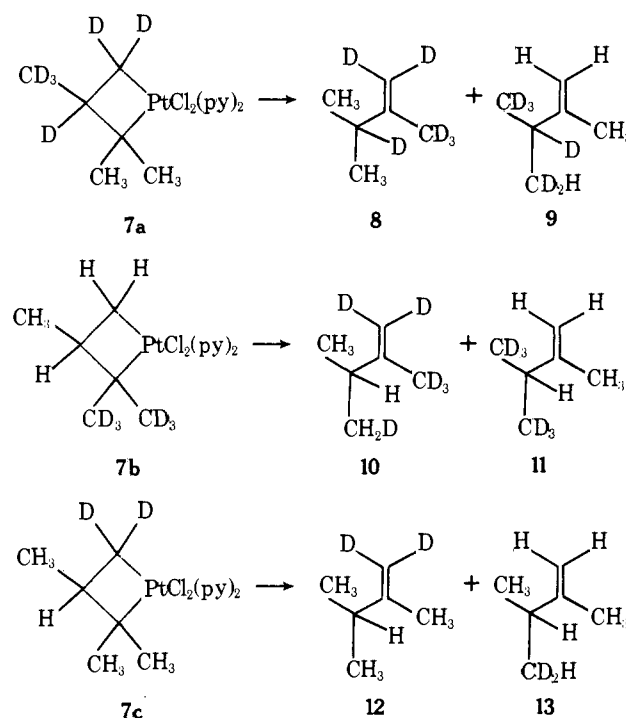
1,3-diyl)platinum(IV) (4). One of three possible routes suggested by Brown to account for this rearrangement was a 1,2-methyl shift in **4** to form **1**.[7] We also sought an answer to this hypothesis in our study.

The three deuterium-labeled compounds used in this study were prepared as shown in Scheme II. The cyclopropanes **6a–c** were independently reacted with Zeise's dimer and subsequently with pyridine to give the platinacyclobutanes **7a–c** and then decomposed in CHCl$_3$ at 25 ± 2 °C to give the olefins shown in Scheme III. The ratios of **8:9, 10:11,** and **12:11** were 1.1, 0.2, and 2.2. These ratios were determined by ^{1}H NMR and the structures were assigned by a combination of ^{1}H NMR and ^{13}C NMR (vide infra).

The analysis and ratio determination of the olefinic products were aided by ^{13}C NMR and ^{1}H NMR. For this purpose, the unlabeled olefin **2** served as a standard for comparison and its peaks are shown in Table I. The various carbons and protons are designated as shown in Figure 1.

In the olefin set of **8** and **9**, the ^{13}C NMR showed a triplet centered at 34.41 ppm in place of the peak at 35.13 ppm consistent with complete deuterium substitution at carbon δ (see Figure 1). The carbon α was now represented by a singlet at 107.5 ppm and a pentuplet centered at 106.94 ppm consistent with a mixture of **8** and **9**. Both of the peaks at 21.35 and 20.02 ppm have clusters of smaller peaks at their base line which overlap with one another and make the exact assignment of multiplicity difficult. One would expect two different septuplets and one pentuplet in addition to the two singlets for **8** and **9**.

The ^{1}H NMR confirms the complete deuteration at carbon δ as the signal at 2.35 ppm was no longer present. The height of the integrated area for the vinylic proton (H$_a$) was 28 mm while the height of the integrated area for the methyl protons (H$_d$) was 110 mm. In this particular set of olefins we do not have a proton which is common to both **8** and **9** as we do for the olefin sets of **10** and **11** and of **12** and **13**. Therefore, we consider this ratio to be in greater error than the ones determined for the other two sets of olefins. Nonetheless, the ratio of **8** to **9** can be determined from the above integrals by the following procedure. The vinyl protons (H$_a$) are due only to **9** and correspond to 14 mm per proton. The methyl protons (H$_d$) are due to both **8** and **9**. The olefin **9**, however, has one proton and five deuteriums substituted on the carbon ε and, therefore, 14 mm (the value for one proton—see above) was substracted from 110 mm to give a value of 96 mm for the protons due to **8**. Compound **8** has six protons and this corresponds to a height for the integrated area of 16 mm per proton. Taking these values per proton we arrived at the ratio of **8:9** as 1.1.

In the olefin set of **10** and **11**, the ^{13}C NMR gave a single peak at 35.10 ppm indicating the substitution of only a proton at the carbon δ. The ^{1}H NMR showed a peak centered at 2.35 ppm in agreement with the ^{13}C NMR results. The methyl peaks were as complex as described for **8** and **9** above. The carbon α was also as described for **8** and **9**. In **10** and **11** the allylic proton (H$_c$) is common to both **10** and **11** (i.e., both **10** and **11** have a proton only substituted at carbon δ). The height

of the integrated areas for H_a, H_b, H_c, and H_d were 58, 89, 35, and 30 mm, respectively. Using the height of the integrated area for H_c as representing 100%, we found that H_a and H_b were 83–84% of the theoretical area if only **11** was present and H_d was only 17% of the theoretical area.[9] This corresponds to the ratio of **10:11** as 0.2.

In the olefin set of **12** and **13**, the ^{13}C NMR looks similar to the other two sets for the vinylic carbon α. However, we now have clean singlets for carbons γ and δ and observed a singlet and a pentuplet for carbon ϵ consistent with the structural assignments of **12** and **13**. The ^1H NMR gave peaks for all of the protons H_a–H_d. The proton H_c is again common to both **12** and **13** (as is H_b) and its integrated area is taken as 100%. The heights of the integrated areas for H_a, H_b, H_c, and H_d were 10.5, 52, 17, and 92 mm, respectively. Using H_c as the standard, we found that H_a was 31% of the theoretical area. The height of the integrated area per proton for **13** is ca. 5.3 mm. This value, times four (for the 4-H_d protons due to **13**), was then subtracted from the integrated area of 92 mm for total H_d protons to arrive at a value of 71 mm for the 6-H_d protons due to **12**. This value was 69% of the theoretical area. In turn, this corresponds to the ratio of **12:13** as 2.2.

Discussion

Olefins **8**, **11**, and **12** are the major olefins in each set and can be formally derived from process (b) in Scheme I. The minor olefins **9**, **10**, and **13** can be formally derived from process (c) in Scheme I. The olefins formed from **7a** and **7b** would not distinguish between an α-hydrogen abstraction and a β-hydrogen abstraction process. However, platinacycle **7c** does distinguish between these two possibilities. An olefin formed via an α-hydrogen abstraction route from **7c** would have the structure **14**. The olefin **14** is distinguishable from **12** and **13**

14
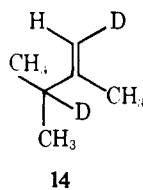
in the following ways. First, **14** would give a triplet for the carbons α and δ in the ^{13}C NMR whereas only a singlet and pentuplet were observed for carbon α and only a singlet was observed for carbon δ. Second, the methyl carbons ϵ would be a broad singlet[12] in the ^1H NMR whereas a doublet was observed indicating the presence of a proton instead of a deuterium at carbon δ. Finally, it is apparent that a mixture of **12–14** would also be observable from both the ^1H NMR and ^{13}C NMR.

In order to determine if the dissociated pyridine played a role in the abstraction process, we decomposed the platinacycle **7a** in the presence of **1** (1:1). Mass spectral analysis of the olefins recovered in this experiment revealed the presence of only 2,3-dimethylbut-1-ene-d_0 and 2,3-dimethylbut-1-ene-d_6, indicating no crossover of deuterium. As indicated earlier in the text, pyridine does play a role in that it must first dissociate from the platinacycle in order that the processes in Scheme I can take place and this dissociation has been previously established. The above experiment would seem to rule out, however, any intermolecular participation by pyridine.

Furthermore, the olefins obtained from **7b** clearly indicate that the rearrangement of **4** to **1** does not occur by a 1,2-methyl migration. Had such a migration occurred then the olefins formed would have been **15** and **16** instead of the observed **10** and **11**. The olefins **10** and **11** can be distinguished from the olefins **15** and **16** in the following manner. The ^{13}C NMR, as previously described, confirmed the presence of a mixture of olefins. However, we would not be able to distinguish between
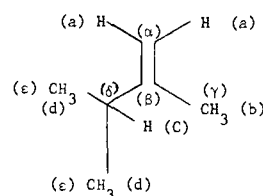
Figure 1. Designation of protons (Roman) and carbons (Greek) for 2,3-dimethylbut-1-ene.

15 **16**
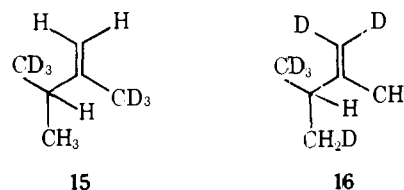
a mixture of **10** and **11** vs. one of **15** and **16** by the ^{13}C NMR. The key difference between the two sets of olefins rests upon the observation that in the olefin set of **10** and **11** the carbons α and γ always contain the same type of hydrogen isotope, i.e., both positions are substituted with deuteriums or both are substituted with protons. In the olefins set of **15** and **16** the opposite case exists, i.e., one of the carbons is substituted with protons while the other is substituted with deuteriums. Thus, if the olefins obtained were **10** and **11**, then the height of the integrated area for H_a to H_b must be 2:3, whereas, if the olefins obtained were **15** and **16**, then the height of the integrated area for H_a to H_b would be the same as the ratio of **15** to **16**. The heights of the integrated areas of H_a and H_b were 58 and 89 mm, respectively. This corresponds to a 2:3 ratio in agreement with the structural assignment of **10** and **11** instead of **15** and **16**. In the case where the ratio of **15** to **16** happened to be 2:3 and, therefore, would give a correct integration for H_a vs. H_b, we can calculate that the height of the integrated area for H_d must then be 174 mm.[14] In fact, the value is only 30 mm, which is, again, consistent with the structural assignment of **10** and **11** and not with **15** and **16**.

The results indicate that the 2,3-dimethylbut-1-ene obtained from **1** occurs by what is formally β-hydrogen abstraction process followed by a reductive elimination reaction. Protons may be abstracted either from the ring of the metallacycle or from substituents as long as they are attached to carbons which are β to the platinum and pyridine appears to play no role in this process other than its initial dissociation from the platinacycle. There is a preference to abstract a ring proton over a proton from a methyl substituent in **1**.[15] The rearrangement of **4** to **1** does not occur via a 1,2-methyl migration.

Experimental Section

The ^{13}C NMR spectra were recorded on a Varian XL-100 spectrometer and the ^1H NMR spectra were recorded on either a Varian T-60 or Varian XL-100 spectrometer. All of the NMR spectra are reported relative to Me$_4$Si using CDCl$_3$ as a solvent. Melting points and boiling points are uncorrected. All of the compounds synthesized in this study are known in their unlabeled form. The preparation of all labeled compounds was first performed on nonlabeled materials and identified by spectroscopic comparison to authentic samples. The position of the deuteriums was determined by comparison with the unlabeled compound.

Methyl 2,2-Dimethyl-3-oxobutanoate-4,4,4-d_3 (5a). To 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel were added 500 mL of anhydrous THF and 50.5 g (0.5 mol) of diisopropylamine. The flask was cooled to −78 °C and 210 mL (0.5 mol) of 2.4 M n-butyllithium was added. After the mixture was stirred at −78 °C for 2 h, 51 g (0.5 mol) of methyl isobutyrate was added over a period of 2 h. After the addition was completed, the reaction mixture was stirred for 0.5 h and then 36 mL (0.5 mol) of acetyl-d_3 chloride (Aldrich) was added over a period of 1.5 h. Then the mixture was allowed to warm to room

temperature and was stirred for 3 h, after which time 125 mL of 6 N HCl and 200 mL of H$_2$O were added to the reaction mixture. The organic layer was separated, washed four times with 100-mL portions of saturated sodium bicarbonate, dried over anhydrous sodium sulfate, filtered, and evaporated in vacuo. The residue was distilled, giving 29.2 g (41%) of **5a**: bp 90–93 °C (30 mmHg); ^{1}H NMR (CDCl$_3$) δ 3.6 (s, 3 H) and 1.3 (s, 6 H).

2,2-Dimethyl-1,3-butanediol-*1,1,3,4,4,4-d$_6$*. To a 1000-mL, three-necked, round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and addition funnel were added 500 mL of anhydrous ether and 9.0 g (0.2 mol) of lithium aluminum deuteride (Stohler Isotopes). To this stirred mixture was added a solution of 33.5 g (0.23 mol) of **5a** in 250 mL of anhydrous ether. The solution was added at a rate which maintained reflux. After the addition was completed, the reaction mixture was refluxed for 3 h. The reaction mixture was then cooled and worked up by adding dropwise amounts of the following reagents: 9 mL of H$_2$O, then 9 mL of 15% aqueous NaOH, and then 12 mL of H$_2$O. This gave a precipitate which was removed by filtration. The filtrate was washed once with 200 mL of H$_2$O, the layers were separated, and the organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The residue was distilled, giving 17.9 g (63%) of the product: bp 78–79 °C (0.3 mmHg); ^{1}H NMR (CDCl$_3$) δ 4.11 (br, 2 H), and 0.82 (s, 6 H).

2,2-Dimethyl-1,3-butanediol-*1,1,3,4,4,4-d$_6$* Dimesylate. To a 1000-mL Erlenmeyer flask, cooled to 0 °C, were added 300 mL of dry pyridine, 32.7 g (0.28 mol) of methanesulfonyl chloride, and 16.8 g (0.14 mol) of the above diol. The Erlenmeyer flask was stoppered and refrigerated for 3 days. The resultant solid was removed by filtration and the filtrate was poured into 1500 mL of ice water. The aqueous solution was extracted with two 450-mL portions of chloroform. The chloroform extract was then washed with eight 150-mL portions of 5% aqueous potassium bisulfate and once with 150 mL of water. The chloroform solution was dried over anhydrous sodium sulfate and then concentrated in vacuo. The resultant oil was taken up in 12 mL of warm methanol and then cooled, whereupon crystallization took place. Filtration of crystals gave 36.1 g (95%) of the product which was used without further purification, mp 68–69 °C.

1,1-Dimethyl-2-methyl-*d$_3$*-cyclopropane-*2,3,3-d$_3$* (6a). To a mechanically stirred suspension of 111 g of zinc dust, 21 g of sodium iodide, 42 g of sodium carbonate, and 277 g of acetamide in a 500-mL, three-necked, round-bottomed flask maintained at 170–175 °C was added, portionwise, 32.1 g (0.12 mol) of the above dimesylate from a 100-mL Erlenmeyer which was connected by means of Gooch tubing to the round-bottomed flask. The product was allowed to distill out of the reaction into a trap which had been precooled to −78 °C. After addition of the dimesylate was completed, the suspension in the flask was thoroughly purged with nitrogen for 15 min to expel any residual amounts of the product. The material in the trap was then microdistilled, giving 1.6 g (16%) of **6a**: bp 55–57 °C; NMR (CDCl$_3$) δ 1.00 (s, 6 H).

Ethyl 2,2-Dimethyl-*d$_3$*-3-oxobutanoate (5b). This compound was prepared in 49% yield by the method of Marshall and Cannon[10] from ethyl acetoacetate and methyl-*d$_3$* iodide (Aldrich).

2,2-Dimethyl-*d$_3$*-1,3-butanediol. This compound was prepared in 85% yield from **5b** and LiAlH$_4$ in the same manner as described for the reaction of **5a** with LiAlD$_4$ except that a 100% excess (0.4 mol) of LiAlH$_4$ was employed.

2,2-Dimethyl-*d$_3$*-1,3-butanediol Dimesylate. This compound was prepared in 94% yield from the above diol and methanesulfonyl chloride in the same manner as described for the previous dimesylate.

1,1-Dimethyl-*d$_3$*-2-methylcyclopropane (6b). This compound was prepared in 21% yield from the above dimesylate by the same procedure used to prepare **6a**: NMR (CDCl$_3$) δ 1.10 (s, 3 H), 0.30–1.00 (br, 2 H), and −0.05 (br, 1 H).

1,1-Dichloro-2,2,3-trimethylcyclopropane. To a solution containing 21.2 g (0.3 mol) of 2-methyl-2-butene, 0.6 g of benzyltriethylammonium bromide, and 60 mL of chloroform was added, under N$_2$, 120 mL of 50% aqueous NaOH over a period of 4 h. After the addition was completed, the reaction mixture was stirred at 50 °C for 1 h. The reaction mixture was then cooled, diluted with 150 mL of H$_2$O, acidified

with 3 N HCl, and extracted with three 150-mL portions of ether. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and then concentrated in vacuo. The residue was distilled, giving 31.4 g (68%) of the product: bp 45–46 °C (30 mmHg); $n^{24}$$_D$ 1.4557 [lit.[11] 64.3–64.7 °C (47 mmHg); $n^{20}$$_D$ 1.4577]; NMR (CDCl$_3$) δ 1.20 (3 H, s) and 1.08 (7 H, s).

1,1,2-Trimethylcyclopropane-*3,3-d$_2$* (6c). To a mechanically stirred suspension of 80 mL of anhydrous diglyme and 17.2 g of finely divided sodium metal was added, dropwise, a solution composed of 28.5 g (0.18 mol) of 1,1-dichloro-2,2,3-trimethylcyclopropane, 37.6 g (0.37 mol) of cyclohexanol-*O-d*, and 3 mL of D$_2$O. The reaction was exothermic and the mixture needed to be cooled intermittently in order to maintain a reaction temperature below 120 °C. Under these conditions, the product distilled out of the reaction into a trap which had been precooled to −78 °C. After the addition had been completed, the reaction mixture was thoroughly purged with N$_2$. The material in the trap was distilled, giving 3.6 g (22%) of **6c**: bp 55–57 °C; NMR (CDCl$_3$) δ 1.02 (9 H, s) and 0.32–0.70 (1 H, br).

Dichlorobis(pyridine)(1,1-dimethyl-2-methyl-*d$_3$*-propane-*2,3,3-d$_3$*-1,3-diyl)platinum(IV) (7a). This compound was prepared from **6a**, Zeise's dimer, and pyridine according to the procedure of Cushman and Brown.[7]

Dichlorobis(pyridine)(1,1-dimethyl-*d$_3$*-2-methylpropane-1,3-diyl)platinum(IV)(7b). This compound was prepared from **6b**, Zeise's dimer, and pyridine according to the procedure of Cushman and Brown.[7]

Dichlorobis(pyridine)(1,1,2-trimethylpropane-*3,3-d$_2$*-1,3-diyl)platinum(IV) (7c). This compound was prepared from **6c**, Zeise's dimer, and pyridine according to the procedure of Cushman and Brown.[7]

Decomposition of Platinacycles 7a–c. These compounds were decomposed in CDCl$_3$ at 25 ± 2 °C according to the procedure of Cushman and Brown.[7] The solutions were analyzed directly by NMR as described in the text for the olefins **8–13**.

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(8) There are many examples of α- and β-hydrogen abstraction as well as reductive eliminations. An excellent review of these processes for σ-alkyl transition metal complexes can be found in the following paper: Schrock, R. R.; Parshall, G. W. *Chem. Rev.*, **1976**, *76*, 243.
(9) For example, the area of H$_a$ in **11** is due to two protons, so one has 58 divided by 2 and obtains 29 mm per proton. However, the theoretical amount is 35 mm and 29 mm is ca. 83% of this theoretical amount. Similar calculations were done for the other protons.
(10) Marshall, F. J.; Cannon, W. N. *J. Org. Chem.* **1956**, *21*, 245.
(11) von E. Doering, W.; Henderson, W. A. *J. Am. Chem. Soc.* **1958**, *80*, 5274.
(12) The predicted^{13} $J_{H,D}$ would be on the order of 1 Hz based upon a $J_{H,H}$ of 6.5 Hz and would be expected to exhibit the usual broadening making this coupling barely resolvable.
(13) $J_{H,H} = J_{H,D} \times 6.514$. See: Jackman, L. M.; Sternhell, S. "Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed.; Pergamon Press: Oxford, 1969; p 142.
(14) This value was calculated in the following manner. The reported value for H$_a$ was 58 mm or 29 mm per proton. There are three H$_d$ protons in **17** which would correspond to a height for the integrated area of 87 mm. The value per proton for **18** would be 43.5 mm (20 × 1.5) and there are two H$_d$ protons in **18** for a value of 87 mm. The sum of these is 174 mm.
(15) Alternatively, the results could indicate a preference for a tertiary over a primary proton. Unfortunately, these two factors are experimentally difficult to separate as the appropriate compounds needed to test such an hypothesis give rise to other reaction pathways and will be reported on later.