

The Platinum(IV)-Carbon σ Bond: Platinum(II)-Facilitated Carbon-Carbon Rearrangement of 2,7,7-Trimethyltricyclo[4.1.1.0^{2,4}]octane

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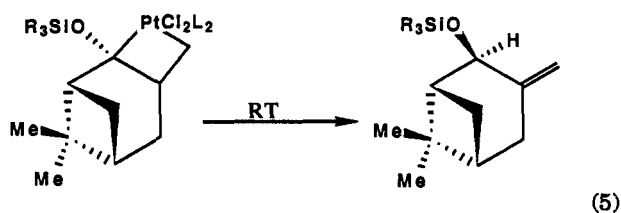
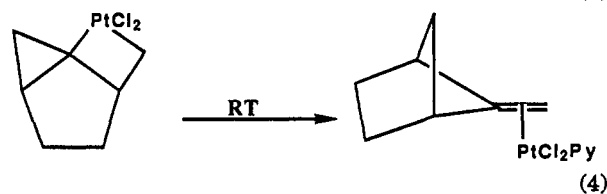
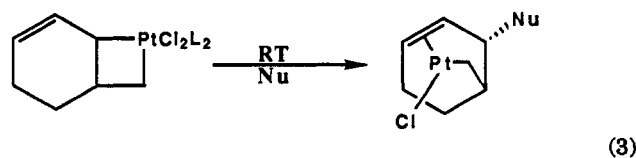
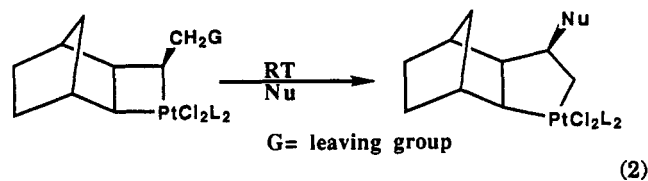
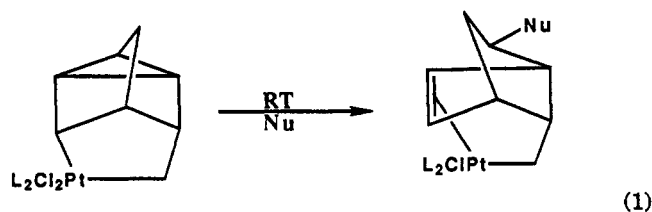
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Summary: The cyclopropanated derivative of α -pinene reacts rapidly with Pt(II) from Zeise's dimer to yield 1,7,7-trimethyl-2-methylidene-endo-6-chlorobicyclo[2.2.1]heptane. In this reaction, the dimethyl bridge rearranges with subsequent capture of Cl. These results coupled with those in the literature strongly suggest that Pt(IV)-carbon σ bonds are polarized Pt (minus), carbon (plus).

Platinum(II) in the form of Zeise's dimer readily reacts with a variety of cyclopropanes which are electron rich to yield platinum(IV)cyclobutane complexes.^{1,2} Structures for these Pt(IV) derivatives have been well characterized by a variety of methods, leaving no doubt as to their existence and octahedral nature. Despite this wealth of examples there are relatively few reactions known for them, thus providing only a modest base for mechanistic generalizations. As a result, we began investigations to explore the nature of the platinum(IV)-carbon σ bond in these cyclobutane complexes.

One might surmise that the highly oxidized Pt(IV) moiety would demand considerable electron density, thereby imparting some level of carbocationic character to the carbons to which it is attached. This conclusion requires that the other ligands are not capable of satisfying the entire electron demand. In the cases cited herein, the other ligands are Cl atoms, which are also electron demanding. Thus, one would expect to see several examples of rearrangements which are characteristic of carbocationic intermediates. However, there appear to be only five cases dealing with Pt(IV).³⁻⁷ Three of these exhibit metal-carbon rearrangements followed by nucleophilic capture,³⁻⁵ one follows the course of carbon-carbon rearrangement, yielding an olefin,⁶ and the fifth example is the only one displaying hydride transfer⁷ (see eqs 1-5). Finally, in a 1976 review article, Bishop cites several rearrangement examples of strained-ring systems which are facilitated by metals. It appears that silver-catalyzed processes develop considerably more ionic



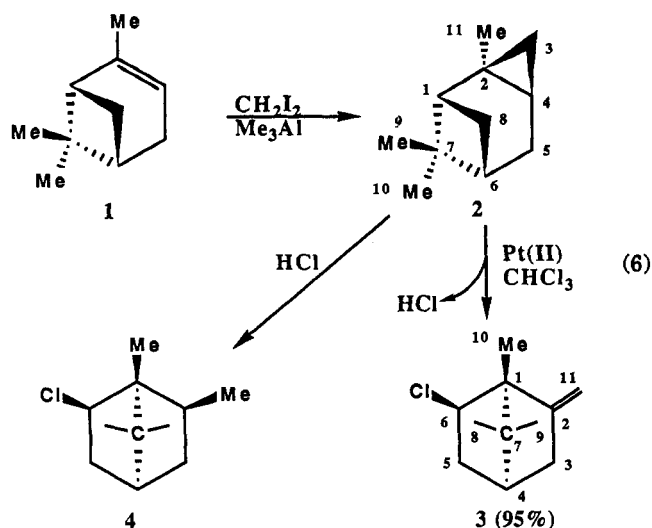
character than those catalyzed by rhodium and other transition metals. Unfortunately, there is no evidence of carbocationic character in the platinum examples cited.⁸

In this communication, we wish to report the first example of a carbon-carbon rearrangement followed by nucleophilic capture which clearly suggests carbocationic character in the reaction. Further, this example will be compared with the example earlier cited in which a hydride transfer occurs because the two substrates are quite similar.

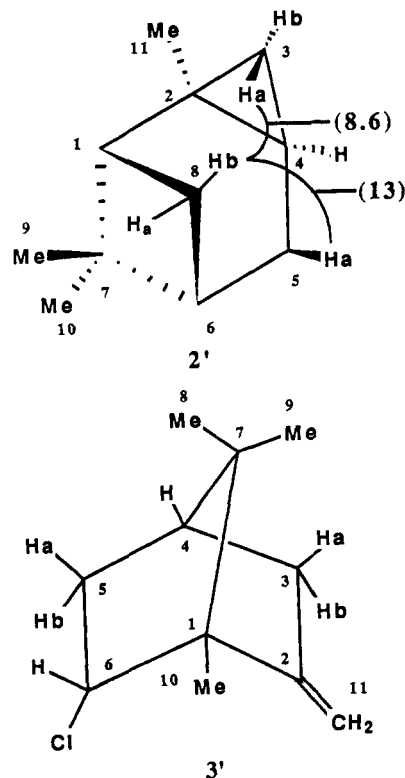
α -Pinene (1) is readily cyclopropanated with Me₂Al and CH₂I₂ to yield 2, which upon reaction with 1 mol of Zeise's dimer yields 3, 4, and HCl (eq 6). As indicated by the alternative arrow from 2, compound 4 is actually derived from the reaction of 2 with HCl, which is liberated in the formation of the primary product 3. Thus, reaction of 2 with Pt(II) in the presence of NaHCO₃ quenches the formation of 4, and 3 is formed exclusively.⁹ This is

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(1) Puddephatt, R. J. *Coord. Chem. Rev.* 1980, 33, 149.
 (2) Reference 1 reports a wide range of platinum(IV)cyclobutanes derived from trans-disubstituted cyclopropane compounds. Since then, several examples of a new series derived from cis-disubstituted cyclopropanes have been reported: Waddington, M. D.; Jennings, P. W. *Organometallics* 1982, 1, 1370. Parsons, E. J.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* 1985, 107, 1793. Parsons, E. J.; Jennings, P. W. *J. Am. Chem. Soc.* 1987, 109, 3973; *Organometallics* 1988, 7, 1435.
 (3) Waddington, M. D.; Campbell, J. A.; Jennings, P. W. *Organometallics* 1983, 2, 1269.
 (4) Neilson, W. D.; Larsen, R. D.; Jennings, P. W. *J. Am. Chem. Soc.* 1988, 110, 8657.
 (5) (a) Burton, J. T.; Puddephatt, R. J. *J. Am. Chem. Soc.* 1982, 104, 4242; *Organometallics* 1986, 5, 1312. (b) Hoberg, J. O.; Jennings, P. W. *Organometallics* 1992, 11, 3453.
 (6) Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. *Tetrahedron Lett.* 1986, 27, 3083.
 (7) Ikura, K.; Rhu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* 1992, 114, 1520.

Table I. ^{13}C and ^1H NMR Data for Compounds 2 and 3

	compd 2		compd 3		
	^{13}C	^1H	^{13}C	^1H	
1	45.4	1.83 t	1	57.6	
2	20.3		2	150.7	
3a	18.9	0.73 m	3a	36.7	2.43 m
3b		0.19 m	3b		1.99 d
4	15.9	0.68 m	4	43.3	1.77 t
5a	27.0	~2.04 m	5a	39.9	2.51 m
5b		~1.65 m	5b		1.36 dd
6	41.6	~1.60 m	6	64.2	4.14 dd
7	40.9		7	48.5	
8a	27.4	0.92 d	8	18.8	0.92 s
8b		~1.98 m	9	21.0	0.83 s
9	26.9	1.24 s	10	10.4	0.94 s
10	21.0	1.03 s	11a	107.9	4.82 m
11	25.4	1.07 s	11b		4.98 m



demonstrated by a total ion current measurement from the GC mass spectral analysis of this product mixture (when base is employed) which shows five peaks: one major peak (3; HRMS found 184.1006, calculated 184.1018) and four very minor peaks with <2% total intensity.

While the information on the inorganic portion of the reaction is not complete, there are two pieces of data that warrant comment. The reaction requires 1 mol of Zeise's dimer or 2 mol of Pt(II) for complete reaction. Second, Pt(0) is the product. Finally, unlike reaction 1, where a 20% yield of methanol-captured product occurred when the reaction was conducted in 50% methanol, reaction 6 yields no detectable yield of a methoxy product as ascertained by proton NMR spectroscopy. Given the low yield of methoxy product in eq 1, it is not surprising that other reactions involving an intramolecular transfer of halogen show low yields of methanol-capture products. Further, MeOH appears to inhibit the reaction.

Confirmation of the Structures of 2 and 3. Typical ^1H and ^{13}C one-dimensional NMR spectra confirmed the presence of the cyclopropyl moiety in 2. The basic structure of 3 is fairly straightforward once the 1D and 2D NMR data are perused (Table I lists the ^1H and ^{13}C assignments). An exocyclic methylene is evident by ^{13}C resonances at 107.9 and 150.7. The latter disappears in the DEPT 135 experiment, indicating a quaternary carbon. Carbons 1 and 7 are also identified in this manner. There are three singlet methyl resonances (^1H and DEPT 135 data). The ^{13}C resonance at 64.2 ppm has one proton which is coupled to protons on C-5 but not to anything else. COSY results show the $^3J_{\text{H,H}}$ relationships between protons on C-6, C-5, C-4, and C-3, which are further confirmed by HETCOR relationships that give the $^1J_{\text{H,C}}$ relationships. Appropriate isotope peaks and the correct *m/e* value from MS confirmed that the chlorine atom was present in 3. The resulting atom assignments for compounds 2 and 3 are listed in Table I.

While it is logical that the cyclopropyl moiety in 2 would be formed on the least hindered side of 1 (away from the dimethyl bridge), further confirmation was sought by the use of the difference method in NOE analysis (see structure 2'). Strong NOE relaxations were observed between proton 8b and proton 3a (8.6%) and between proton 8b and proton 5a (13%) when 8b was irradiated. Since there was no

NOE between any of the cyclopropyl protons and the bridge methyl groups (9 or 10), it is reasonable to conclude that the cyclopropyl moiety is indeed cis to the methylene bridge.

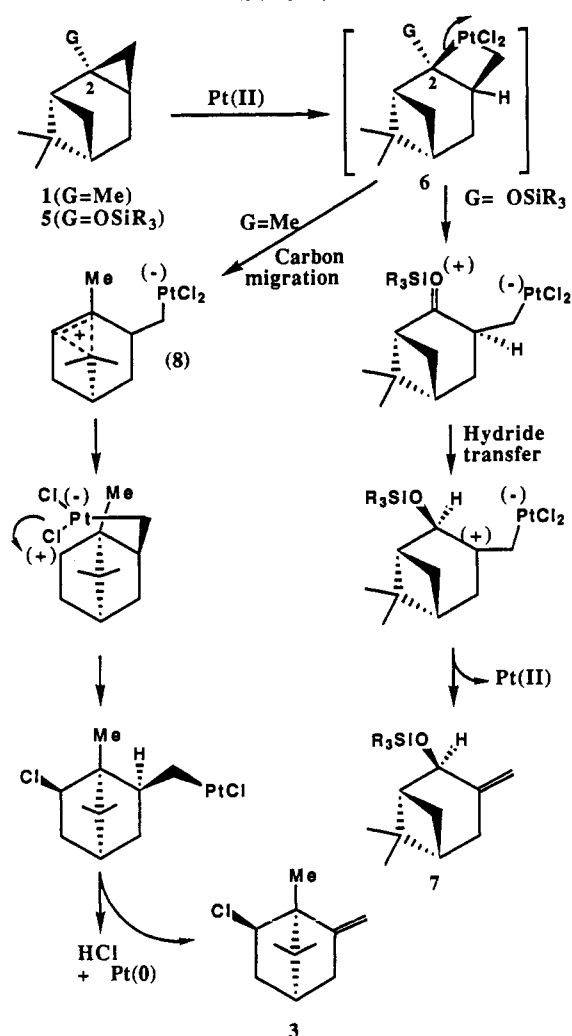
With the regiochemistry in 3 readily assigned via HETCOR and COSY spectra, the stereochemistry of the chlorine was investigated by measuring the coupling constants between 6H and its cis 3J proton (5H_a or 5H_b) (see structure 3'). To identify proton 5H_a, one needs to relate it to proton 4H. In these bicyclo[2.2.1] systems, proton 4H is coupled to the exo proton 5H_a by 2–5 Hz and to 5H_b by 0.0 Hz.¹⁰ Further, the coupling of exo 6H to cis 5H_a is typically 8–12 Hz and to trans 5H_b is 2–5 Hz. If 6H were endo, it would be coupled to 5H_b by 8–10 Hz and to 5H_a by 3–5 Hz.

For 3, 4H was coupled to 5H_a by 4.4 Hz (0.0 Hz to 5H_b), firmly establishing which proton signal is attributed to 5H_a. Subsequently, 5H_a was found to be coupled to 6H by 10.3 Hz (5-Hz coupling was observed between 6H and 5H_b). Thus, it appears clear that the Cl atom in structure 3 is endo.

(9) Since the emphasis in this investigation deals with a metal-facilitated process, the structure of 4 was not rigorously established.

(10) Moats, R. Ph.D. Thesis, Montana State University, 1990; unpublished results.

Scheme I



Mechanistic Comparison. With the details and structures of eq 6 understood, it is important to compare this reaction with the one mentioned earlier in which hydride transfer was observed.⁷ These reactions are compared in detail in Scheme I. While the platina(IV)-cyclobutane intermediate 6 has not been isolated in either reaction, there is adequate precedent which establishes that Pt(II) will insert into trisubstituted and even tetra-

substituted cyclopropane derivatives.^{1,11} If the insertion actually occurs into the least substituted bond, it can rearrange to the structure shown as 6, from which we propose further reaction to occur.¹² Thus, both substrates proceed to 6 and the platinum anion dissociates from the trisubstituted carbon. Divergence in the pathway occurs at this point as shown, in which hydride is transferred to the incipient cation when G = OSiR₃, whereas the dimethyl bridge migrates when G = Me.

The divergence may be explained by the fact that OSiR₃ is considerably better than CH₃ at stabilizing the incipient cation derived from 6. Thus, it is reasonable to suggest that the former reacts from an earlier transition state than does the methyl derivative.¹³ In 6 (G = OSiR₃) there is insufficient electron demand or charge development to require carbon rearrangement for stabilization. In contrast, with a later transition state and considerably more electron demand, it is necessary to lower the energy barrier by delocalization via carbon rearrangement, which provides a transition state like that shown as 8. Neither the methyl moiety nor the α -hydrogen can provide as much transition-state stabilization as the migrating carbon bridge.¹³

Summary. Since this reaction proceeds along a pathway similar to one clearly established in the carbocation literature and since there appear to be additional examples pointing in the same direction, it appears quite reasonable to conclude that Pt(IV)-carbon σ bonds in platina(IV)-cyclobutanes may proceed along a surface having carbocationic intermediates. Further, the one example shown as eq 1 prompts the suggestion that five-membered rings may behave in the same manner.

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OM920836D

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(13) Lowry, T. H.; Richardson, K. S. In *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row: New York, 1978; pp 385-391.