New Platinacyclobutanes from *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene and *exo,exo*-Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane

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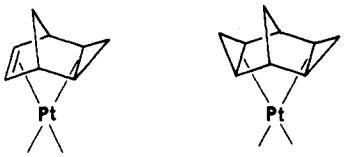
Two new platinacyclobutane complexes have been prepared from tricyclooctene 1 and tetracyclononane 2. They are, in fact, the compounds in solution when one dissolves the rather insoluble, initially formed platinum complexes in THF or Me_2SO. They were characterized by ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy as platinacyclobutanes which have the exo configuration relative to the bicyclic structure. Moreover, they are unique in that there are no previously characterized platinacyclobutanes which have cis disubstitution.

Metallocyclobutane complexes have received considerable attention over the last few years because they are thought to be intermediates in a number of organic transformations.[1-3] Platinacyclobutanes have been particularly interesting because they often have slow reaction rates and stable intermediates. Moreover, the phenyl-substituted platinacyclobutanes have been shown to exhibit a very intriguing stereospecific intramolecular rearrangement.[4,5]

In 1969, Volger[6] reported on the reactions of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, **1**, and *exo,exo*-tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane, **2**, with various transition-metal complexes. He found that **1** was quantitatively converted to **3** by using $Rh_2(CO)_4Cl_2$ via an uncharacterized yellow intermediate. Katz[7] subsequently reported that the rhodium complex $(Ph_3P)_3RhCl$ not only converted **1** to **3** but also to **4** and **5**. From the results of an elegant deuterium-labeling experiment, he suggested that an endo rhodium π-allyl complex was responsible for the formation of **4** and **5**. According to Volger,[6] the tetracyclohydrocarbon **2** also reacted with $Rh_2(CO)_4Cl_2$, forming a yellow complex, but failed to rearrange to analogues of **3** and **4**.

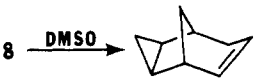
1 **3** (32%) **4** (6%) **5** (62%)

Volger further showed that Zeise's dimer, $[(C_2H_4)PtCl_2]_2$, reacted with **1** and **2** to form insoluble pale yellow derivatives which he postulated to have structures **7** and **8**, respectively. These platinum complexes were proposed to require bis-endo coordination to the edge of the cyclopropane.



7 **8**

In 1980, Johnson[8] reported further on the reactions of complex **8**. He found it to be insoluble in THF and CH_3CN. When it reacted with pyridine, starting hydrocarbon **2** was regenerated, rather than forming the typical bis(pyridine), six-coordinate platinacyclobutane. In Me_2SO, a facile and quantitative rearrangement occurred to yield **6**, which is analogous to the π-allyl rearrangement advanced by Katz. Like Volger, Johnson concluded that **8** was indeed a bis-endo edge-bound platinum complex.



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Results

In this article, we present evidence which shows that complexes **7** and **8** are, or are easily converted to, platinacyclobutanes **9** and **10**, respectively. In these experiments, hydrocarbon **1** or **2** was added dropwise to Zeise's dimer in ether. The characteristically orange solid, Zeise's dimer, was quickly consumed and replaced by a pale yellow suspension which was filtered, washed with ether, and dried in a vacuum desiccator containing anhydrous calcium sulfate. The platinum complex of **1** was darker yellow than that from **2**. In order to characterize these two initially formed solids, they were solubilized in THF.

9 **10**

NMR Spectral Interpretation. Although these complexes were not very soluble in THF as previously reported, they were sufficiently soluble to determine ^{13}C NMR spectra by using a high-field 250-MHz spectrometer. The NMR data for the proposed complexes **9** and **10** are shown in Table I.

When these data were first observed, the most striking characteristic was the unexpected number of unique ^{13}C resonances. If structures **7** and **8** were correct, one would have observed five and four unique resonance lines, respectively. The data obtained and listed in Table I were totally inconsistent with **7** and **8**. The fact that only one ^{195}Pt NMR resonance was observed for complex **8** ensured the homogeneity of the sample. In discussing the ^{13}C NMR

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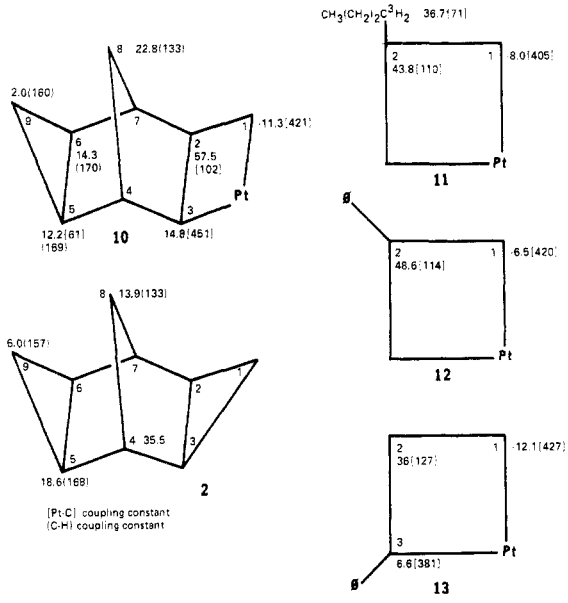
Table I. ^{13}C NMR Data for 9 and 10 in Tetrahydrofuran

carbon	9 δ	9 $J_{Pt,C}$, Hz	9 $J_{C,H}$, Hz	10 δ	10 $J_{Pt,C}$, Hz	10 $J_{C,H}$, Hz
1	−3.1 t[a]	435	148	−11.3 t	421	149
2	54.0 d	88	144	57.5 d	102	146
3	13.4 d	457	159	14.8 d	451	157
4	47.3 d	12	151	40.5 d	13	148
5	134.4 d	56	169	12.2 d	61	169
6	137.8 d		169	14.3 d		170
7	47.3 d	33	151	42.2 d	33	148
8	45.2 t		134	22.8 t		133
9				2.0 t		160

[a] Multiplicity of resonance peak with gated decoupling.

assignments in detail, structure **10** will be exemplified. Structures **2**, **11**, **12**, and **13**, which have well-characterized NMR spectra, will be used as analogues.[9]



Carbon 1 has three unique characteristics. First, it is coupled to ^{195}Pt by 421 Hz which is consistent with a σ bond to platinum. Second, it exhibits triplet multiplicity in the gated decoupled spectrum, confirming that it is a CH_2 moiety. Third, it is upfield of Me_4Si, which is in accord with the analogous carbons of structures **11**, **12**, and **13**.

The large platinum coupling constant of 451 Hz and the doublet character of the gated decoupled spectrum established the resonance for C-3. The reduced ^{195}Pt coupling to C-2 and its chemical shift are consistent with the analogous carbons of structures **11**, **12**, and **13**.

There are two additional carbons that exhibit triplet multiplicity in the gated decoupled spectrum. The high-field resonance at 2.0 ppm with a $^1J_{C-H}$ value of 160 is assigned to the cyclopropyl carbon 9, basically because of the analogous $^1J_{C-H}$ coupling in structure **2**. The 4.0 ppm shift to higher field for C-9 in structure **10** vs. that carbon in structure **2** is not understood. The other triplet resonance at 22.8 ppm with a $^1J_{C-H}$ of 133 Hz was consequently assigned to C-8.

Carbons 4 and 7 have not been adequately investigated to permit accurate assignment. However, we tentatively suggest that C-4 is at 40.5 ppm with a $^2J_{Pt,C}$ value of 13 Hz and C-7 is at 42.2 ppm with a $^3J_{Pt,C}$ value of 33 Hz.

(9) NMR resonance positions for compounds **2**, **11**, **12**, and **13** were established in our own laboratory after synthesizing the compounds by literature methods.

Carbons 5 and 6 are obviously part of an intact cyclopropane moiety because of their C–H coupling constants which are analogous to those in structure **2**. Carbon 5 is also unique in that the $^3J_{Pt,C}$ value is 61 Hz. This is analogous to C-3 of structure **11**. To explain the relatively large coupling constant to C-5, we propose to employ a Karplus-type relationship. For C-5, the dihedral angle is near 180°. If this idea is extended to C-7, a value of 33 Hz is reasonable for an estimated angle of 100° in either of the two possibilities. Finally, the $^3J_{Pt,C}$ value for C-8 is near 0, suggesting an angle of 80–90° which is also reasonable if the platinacyclobutane moiety is puckered at an angle of 150–160°. A similar distortion in platinacyclobutanes has been observed previously.[10] The Karplus-type relationship has also been used previously to explain coupling constants in organotin[11] and organoselenium[12] complexes.

Arguments similar to those used above can be employed to justify structure **9**. The exo stereochemistry for both platinacyclobutane moieties is assumed from the stereochemistry of the starting hydrocarbons **1** and **2**.

Chemical Characterization. If the initially formed platinum complexes were dissolved in Me_2SO-d_6 at room temperature, they slowly formed compounds **5** and **6**. During this dissolution and subsequent rearrangement, we were able to detect complexes **9** and **10** by ^1H NMR spectroscopy. Their half-lives at 25 °C were 3.0 h and 28 min, respectively.

If, to a $CDCl_3$ suspension of the initially formed platinum complexes of **1** or **2** in an NMR tube, 2.5 equiv of pyridine were added, the complexes dissolved to form **9** and **10**, respectively. There was no NMR spectral evidence for the formation of **1** or **2** as previously reported.[8] Addition of 3.5 equiv of Ph_3P to this pyridine derivative in $CDCl_3$ did regenerate compounds **1** and **2**. When 3.5 equiv of Ph_3P were added to either of the $CDCl_3$ suspensions, **1** and **2** were quantitatively regenerated.

Discussion

In this reaction sequence, Zeise's dimer in ether reacts rapidly with hydrocarbon **1** or **2** to form initial platinum complexes (IPC) which have not been fully characterized. They have been proposed to be endo-platinum complexes which are bound to the edge of the cyclopropane moiety.[6,8] However, in the present work we show that dissolution of these IPC complexes in THF, $CHCl_3$ containing pyridine, or Me_2SO yields the *exo*-platinacyclobutanes **9** and **10**, respectively.

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Evidence for proposing structures **9** and **10** is garnered from ^{13}C and ^{195}Pt NMR spectroscopy. The chemical shift values observed are consistent with the proposed structures when compared to model systems **2**, **11**, **12**, and **13**. A great deal of structural assignment weight was put on the $J_{Pt,C}$ values which are not only indicative of platinum–carbon σ bonds but also are analogous to known platinacyclobutanes.

The only piece of information for which there are little data is the exo configuration of the platinacyclobutane. However, the facts that the original cyclopropane moieties in **1** and **2** were exo and that they were regenerated from complexes **9** and **10** on treatment with Ph_3P strongly suggest that the exo platinacycle is correct. There is a 1–2 ppm downfield shift for one proton on C-8 in going from **1** to **9** or **2** to **10**, but there is inadequate precedent to use these data for structural assignments.

These complexes (**9** and **10**) are the first examples to be characterized as cis-1,2-disubstituted platinacyclobutanes. All previous examples of stable 1,2-disubstituted platinacyclobutanes were derived from trans-disubstituted cyclopropanes. However, there are three reports in which cis-substituted cyclopropanes were reacted with platinum. McQuillin[13] reported in 1972 that *cis*-1-methyl-2-*n*-butylcyclopropane reacted with Zeise's dimer to form a mixture of 2- and 3-octene. Further, he found that bicyclo[4.1.0]heptane reacted to give a platinum complex which, upon treatment with KCN, gave methylenecyclohexane, 1-methylcyclohexene, and cycloheptene. In neither of these two cases was a platinacyclobutane characterized or proposed.

In 1979, Johnson[14] reported that *cis*-1,2-dimethylcyclopropane reacted with Zeise's dimer to give 1-pentene (23%), *cis*-2-pentene (20%), 2-methyl-1-butene (15%), 3-methyl-1-butene (6%), and 2-methyl-2-butene (36%). Although a platinacyclobutane was not observed, it was proposed as a possible intermediate.

Finally, in 1980, Puddephatt[4] reported that *cis*-1,2-diphenylcyclopropane reacted sluggishly with Zeise's dimer to yield possibly a diphenylallyl derivative of platinum. Further characterization was not carried out, but a platinacyclobutane was proposed as an intermediate.

Thus, it appears that hydrocarbons **1** and **2** either form platinum complexes which are different from the cis-disubstituted cyclopropanes previously investigated or the decomposition reaction of the platinacyclobutanes from **1** or **2** is retarded. In fact, McQuillin[13] favored a π-allylplatinum complex over the platinacyclobutane to explain the differences in reactivity and products between cis and trans complexes. It is therefore reasonable to suggest that the exo platinum complexes **9** and **10** are unusually stable because they are unable to achieve coplanarity with the β hydrogen to form olefinic products via β elimination. Further investigation is continuing on these aspects.

Experimental Section

General. NMR spectra were recorded on a Bruker WM 250 spectrometer. K_2PtCl_4 was obtained from Aldrich and used without further purification. THF-d_8 was purchased from Stohler and Me_2SO-d_6 from Wilmad. Analytical analyses were carried out by Galbraith Laboratories.

Preparation of Zeise's Dimer $[(C_2H_4)PtCl_2]_2$. This compound was prepared from K_2PtCl_4 exactly as described by Littlecott.[15]

Preparation of *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene (1) and *exo,exo*-Tetracyclo[3.3.1.0^{2,4}.0^{6,8}]nonane (2). These compounds were prepared by the methods described by Kottwitz.[16] The NMR spectral data for these hydrocarbons agreed with the published values.[6]

Reaction of 1 and 2 with Zeise's Dimer. To a vial containing 110 mg (0.185 mmol) of $[(C_2H_4)PtCl_2]_2$ in 10 mL of dry ether was added dropwise 80 μL($\sim$0.8 mmol) of **1** or **2**. The orange dimer was quickly consumed, as the yellowish cream-suspended product formed. After the mixture was stirred with a magnetic stirrer for 10 min, the suspension was filtered and the solid product was crushed, resuspended in 10 mL of ether, and again filtered by suction. After this was dried in a vacuum desiccator containing anhydrous $CaSO_4$, a yield of 80–90% was obtained. Larger quantities (to 1.5 g) were prepared in a similar manner.

The products **7** and **8** gradually darkened in color with increasing temperature: **7**, mp 130–140 °C dec; **8**, mp 145–155 °C dec. Anal. Calcd for $C_8H_{10}PtCl_2$ (**7**): C, 25.82; H, 2.71. Found: C, 25.60; H, 2.70. Anal. Calcd for $C_9H_{12}PtCl_2$ (**8**): C, 27.99; H, 3.13. Found: C, 27.98; H, 3.23.

Dissolution of 7 and 8 in THF. To 1.5–2 mL of THF was added 100 mg of **7** or **8**, resulting in a yellow solution for ^{13}C NMR analysis. During the time required for the ^{13}C determinations (at 35 °C), the solutions of **7** and **8** gradually darkened, with the production of small amounts of **1** and **2** as the only detectable decomposition products. Solutions of 2–4 mg of **7** or **8** in 100 μL of THF-d_8 were used for ^1H NMR analysis.

Dissolution of 7 and 8 in $CdCl_3$ and Pyridine, and Subsequent Reaction with Ph_3P. The addition of 6 μL (0.075 mol) of pyridine to a suspension of 5 mg ($\sim$0.014 mmol) of **7** or **8** in 0.5 mL of $CDCl_3$ resulted in a yellow solution for ^1H NMR analysis. Larger quantities were used to prepare solutions suitable for ^{13}C NMR analysis. The addition of 0.5 mL of a 0.095 M solution of Ph_3P in $CDCl_3$ (containing 0.048 mmol of Ph_3P) to the above 0.5-mL solutions of **9** or **10** resulted in the quantitative production of **1** and **2**, respectively, as determined by ^1H NMR spectroscopy.

Reaction of 7 and 8 with Ph_3P in $CdCl_3$. To $\sim$0.5 mL of a 0.095 M solution of Ph_3P in $CDCl_3$ (containing 0.048 mmol of Ph_3P) was added 5 mg ($\sim$0.014 mmol) of **7** or **8**, resulting in dissolution of the platinum compound and quantitative production of **1** and **2**, respectively as determined by ^1H NMR spectroscopy.

Dissolution of 7 and 8 in Me_2SO-d_6. To 0.6 (or 1.5) of mL Me_2SO-d_6 was added 23 (or 100) mg of **7** or **8**, yielding yellow solutions of **9** or **10**, respectively, as determined by ^1H NMR spectroscopy. The slow decomposition to form **5** or **6**, respectively, along with small amounts of **1** and **2**, respectively, was followed by ^1H NMR spectroscopy.[17] The products were identified by ^1H and ^{13}C NMR spectroscopy:[18,19] ^{13}C NMR for **5** (ppm) 13.4 (d, 2C), 15.4 (d), 27.5 (t, 2 C), 31.4 (d), 127.2 (d), 128.8 (d); ^{13}C NMR for **6** (ppm) 6.1 (t), 17.7 (d), 25.6 (d), 26.9 (t), 33.5 (d), 33.7 (d), 34.7 (t), 125.2 (d), 136.3 (d).

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Registry No. **1**, 3635-94-7; **2**, 24506-61-4; **5**, 3725-23-3; **6**, 42836-55-5; **9**, 79647-66-8; **10**, 79647-67-9; $[(C_2H_4)PtCl_2]_2$, 12073-36-8.

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(17) NMR analysis suggests the presence of other minor decomposition products from **9**, but no **4** was detected.
(18) ^1H NMR of **5**: Sauers, R. R.; Shurpik, A. J. *J. Org. Chem.* **1968**, *33*, 799.
(19) ^{13}C NMR of **6** agrees with data of Johnson.[8]