

Reactivity of (η^3 -Butadienyl)platinum(II) Complexes: Revised Mechanism for the Formation of a Silacyclobutenyl Complex

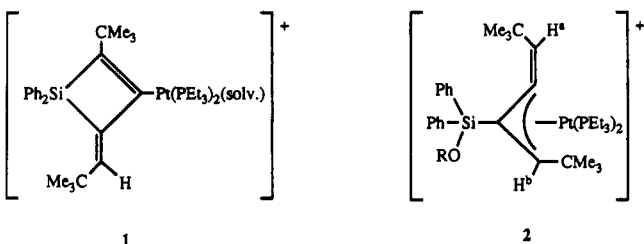
Anne C. Dema and Charles M. Lukehart*

Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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Summary: When a (η^3 -butadienyl)Pt^{II} complex containing a SiPh₂(OH) substituent at the central position of the allyl fragment is treated with Et₃N, elimination of Ph₂SiO as an oligomer occurs and a new (η^3 -butadienyl)-Pt^{II} complex is formed having a hydrogen atom replacing the original silanol substituent. This product complex provides an independent method for assigning the butadienyl proton resonances of the starting complex which has mechanistic implications. NMR data indicate that the original proton assignments are incorrect. A revised mechanism for the formation of these η^3 -butadienyl complexes and a silacyclobutenyl complex is proposed. Other reactivity is also discussed.

We recently reported that the cationic platinum-hydride complex [*trans*-PtH(PEt₃)₂(THF)]⁺ reacts with the dialkynylsilane, Ph₂Si(C≡CCMe₃)₂ to give the (η^1 -4-alkylidene-1-silacyclobutenyl)Pt^{II} complex 1.¹ Subsequent



results revealed that when this reaction is conducted in the presence of water or alcohol, an intermediate is apparently trapped by these hydroxyl-containing reagents to give (hydroxyl)silyl- or (alkoxy)silyl-substituted η^3 -butadienyl complexes like 2.² Repetition of the synthesis of 2 using the corresponding Pt-D⁺ reagent and repetition of this trapping reaction using either H₂O or D₂O as the trapping agent clearly indicate that the butadienyl hydrogen atoms of 2, H^a and H^b, are derived solely from either the Pt-hydride or the hydroxy group of the trapping agent. On the basis of the initial assignment of the butadienyl ¹H NMR resonances to protons in sites H^a or H^b, we proposed a mechanism of formation of 1 and 2 that involves a bis(alkylidene)silacyclopropane intermediate.² A critical feature of this mechanism is the proper assignment of the observed butadienyl proton resonances of 2 to protons in sites H^a and H^b. The initial assignment of these resonances was complicated by the similar values of *J*_{PtH} and *J*_{PH} coupling constants observed for both of these resonances. Reversing these assignments could suggest an alternative mechanism.³ We now report an unusual reaction of the hydroxylsilyl-(η^3 -butadienyl) complex 2 (R

= H) or 3. The product of this reaction provides a suitable system for determining the correct assignments of the protons at sites H^a and H^b in complexes like 2. These results strongly indicate that the original assignments of these proton environments should be reversed. A revised mechanism for the formation of the η^3 -butadienyl complexes 2 and the silacyclobutenyl complex 1 is proposed on the basis of these data. Additional chemical reactivity unrelated to this question of mechanism is also presented.

Experimental Section

Materials and Methods. Procedures specifying solvent purification, ambient conditions, the syntheses of compounds of types 1-3, the instrumentation and acquisition of spectroscopic data, and the commercial source of microanalytical data are provided elsewhere.²

Preparation of [Pt(η^3 -C(H)(CMe₃)C(H)C=C(H)(CMe₃)]-(PEt₃)₂[SbF₆] (4). To a solution of 0.200 g (0.194 mmol) of 3 in 10 mL of diethyl ether was added 0.027 mL (0.194 mmol) of Et₃N. After 30 min of reaction, the solvent was removed under reduced pressure. The reaction residue was extracted with methanol, and filtration of the extractant mixture permitted the isolation of the known oligomer [Ph₂SiO]₃ (0.023 g, 60% yield). This oligomer was identified by ¹H NMR and by melting point; mp 175-183 °C (lit.⁴ mp 187-189 °C). Complex 4 was isolated by crystallization from methanol/diethyl ether solution at -20 °C to give 0.111 g (68%) of 4 as colorless crystals: mp 83-86 °C; ¹H NMR (CDCl₃) δ 1.05 (s, 9, CMe₃), 1.11 (m, 18, PCH₂CH₃), 1.18 (s, 9, CMe₃), 2.1 (m, 12, PCH₂CH₃), 4.73 ("d of t", 1, H^c, ³*J*_{H^cH^c} = ³*J*_{PH} = 3 Hz, ⁴*J*_{H^cH^c} = 10 Hz, ²*J*_{PH} = 43.5 Hz), 5.25 (d of d, 1, H^b, ⁴*J*_{H^bH^c} = 10 Hz, ⁴*J*_{PH} = 3 Hz, ³*J*_{PH} \approx 0 Hz), 5.70 (d of m, 1, H^a, ³*J*_{H^aH^c} = 3 Hz, ³*J*_{PH} = 1.5 and 7 Hz, ²*J*_{PH} = 20 Hz); ³¹P{H} NMR (CDCl₃) δ 3.9 (d, PEt₃, ²*J*_{PP} = 12 Hz, ¹*J*_{PtP} = 3102 Hz), 10.5 (d, PEt₃, ²*J*_{PP} = 12 Hz, ¹*J*_{PtP} = 3888 Hz). Anal. Calcd for C₂₄H₅₁F₆P₂PtSb: C, 34.63; H, 6.17. Found: C, 35.03; H, 6.10.}}}}}}}}}}}

Preparation of Pt(η^1 -C(H)(CMe₃)=C(H)C=C(H)-(CMe₃)](PEt₃)₂Cl (5). To a solution of 0.138 g (0.165 mmol) of 4 in 10 mL of CH₂Cl₂ was added 0.030 g (0.181 mmol) of Et₃NCl·H₂O. The reaction was stirred for 4 h, and then the solvent was removed under reduced pressure. The reaction residue was extracted with benzene, and the extractant mixture was filtered to remove undesired salts. Concentration of the filtrate gave 0.075 g (72%) of 5 as a powder: mp 58-64 °C; ¹H NMR (CDCl₃) δ 1.05 (s, 9, CMe₃), 1.15 (m, 18, PCH₂CH₃), 1.25 (s, 9, CMe₃), 1.9 (m, 12, PCH₂CH₃), 5.00 (d, 1 H^b, ³*J*_{HH} = 13.4 Hz, ⁴*J*_{PH} = 26 Hz), 5.24 (d, 1, H^a, ³*J*_{PH} = 104 Hz, ⁴*J*_{HH} = 2.7 Hz), 5.89 (d of d, 1, H^c, ³*J*_{PH} = 39 Hz, ³*J*_{HH} = 13.4 Hz, ⁴*J*_{HH} = 2.7 Hz); ³¹P{H} NMR (CDCl₃) δ 6.9 (s, PEt₃, ¹*J*_{PtP} = 3086 Hz). Anal. Calcd for C₂₄H₅₁ClP₂Pt: C, 45.60; H, 8.13. Found: C, 45.79; H, 8.37.}}}}}}}}

Results and Discussion

The silanol complex 3 is a known compound that has been characterized spectroscopically and through X-ray

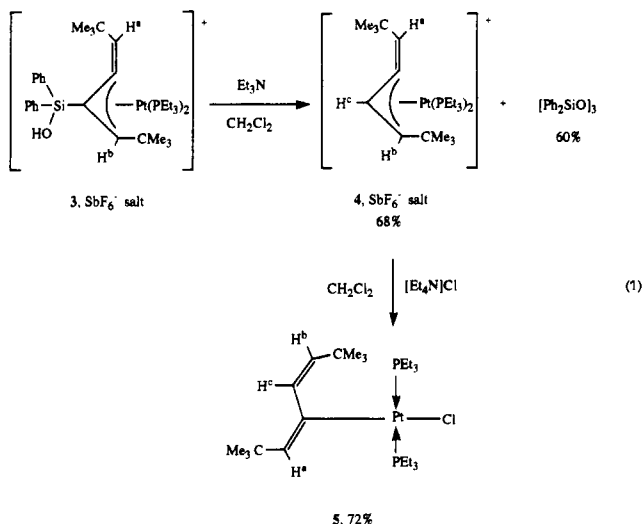
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(3) We are grateful to a reviewer of other work for this insight.

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diffraction.² When **3** is treated with triethylamine, the known siloxane oligomer, $[\text{Ph}_2\text{SiO}]_3$, and the $(\eta^3\text{-butadienyl})\text{Pt}^{\text{II}}$ complex **4** are formed in good yield, as shown in eq 1. The siloxane is identified by ^1H NMR and melting



point. Complex **4** has a hydrogen atom, H^c , bonded to the central carbon atom of the allyl fragment, so the overall conversion of **3** to **4** represents a very unusual base-promoted elimination of Ph_2SiO from complex **3**. Although the condensation of primary, secondary, or tertiary silanols to disiloxanes, oligomers, or solid polymers is well documented,⁵ the cleavage of a Si-C bond, such as the Si-C(allyl) bond of **3**, during such a process is unprecedented to our knowledge. Base-catalyzed condensation of silanols presumably proceeds through a silanolate ion intermediate.⁶ Similar silanolate formation in eq 1 would give an overall neutral, zwitterionic $(\eta^3\text{-butadienyl})\text{Pt}^{\text{II}}$ intermediate. Cleavage of the Si-C(allyl) bond in this intermediate might be favored due to stabilization of the leaving fragment through coordination to the Pt(II) ion. At some point in the mechanism, protonation of the allyl fragment occurs to give **4**.

Complex **4** exhibits characteristic NMR resonances expected for $[(\eta^3\text{-butadienyl})\text{Pt}(\text{PEt}_3)_2]^+$ compounds.^{2,7} The ^{31}P NMR spectrum shows two doublets for the nonequivalent phosphine ligands at δ 3.9 and 10.5 with $^2J_{\text{PP}}$ coupling of 12 Hz. The ^1H NMR resonances of the $\eta^3\text{-butadienyl}$ fragment show two singlets for the nonequivalent *tert*-butyl substituents and three separated resonances for the butadienyl protons H^a , H^b , and H^c . Proton-decoupling experiments lead to the unambiguous assignment of the resonance at δ 4.73 to H^c . Difference NOE spectra provide unambiguous assignment of the remaining two resonances at δ 5.25 and 5.70 to H^b and H^a , respectively. NOE enhancements of 9–12% are observed

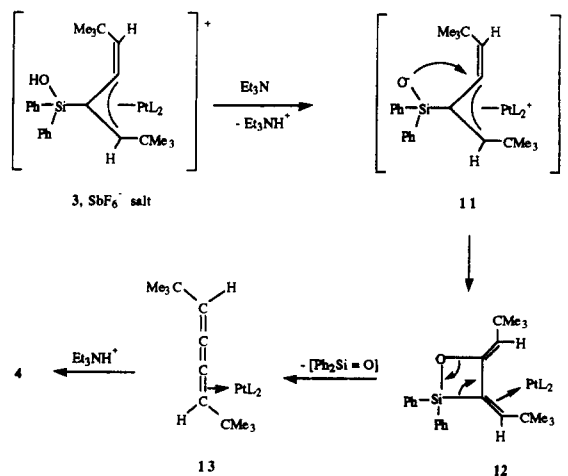
between the resonance of H^b and H^c . No other NOE effects are observed among these three resonances.

The assignment of observed proton resonances of **4** to the two hydrogen atoms in sites H^a and H^b permits a possible independent check on the assignment of the corresponding resonances of **3**. To correlate the proton assignments of **4** to those resonances observed for **3**, the known monodeuterated isotopomer of **3**, **3-*d***₁, obtained from a D_2O trapping experiment, was treated with triethylamine. Before reaction, complex **3-*d***₁ exhibits a butadienyl proton resonance of full intensity centered at δ 5.59 and a Si-OH resonance at higher field. The butadienyl proton resonance at δ 5.51 is absent. After reaction with triethylamine, the isolated isotopomer **4-*d***₁ exhibits the expected resonance at full intensity for the butadienyl proton H^c at δ 4.73. In addition, butadienyl proton resonances of relative intensities of 70:30 are observed at δ 5.25 and 5.70, respectively. These results indicate that the butadienyl proton of **3** obtained from water as a trapping agent is transferred with some selectivity to site H^a of **4** upon reaction with triethylamine. By assuming that deuterium scrambling is limited to the extent observed, we conclude that the proton in site H^a of **3** is that hydrogen atom derived from water. This assignment is opposite to that proposed earlier.²

We account for the formation of the minor isotopomer of **4-*d***₁ by proposing the intermediate formation, to some extent, of a neutral $(\eta^2\text{-butatriene})\text{PtL}_2$ complex through rearrangement of the zwitterionic intermediate formed following cleavage of the Si-C(allyl) bond.⁸ Because the resonance of H^a for this minor isotopomer of **4-*d***₁ reveals a greatly reduced value of J_{PH} from that value observed for **4-*d***₁, we suggest that this H-D exchange is accompanied by a syn-anti rearrangement of the *exo*-alkylidene terminus of the butadienyl ligand. Such a syn-anti arrangement during the formation of unlabeled **4** would not normally be observed due to overlapping resonances for H^a and the relative small abundance of this minor isotopomer.

We now propose a revised mechanism for the formation of the silacyclobutenyl complex, **1**, and the silyl-substituted $\eta^3\text{-butadienyl}$ complexes, **2**, as shown in Scheme I. Regio-

(8) A referee has suggested a specific mechanism by which such a $(\eta^2\text{-butatriene})\text{PtL}_2$ complex could be formed as a precursor to **4**. As shown below, deprotonation of the silanol group of **3** gives the siloxide zwitterionic complex **11**. Internal nucleophilic attack by the siloxide group on the cationic allyl ligand would give a bis(*exo*-alkylidene)siloxetane complex **12** that would eliminate $\text{Ph}_2\text{Si}=\text{O}$ and form the $(\eta^2\text{-butatriene})\text{PtL}_2$ complex, **13**. Protonation of **13** would give **4**.

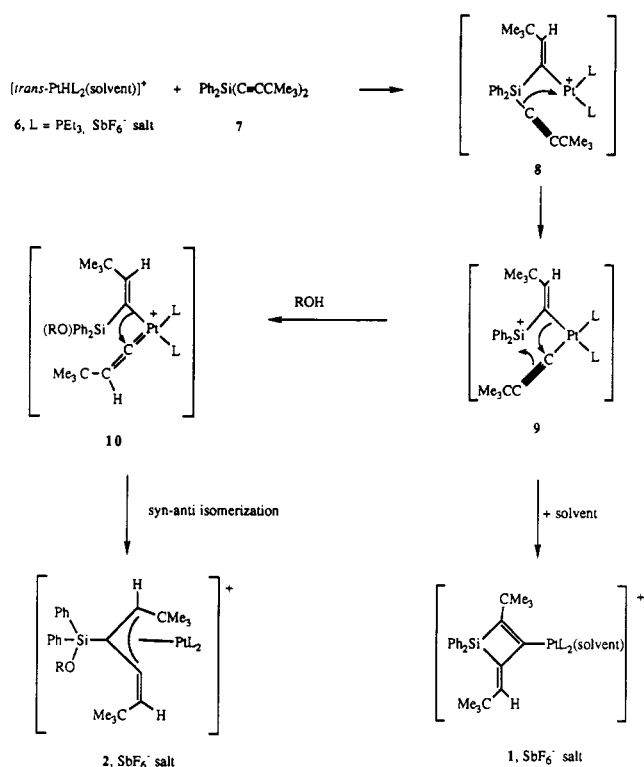


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(7) For examples of other $\eta^3\text{-butadienyl}$ complexes, see: (a) Benyunes, S. A.; Brandt, L.; Green, M.; Parkins, A. W. *Organometallics* 1991, 10, 57. (b) Brisdon, B. J.; Deeth, R. J.; Hodson, A. G. W.; Kemp, C. M.; Mahon, M. F.; Molloy, K. C. *Organometallics* 1991, 10, 1007. (c) Bruce, M. I.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *Organometallics* 1988, 7, 343. (d) Bruce, M. I.; Hambly, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* 1985, 4, 501. (e) Bruce, M. I.; Hambly, T. W.; Snow, M. R.; Swincer, A. G. *Organometallics* 1985, 4, 494. (f) Nesmeyanov, A. N.; Aleksandrov, G. G.; Bokii, N. G.; Zlotina, I. B.; Struchkov, Yu. T.; Kolobova, N. E. *J. Organomet. Chem.* 1976, 111, C9. (g) Nesmeyanov, A. N.; Kolobova, N. E.; Zlotina, I. B.; Lokshin, B. V.; Leshcheva, I. F.; Znobina, G. K.; Anisimov, K. N. *J. Organomet. Chem.* 1976, 110, 339.

Scheme I



and stereoselective addition of the Pt-H bond of 6 to an alkenyl substituent of 7 gives the Pt, Si- μ -alkenylidene intermediate 8. Alkenyl transmetalation from Si to the Pt(II) ion forms the alkenyl complex 9. Electrophilic attack by the silyl cation at the alkenyl ligand and intramolecular nucleophilic addition to C(α) of the alkenyl ligand, as shown, would give the silacyclobutenyl complex, 1. In the presence of hydroxyl species, formation of the Si-OR substituent is favored and protonation of the alkenyl ligand occurs to convert 9 to the cationic η^1 -alkenylidene complex 10. Rotation about the Pt(II)-C(alkenylidene) bond should not be strongly hindered. Intramolecular nucleophilic addition to C(α) of the alkenylidene ligand followed by a η^1 -to- η^3 -allyl transformation and a subsequent syn-anti isomerization would form complexes of type 2.

When complex 4 is treated with chloride, the corresponding neutral (η^1 -butadienyl)Pt^{II} compound, 5, is obtained in good yield. The ¹H NMR data for 5 are consistent with the structure shown and with data reported for other alkenyl or η^1 -butadienyl complexes of Pt(II).⁹ Proton resonances of the butadienyl protons H^a, H^b, and

H^c are observed at δ 5.24, 5.00, and 5.89, respectively. The bromo derivative of 5 has been prepared similarly and has been characterized spectroscopically. The ³¹P NMR data for 5 are consistent with a *trans*-PtL₂Cl geometry. The formation of (η^1 -butadienyl)Ru complexes has been reported recently by Bruce and co-workers.¹⁰

Conclusions

The unusual elimination depicted in eq 1 gives the (η^3 -butadienyl)Pt^{II} complex 4 in which the correct assignment of observed butadienyl proton resonances to hydrogen atoms in sites H^a, H^b, and H^c can be made. When this reaction is conducted with a monodeuterio isotopomer of 3, the assignment of observed butadienyl proton resonances of 3 to hydrogen atoms in sites H^a and H^b can be made with some confidence. These assignments lead to a new proposed mechanism for the formation of the η^3 -butadienyl complexes 2 and of the silacyclobutenyl complex, 1. An important feature of this mechanism is alkenyl transfer from the silicon atom to the platinum ion. This mechanism represents a more unified mechanism for the formation of heterocyclic ligand systems from Pt-H⁺ addition to dialkynylelementa molecules. A similar mechanism has been proposed for the formation of 2-alkylidene-1,2-dihydrophosphate *P*-oxide ligands by this method.¹¹ The extent to which this mechanism applies to the analogous formation of *exo*-alkylidene- η^1 -thiete 1,1-dioxide, - η^1 -1,2-dihydroarsete *As*-oxide, or - η^1 -cyclobutenone ligands is uncertain.¹²

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Supplementary Material Available: ¹H NMR and ³¹P NMR spectra of compounds 4 and 5 and selected ¹H NMR spectra relevant to the assignment of butadienyl proton resonances (12 pages). Ordering information is given on any current masthead page.

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