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REACTION OF *exo*-TRICYCLO[3.2.1.$0^{2,4}$]-6-OCTANONE WITH ZEISE'S DIMER

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Summary

Reaction of *exo*-tricyclo[3.2.1.$0^{2,4}$]-6-octanone with platinum(II) gave two isomeric platinacyclobutane products in a ratio of 2.3/1. The major isomer was shown by NMR spectroscopy to have resulted from insertion of the platinum into the least substituted cyclopropyl bond which is nearer the ketone. These platinum(IV) complexes were also shown to be surprisingly inert.

Introduction

McQuillen [1] reported in 1971 that the following order or reactivity had been observed for the reaction of mono-substituted cyclopropanes with Zeise's dimer, $(C_2H_4PtCl_2)_2$: n-C_6H_{13} > $PhCH_2$ > Ph. Further, he reported that when the substituents were CO_2CH_3, $COCH_3$ or CN, no reaction occurred.

Our goals in this reported endeavor were twofold. First, we wanted to remove the electron-withdrawing functionality far enough away from the cyclopropane moiety to achieve reaction but not so far as to remove its entire influence. Second, we wanted the cyclopropyl substrate to be asymmetrically substituted so as to present three different edges for platinum insertion. We now wish to report the successful results on the influence of a ketone on platinum(II) insertion into an asymmetrically substituted cyclopropane.

Experimental

General. The ^1H, ^{13}C and ^{195}Pt NMR spectra were obtained on a Bruker WM-250 spectrometer. Nominal mass spectra were recorded from a VG/MM16F spectrometer while accurate mass measurements were obtained from a VG/7070E spectrometer. Diazald and 2-norborene-5-ol were obtained from Aldrich and used without further purification. Elemental analyses were performed by Galbraith or on the VG/7070 mass spectrometer at MSU.

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Preparation of compound 1. The cyclopropanation of 2-norbornene-5-ol (mixture of *exo* and *endo* isomers) was carried out by the method of Kottwitz [2]. To 12 g of dry Sarett reagent in 200 ml of CH_2Cl_2 at 0°C was added 2.8 g of the mixture isomers of the cyclopropanation reaction. The reaction mixture was allowed to warm up to room temperature, filtered and the CH_2Cl_2 rotoevaporated. Chromatography on silica gel with hexane afforded 2.6 g of a yellow oil composed of 72% ketone 1 and 20% of the starting alcohol. Ketone **1** was purified by the preparative GC on 10′ × 3/8″ 10% SE-30 on Chromosorb W-NAW column. NMR data for **1**: ^{1}H NMR ($CDCl_3$): 2.4(2H,dd); 1.2(2H, m); 0.4(1H, dd); 0.9(1H, m); 1.9(2H, m); 0.8–0.9(2H, m) ppm. ^{13}C NMR ($CDCl_3$): 214.9(s); 48.0(d, *J*(C,H) 150 Hz); 44.5 (t,144); 34.3(d,142); 25.1(t,135); 16.4(d,171); 9.2(d,174); 5.29(t,160) ppm. MS: *m/e* (relative intensity); 122(M^+,18), 93(10), 80(92), 79(100), 78(43), 77(23), Accurate mass for $C_8H_{10}O$: found 122.0734; calcd. 122.0732.

Preparation of platinacyclobutanes 2 and 3. To a suspension of 0.5 g (0.86 mmol) of Zeise's dimer $(C_2H_4PtCl_2)_2$ in 10 ml of dry ether was added 0.3 g (2.5 mmol) of **1**. The mixture was stirred under reflux for 4 h during which time a yellow solid precipitated (complexes **2** and **3**, L = Cl) as the orange Zeise's dimer disappeared. After filtration, the yellow solid was dried in vacuo overnight to give 0.64 g (97% yield). To 0.4 g of this solid suspended in 10 ml $CDCl_3$ was added 4 equivalents of pyridine. The solid was dissolved and the volatiles removed by evaporation leaving a yellow oil. On mixing the yellow oil with pentane, a yellow solid formed (complexes **2** and **3**, L = Py). Upon repeated trituration with pentane 0.55 g (98% of yield) of **2** and **3** were obtained after drying. The ratio of isomers **2** and **3** was 2.3/1.

Preparation of compound 4. Ketal **4** was prepared by the normal procedures using **1**, ethylene glycol and a trace of *p*-toluenesulfonic acid in 88% yield. NMR spectra for **4**: ^{13}C NMR ($CDCl_3$): 117.6(s); 64.4(t); 63.8(t); 43.6(t); 42.7(d); 34.8(d); 25.5(t); 15.06(d); 9.14(d); 3.42(t)ppm. Accurate mass for $C_{10}H_{14}O_2$: found 166.0997; calcd. 166.0993.

Preparation of complexes 5 and 6. In an analogous procedure to the preparation of **2** and **3**, compound **4** (0.35 g) was treated with 0.5 g of Zeise's dimer to form 0.7 g

TABLE 1

^{13}C NMR DATA FOR COMPOUNDS **5** AND **6**

5					**6**				
	ppm	Mult.	*J*(C–H)	*J*(Pt,C)		ppm	Mult.	*J*(C–H)	*J*(Pt,C)
C(1)	−11.2	t	143	352.3	C(1)	−12.9	t	147	355.8
C(2)	47.8	d	146	98.4	C(2)	54.0	d	133	97.6
C93)	2.7	d	153	408.2	C(3)	9.5	d	143	399.3
C(4)	48.8	d	141	26.0	C(4)	48.1	d	141	small
C(5)	113.9	s	–	50.6	C(5)	44.0	t	136	43.6
C(6)	42.0	t	129	small	C(6)	115.7	s	–	small
C(7)	40.4	d	143	0	C(7)	40.4	d	143	0
C(8)	34.3	t	140	0	C(8)	34.6	t	140	0
Ketal	63.35	t	148		Ketal	63.5	t	148	
	64.0	t	148			64.3	t	148	
^{195}Pt NMR [a] 3321.5 ppm					3333.1 ppm				
1.43 integral					2.01 integral				

[a] Relative to an external standard of 1.0 *M* solution of $Na_2Pt(CN)_4$ in D_2O at 23°C.

TABLE 2

RELATIVE CONCENTRATION OF COMPOUNDS 5 AND 6

Time (h)	5	6
0	1	1.4
1	1	1
18	2.5	1
42	3.0	1

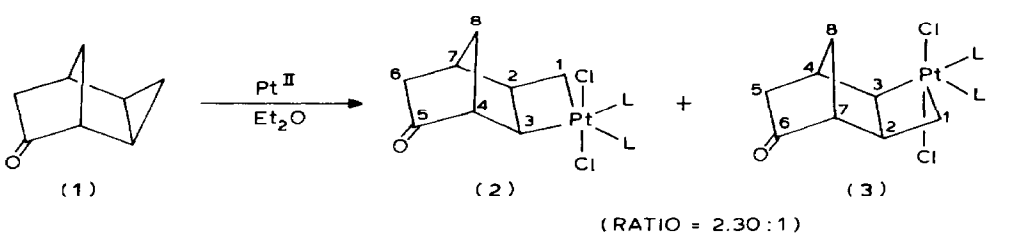
(94%) of **5** and **6** (L = Cl). To 0.4 g of this material in $CDCl_3$, pyridine was added to give 0.52 g (96%) of **5** and **6** (L = Py). The ratio of **5** to **6** was 1/1.4. The ^{13}C NMR data for each isomer are given in Table 1.

Hydrolysis of complexes 5 and 6. To 0.1 g of the mixture of **5** and **6** in 2 ml of $CDCl_3$ was added 1 ml of 3 *M* HCl. After shaking for 1 min, the aqueous layer was separated and the chloroform layer was washed with 1 ml of 5% $NaHCO_3$ and 1 ml of saturated NaCl. Separation of the $CDCl_3$ layer and drying over anhydrous $MgSO_4$ gave a light yellow solution of **2** and **3** which was analyzed by NMR spectroscopy. Both ^{195}Pt and ^{13}C NMR data gave the ratio of products as 1/1.48, which is the same as the ketal mixture.

Equilibrium between 2 and 3. The above mixture was subsequently refluxed in chloroform with periodic analyses of the ^{195}Pt NMR spectrum. The results are shown in Table 2.

Results

The proposed structures for the reaction products are shown in eq. 1. Although there are two structures shown for the products in this reaction, we have had no



(1)

success in separating them. Thus, the structure analyses are based on the isomeric mixture.

Structure assignments for compounds 2 and 3. There are two platinum resonances of unequal intensity at 3390.4 and 3367.9 ppm downfield relative to an external standard, 1.0 *M* solution of $Na_2Pt(CN)_4$ in D_2O at 23°C (Fig. 1). These data are significant in that they indicate that there are two different platinum compounds in a ratio of 2.3 to 1 rather than one compound with two platinum atoms. The ^{13}C NMR data also suggests a mixture with a ratio of 2.3/1. Using this assumption, we were able to decipher and assign ^{13}C NMR resonances for each isomer (Table 3).

These data are analogous to other platinacyclobutanes prepared in our laboratory [3,4]. The key features in these types of complexes are that there is strong coupling

between the metallacyclobutane carbons and ^{195}Pt, and that the CH_2 which is attached directly to the platinum atom resonates upfield of TMS by 10–20 ppm. Furthermore, in all examples which we have investigated to date, the $^3J(Pt,C(5))$ is on the order of 50 Hz [3,4]. This is particularly useful, in this case, for assigning the structures of **2** and **3**. In the major isomer, **2**, (C(5)) is the carbonyl carbon which is readily distinguished by ^{13}C NMR spectroscopy. Its coupling constant to platinum is 46.3 Hz. In contrast, the carbonyl carbon in isomer **3** is not coupled to platinum. Instead a resonance at 46.4 ppm, which is a triplet in the gated decoupled spectrum, is coupled to ^{195}Pt by 49 Hz. Results from proton–proton and proton–^{13}C NMR decoupling experiments are consistent with the structures shown. Finally, the C, H and N analyses of the mixture were correct.

Kinetic vs. thermodynamic product formation. Due to the observed ratio of compounds **2** and **3** being somewhat of a surprise, it was important to determine whether they were formed by direct insertion or resulted from an equilibrium reaction after formation. Two experiments were conducted. In the first experiment a mixture of **2** and **3** was heated in $CDCl_3$ at 58°C for 24 h. Another sample was kept at −20°C for one week. In both samples the ratio between isomers **2** and **3** remained constant as determined by NMR spectroscopy.

In the second experiment, a different ratio of **2** and **3** was prepared by an

TABLE 3

^{13}C NMR SPECTRA FOR COMPLEXES **2** AND **3**

	Structure **2**		Structure **3**	
	ppm	J(Pt,C) (Hz)	ppm	J(Pt,C) (Hz)
C(1)	−10.65(t)	351.5	−13.56(t)	362
C(2)	52.71(d)	98.3	47.16(d)	100
C(3)	−2.21(d)	429.3	5.20(d)	412
C(4)	54.4(d)	11	39.63(d)	small
C(5)	212.5(s)	46.3	46.38(t)	49
C(6)	44.47(t)	–	216.47(s)	–
C(7)	39.83(d)	25.4	55.22(d)	27
C(8)	34.20(t)	–	34.36(t)	–

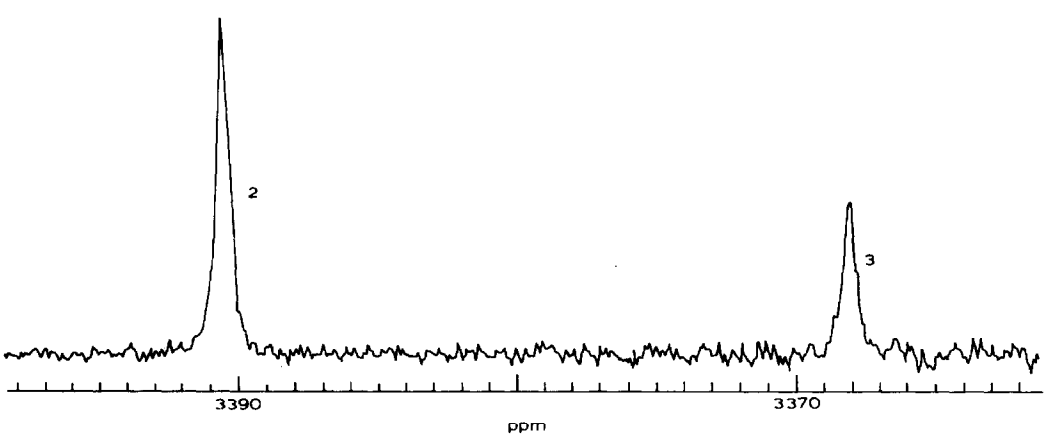
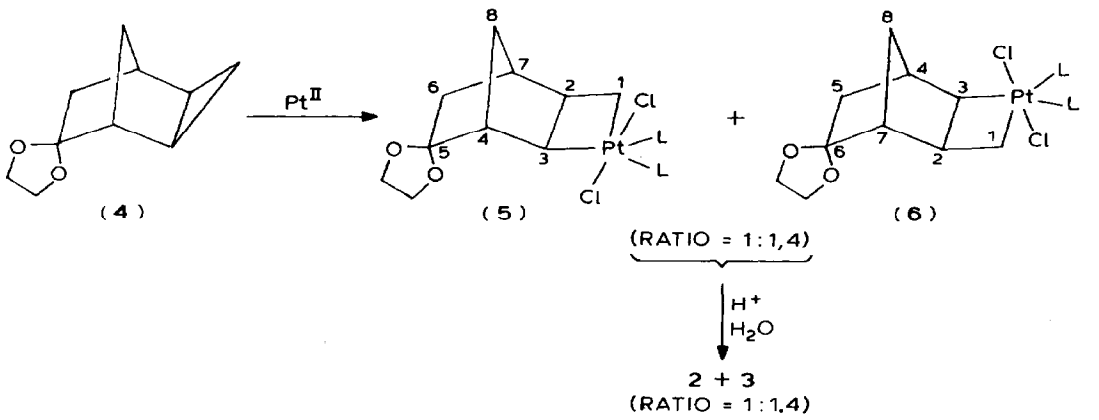


Fig. 1. ^{195}Pt NMR spectrum of **2** and **3** relative to an external standard of 1.0 M of $Na_2Pt(CN)_4$ in D_2O at 23°C.



SCHEME 1

independent sequence of chemical reactions (Scheme 1). The spectral data for compounds **4**, **5** and **6** is given in the experimental section, and the logic used for structure assignments is the same as that discussed for **2** and **3**. As can be seen in Scheme 1, the isomeric ratio from this procedure is significantly different from that shown in eq. 1. On standing at room temperature in $CDCl_3$ for several hours the ratio remained constant. However, upon refluxing in $CDCl_3$ for 42 h the ratio of isomers changed to 3/1. There was a negligible amount of decomposition during this procedure.

Discussion

There is no question that the carbonyl group is reducing the activity of the cyclopropane toward the platinum(II) insertion reaction. In a reaction of the non-keto hydrocarbon system with Zeise's dimer, the insertion reaction is complete in 2–3 h in refluxing ether. With **1** the reaction is complete in 5 h in refluxing ether.

Another interesting feature of this reaction is the disposition of the platinum in the final product. Even though the carbonyl group appears to have a negative influence on the cyclopropane reactivity toward platinum insertion, the platinum atom for the major product has inserted into the least substituted edge which is, in fact, closer to the deactivating group. This product could, however, result from a "Puddephatt type" [5] equilibrium and, therefore, would not actually reflect the kinetic insertion product. To test this possibility, the isomeric mixture in chloroform was subjected to two different temperatures to see if the isomer concentrations would change. The mixture was heated to 58°C for 24 h and another sample was cooled to −20°C and allowed to remain at that temperature for one week. Under neither of these conditions did the concentrations of the mixture change.

As a second check on the potential equilibrium between **2** and **3**, they were synthesized by another route in hopes of generating a different ratio. The synthetic sequence and product ratios are shown in Scheme 1. It is clear that the experiment was successful in generating a different ratio of isomers from that observed from reaction 1. It is interesting to note that isomeric ratio for the ketal and subsequently the ketones **2** and **3** was slightly in favor of **3**, which is in contrast to the results of

reaction 1. On standing at room temperature, the concentrations did not change. However, on boiling in $CDCl_3$ ($\sim 60°C$) for 18 hours the ratio changed to 2.5/1, and after 42 h it had leveled off at 3/1.

It is clear that **2** and **3** are in equilibrium but it is slow to establish itself at 60°C. Thus, it is virtually stopped at room temperatures. Further, the observed ratio from reaction 1 is not the ultimate ratio observed after heating and cooling in chloroform. Thus, it seems reasonable to suggest that the observed ratios in reaction 1 and Scheme 1 reflect the propensity for platinum(II) to insert into the respective bonds.

A brief foray into the chemistry of the isomeric mixture was done in an effort to differentiate between the two compounds. The overall conclusion is that complexes **2** and **3** are both very stable. In refluxing chloroform [6], or under 80 psi pressure of carbon monoxide [6], or in reaction with DMSO in $CHCl_3$, the complexes were impervious. On treatment with a 3 *M* HCl solution, the chloroform layer decolorized and the yellow colored complexes migrated to the aqueous phase. Separation of the aqueous phase and neutralization with $NaHCO_3$ gave complexes **2** and **3** in virtually quantitative yield. It had been hoped that the acid would protonate the carbonyl oxygen which would then activate one or the other of the platinacyclobutane rings. Apparently all that occurs is removal of the pyridine ligands by protonation, aquation and subsequent solubilization in the aqueous phase. Finally, on treatment of the isomeric mixture in chloroform with 2.3 equivalents of triphenylphosphine, reductive elimination occurred yielding the original cyclopropane **1**.

In conclusion, this is the first example of a cyclopropane substrate which is pseudo conjugated to a ketone function that has been shown to react with Zeise's dimer. An isomeric mixture of platinecyclobutane complexes was obtained. The major isomer which is apparently coming from a Puddephatt type equilibrium, has inserted the platinum into a cyclopropane edge which is closer to the carbonyl moiety. Finally, the pyridine solubilized platinacyclobutane complexes **2** and **3** are relatively inert to reactions which are generally operative in hydrocarbon analogues.

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6 Work in progress in our laboratories on the hydrocarbon analogues which will be reported later.