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TRANSFORMATIONS OF CYCLOPROPANE IN RIGID HYDROCARBON SYSTEMS USING PLATINUM(II)

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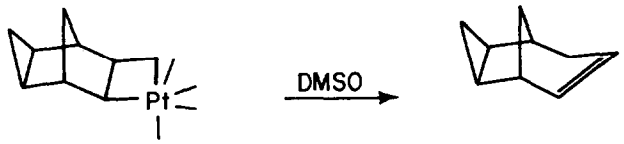
Summary

Using the cyclopropane adducts of the norbornyl system, platinacyclobutane complexes were prepared. In this article, the reactions of these platinum(IV) complexes with heat, CH_2N_2 and DMSO are discussed. In each case, a unique olefinic product has been produced. In another reaction, the platinacyclobutane of phenylcyclopropane is treated with CH_2N_2 to produce styrene.

Introduction

It is clear from the literature that cyclopropanations of olefins can be effected and that transition metals can be used to convert these to new compounds. Many such transformations involve the reaction between the organic functionality and a transition metal to generate a desired organic product in which the organometallic intermediates are often either too unstable or not a desired product. With platinum(II) and cyclopropane derivatives, however, the intermediate platinacyclobutanes have been shown to be quite stable. This stability represents a very nice opportunity to explore both new reaction routes of synthetic utility and the mechanistic features of cyclopropane transformations in general. To date, most of the reported reactions of platinum(II) with cyclopropane and subsequent transformations of the platinacyclobutanes have been conducted with simple alkyl- or aryl-cyclopropane derivatives [1]. One exception was reported by Johnson [2] in 1980 and is shown below:



Our goal has been to investigate the reactions of platinacyclobutanes which would provide routes to new and novel organic compounds and details on their mechanistic

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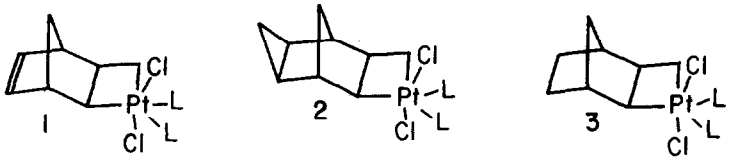
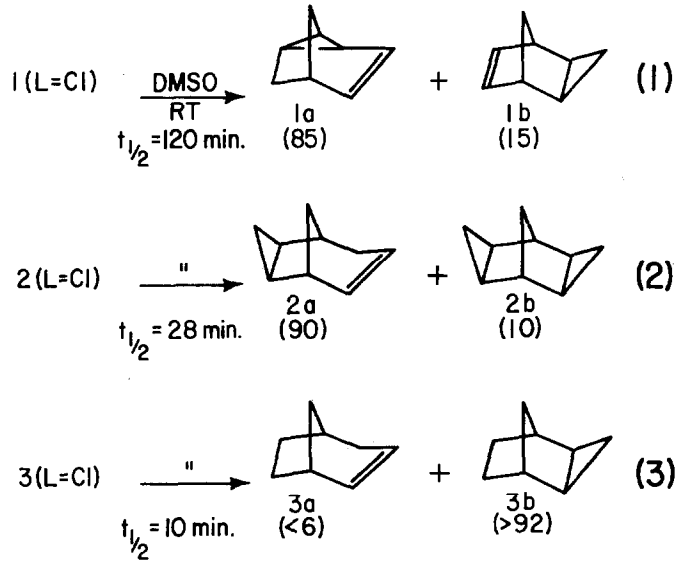
sequences. Since we wanted to study substrates which were highly reactive and sensitive to cationic intermediates, norbornyl type systems were selected for investigation. In this article, we wish to report the reactions of the platinacyclobutanes **1**, **2**, and **3** with (a) DMSO in $CDCl_3$, (b) heating in $CDCl_3$ and (c) CH_2N_2 [3].



L = Cl, Pyridine (Py) or DMSO

Results and discussion

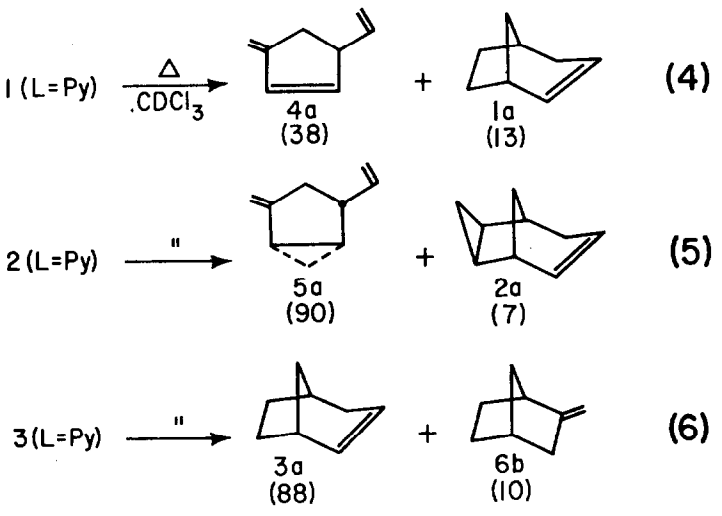
Dimethylsulfoxide. As stated earlier, Johnson had shown that complex **2** reacted very efficiently. Since this represents a new and significant methodology for ring homologation, it was decided to investigate it in analogous systems. The results shown in eq. 1, 2 and 3 clearly show that the reaction is reasonable for substrates **1** and **2**. While there is competition from a reductive elimination pathway to form the original cyclopropane, it is less severe in the first two cases than in the third reaction where it is the major pathway. Structural assignments for the reaction products were garnered from comparison with those reported in the literature [3,4]. An intermediate in these reactions that is easily discerned by NMR spectroscopy, is **1** or **2** in which L = DMSO.



While the mechanisms of these reactions are presently being investigated, it is reasonable to suggest that the first two reactions result from an intermediate in which the platinum has rearranged to an *endo* position. Such a species would derive stabilization from the transannular olefin and cyclopropane functionalities. For substrate **1**, this is similar to results published earlier by Katz using rhodium(I) [4].

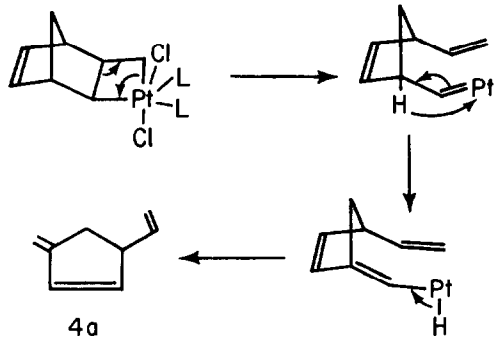
In light of this reasoning, the results of reaction 3 are reasonable since an *endo* platinum intermediate would derive no transannular stabilization. Efforts to optimize the yields of these reactions are pending further mechanistic study.

Heating in $CDCl_3$. These results were prompted by the idea that platinacyclobutanes were thought to be too stable to react. Thus, we initiated a study on the thermal stability of these complexes with the results shown in eq. 4, 5, and 6. Compounds **4a** and **5a** were assigned structures from the results of ^1H and ^{13}C NMR spectroscopy.



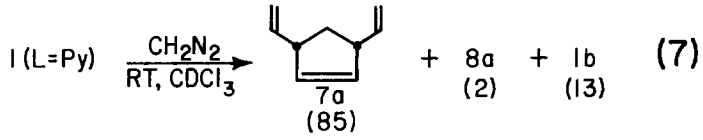
Again, this is a very reasonable way of converting complex **2** to a five-membered ring diene, but the conditions are too harsh for the relatively unstable triene from substrate **1**. It is interesting to note that this method is now reasonable for making the ring homologated product from **3** which the other two substrates gave on treatment with DMSO.

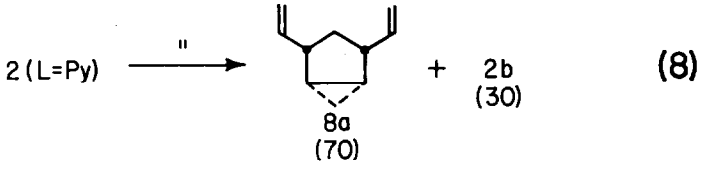
One proposed pathway for the formation of compounds **4a** and **5a** is that in which the platinacyclobutane moiety cleaves to form the metallocarbene olefin complex as shown in Scheme 1.

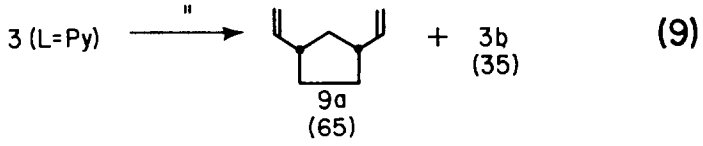


SCHEME 1

Reactions with diazomethane. The fact that platinacyclopentanes and other higher homologs are difficult to make prompted us to investigate means of expanding platinacyclobutane rings. To this end, our first probe was with diazomethane. It was anticipated that either the entire diazo system or the CH_2 would coordinate to the platinum with subsequently insertion into the platinacyclobutane ring. Further reaction with CH_2N_2 would, perhaps, expand the ring further. While several various sized rings might be generated, it was our hope that conditions might be arranged to generate one ring size as the major product. The surprising results are shown as eq. 7, 8, and 9.





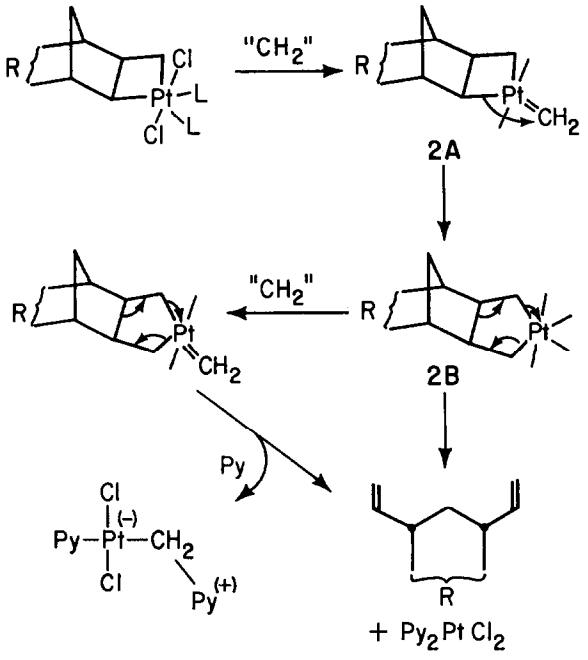


It is obvious from these results that the original goal of preparing metallocyclic rings by this procedure is not reasonable. However, the types and stereochemistry of products formed make the reaction even more interesting. Reaction conditions are being studied to improve the reaction yield and specificity. Structural evidence for these compounds was obtained from ^1H and ^{13}C NMR spectroscopy and mass spectrometry (see experimental section). The key features in structuring all three compounds are the terminal vinyl moiety and the symmetry.

While it appears that the original ring expansion idea was wrong, a reasonable postulate for the reaction pathway in these reactions does in fact involve a platinacyclopentane ring as shown in Scheme 2.

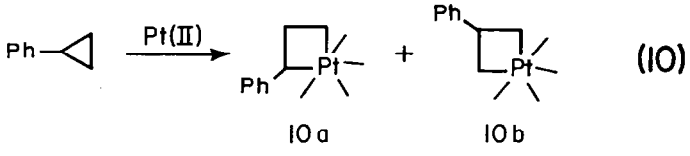
The viability for this scheme is bolstered by the fact that platinacyclopentane complexes are known to decompose to diolefins [5] and that dipyridineplatinum(II) dichloride was isolated. However, the isolation and characterization of another platinum complex, of $PyPtCl_2CH_2Py$ from this reaction suggests that a pathway involving the reaction of the platinacyclopentane intermediate with a second mole of diazomethane may also be occurring as shown in Scheme 2 [6]. If the overall scheme is correct, it is required that the symmetrical intermediate **2B** be formed rather than the unsymmetrical isomer. The reason is that in the latter a simple norbornene derivative and ethylene would have been obtained rather than the symmetrical dienes that are observed.

To further test the generality of this type of reaction, phenylcyclopropane was chosen. Platinum(II) reacts with phenylcyclopropane to generate two platinacyc-



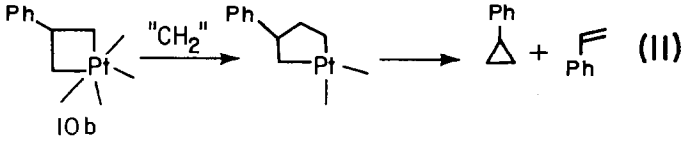
SCHEME 2

lobutane complexes as shown in eq. 10 [1].



(10)

On reaction of the mixture of **10a** and **10b** with CH_2N_2, styrene and phenylcyclopropane were generated as shown in eq. 11 for isomer **10b**. While one obtains more cyclopropane than styrene at room temperature, at 0°C, one obtains a 5 fold excess of styrene.



(11)

In this case it does not matter which platinacyclobutane isomer one starts with or which platinacyclopentane is generated since one will always obtain styrene and ethylene. The results therefore corroborate the earlier findings that diazomethane reacts very nicely with platinacyclobutanes to add one carbon atom and to form diolefin products.

Conclusion

Although the yields and conditions for the reaction of platinacyclobutanes with DMSO, heat in $CDCl_3$ and diazomethane have not been optimized, there is reason

to expect that these reactions can be developed and used to facilitate carbon–carbon bond formation. With DMSO, one obtains a ring homologated product. This transformation may appear to be trivial, but it is not if one considers carrying out the same transformation with typical organic reagents.

In the reactions with heat in chloroform or CH_2N_2, one, in principle, has the option to prepare α–ω dienes with either one or two carbons added to the original olefin. Finally, in the reactions with CH_2N_2, the product is exclusively a *cis*-1,3-diene.

Experimental

General. All solvents were reagent grade and used as such. NMR spectra were obtained on a Bruker WM-250 spectrometer and mass spectra were acquired from VG/MM16F and VG/7070E spectrometers. Analytical data were obtained by accurate mass measurements using the VG/7070E spectrometer or from Galbraith laboratories. Preparative chromatography separations used apiezon L on Chromasorb W-NAW.

Preparation of platinacyclobutane complexes 1, 2 and 3. The cyclopropane adducts were prepared from the appropriate norbornyl derivative using diazomethane (Diazald) and palladium acetate [7]. Subsequent reaction of the cyclopropane derivative with Zeise's dimer in ethyl ether at room temperature gave quantitative yields of the tetrameric IPC (initially precipitated complex) for complexes **1** and **2** [1,3]. For complex **3** it was necessary to reflux the ether solution for 5 h to achieve complete reactivity. On treatment of the IPC of **1**, **2** or **3** with pyridine, the monomeric dipyridinebis(dichloroplatinacyclobutane) complexes were prepared. They were purified by precipitation out of chloroform with pentane followed by repeated trituration in pentane. The final product is obtained by filtration and drying in vacuo.

Reaction of the IPC (initially precipitated complex) of 1, 2, or 3 with DMSO-d_6. To 0.6 ml of DMSO-d_6 was added 23 mg of **1**, **2** or **3** (L = Cl). The resulting yellow solution was chracterized by NMR spectroscopy as **1**, **2**, and **3** in which L = DMSO-d_6. On standing at room temperature the DMSO complexes decomposed to **1a** ($t_{1/2}$ 120 min), **2a** ($t_{1/2}$ 28 min) and **3a** ($t_{1/2}$ 10 min). The percent yields of total products were 92% for **1**, 95% for **2** and 83% for **3** with the product ratios given in eq. 1, 2 and 3. NMR data for **1a** and **2a** were identical with that previously reported [3,8]. For compound **3a** the ^1H NMR data ($CDCl_3$) are 2.3 (m, 2H); 5.35 (m, 1H); 5.8 (m, 1H); 1.2–1.9 (m, 8H) ppm. Selected mass spectral data for **3a** are *m/e* 108 (M^+, 27); 93(20); 80(39); 79(100); 67(37), 66(57).

Thermal decomposition of 1, 2 and 3 (L ≡ pridine) in $CDCl_3$. A solution of 450 mg of **2** (L = Py) in 10 ml of $CDCl_3$ was placed in a flask equipped with a reflux condenser and an anhydrous $CaSO_4$ drying tube and stirred at reflux for 30 h. During the refluxing period the yellow solid Py_2PtCl_2 precipitated out. On cooling and filtration the solution analyzed, by NMR spectroscopy, to be 90% **5a**, 7% **2a** and 3% **2** (L = py). ^{13}C NMR ($CDCl_3$): 152.1(s) 143(d), 112.7(t), 104.1(t), 42.9(d), 34.6(t), 25.5(d), 23.9(d), 10.8(t) ppm. Anal. Found: C, 89.74; H, 10.17. C_9H_{12} calcd.: C, 89.94; H, 10.06%.

In a similar fashion complex **1** (14 h) and **3** (8 h) were thermally decomposed. For **1** the overall loss of starting material was 80% but the product mixture is composed

of several components. Compound **4a** represents 38% of the total mixture. ^{13}C NMR data for **4a**: ($CDCl_3$) 154.1(s), 141.7(d), 141.8(d), 134.9(d), 113.8(dd), 103.3(t), 49.2(d) and 36.6(t) ppm. Compound **4a** is quite unstable and decomposed during the NMR procedure.

For complex **3**, 90% of the starting material decomposed in 8 h to give compounds **3a** and **6b** in a ratio of 9 to 1. The spectral data for **3a** and **6b** were in agreement with that reported in the literature [9].

Reaction of platinacyclobutane complexes 1, 2 and 3 (L ≡ pyridine) with diazomethane. To a solution of **1** (0.5 g, 0.95 mmol) in 5 ml of $CDCl_3$ was bubbled CH_2N_2 from a 3 fold excess of diazald (0.59 g, 2.76 mmol). The addition was completed in 15 min with an additional 15 min given for stirring. Subsequently, the volatile portion was separated by flash distillation and the individual components isolated via preparative chromatography. The overall yield of 82% was composed of compounds **7a**, **8a** and **1b** in a ratio of 1.0/0.2/0.15, respectively. This analysis was garnered from ^1H NMR data on the mixture using the allylic protons for **7a** (3.30 ppm), the cyclopropyl proton (0.12 ppm) for **8a** and olefinic protons (6.38 ppm) for **1b** [3,8]. After separation via GC the individual components were analyzed by NMR and mass spectroscopy. The results are listed below.

7a: ^1H NMR: 5.77(2H,dq), 5.54(2H,s), 4.97(2H, bd), 4.92(2H, bd), 4.92(2H,bd), 3.30(2H, q), 2.33(1H, dt), 1.31(1H, dt) ppm; ^{13}C NMR: 142.5(d), 134.4(d), 113.3(t), 49.8(D), 37.8(t) ppm; MS: *m/e* 120(8.5), 106(40), 105(40), 91(85), 78(100), 66(27).

8a: ^1H NMR: 5.92(2H, dt), 5.0(2H, dm), 4.86(2H, dm), 2.65(2H, bt), 1.73(1H,ddd), 1.38(1H, d), 1.28(2H, dd), 0.47(1H, ddd), 0.12(1H, ddd) ppm; MS: *m/e* 134(6), 120(30), 105(100), 93(58), 91(51), 79(82), 77(52), 67(39); M^+ (Calcd) 134.1095, M^+ (Obsd) 134.1085.

In an analogous procedure, complex **2** was treated with CH_2N_2. The overall yield was 75% with products **8a** and **2b** being formed in a ratio of 1/0.29. ^1H data for **8a** are reported above.

For complex **3** there was 48% unreacted platinacyclobutane. Of that which reacted, compounds **9a** and **3b** were formed in a ratio of 1/0.35. Compounds **9a** and **3b** [3,8] were isolated by flash distillation and analyzed by NMR and mass spectroscopy. NMR and MS data for compound **9a** are: ^1H NMR: 5.78(2H, dq), 4.96(2H, bd), 4.85(2H, bd), 2.55(2H, m), 1.78(1H, dd), 1.45(2H, m), 1.32(2H, m), 1.27(1H, m) ppm; ^{13}C NMR: 143.4(d), 112.4(t), 44.2(d) 31.6(t), 29.7(t) ppm; MS: *m/e* 122(41), 110(30), 109(77), 94(100), 78(82), 67(41), 50(30). M^+ (calcd) 122.1096, M^+ (obsd) 122.1104.

Isolation and characterization of $PyPtCl_2CH_2Py$ The nonvolatile portion of the CH_2N_2 reaction with **2** (L = Py) was placed on a silica gel column using CH_2Cl_2. Elution with CH_2Cl_2 gave unreacted complex **2**. Subsequent elution with a 1/1 mixture of hexane and EtOAc gave the complex $PyPtCl_2CH_2Py$. The following spectral data were subsequently collected. ^1H NMR: 9.05(2H, m), 8.29(3H, brt), 8.08(1H, brt), 7.62(2H, m), 7.25(2H, m), 5.45(2H, s) ppm; ^{13}C NMR: 151.7(d), 143.3(d), 139.8(d), 137.1(d), 126.6(d), 124.6(d), 30.1(t, J(PtC) 751 Hz) ppm. This complex has now been crystallized and subsequently structured by X-ray crystallography. A formal report of the origins and the structural aspects of this complex will be reported in a separate article.

Reaction of 2 and 3 phenylplatinacyclobutane (10) with diazomethane. To a stirred solution of the mixture of phenylplatinacyclobutanes (200 mg) in 15 ml of $CDCl_3$ at

0°C was bubbled a large excess of diazomethane (Diazald). The reaction mixture was stirred for an additional hour, brought to room temperature and the volatiles removed by vacuum distillation. Styrene and phenylcyclopropane which are formed in a ratio of 5/1 were identified with mass spectroscopy by comparison to authentic compounds. Two very minor products with a *m/e* of 118 were also detected. The overall yield of products was 83% and was improved by the slow addition of diazomethane. The experiment that was run at room temperature following the same procedure as outlined above except for the obvious difference in temperature. Styrene and phenylcyclopropane were formed in a ratio of 1/3 with an overall yield of 80%.

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