Rearrangement of a σ-2-(Cycloprop-2-enyl)vinyl- to an η^3-Cyclopentadienylplatinum(II) Complex. Selective Protonolysis of the Platinum−Methyl Bond

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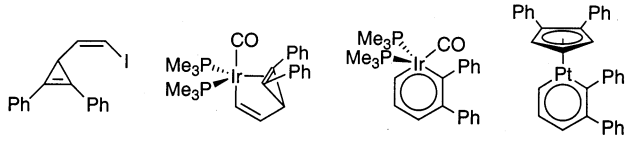
The σ-2-(cycloprop-2-enyl)vinylplatinum(II) complex $(PEt_3)_2Pt(Me)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (**5**) was prepared and characterized by NMR spectroscopy and X-ray crystallography. Treatment of **5** with Bronsted acids results in selective splitting of the Pt−methyl bond to give chloro derivative $(PEt_3)_2Pt(Cl)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (**6**), or the rearranged η^3-diphenylcyclopentadienyl cation $\mathbf{7}^+$, depending on the acid employed. Formation of cation $\mathbf{7}^+$ could also be accomplished by treatment of **6** with $TlPF_6$. Monitoring the protonolysis reactions by NMR spectroscopy at −60 °C, however, showed no evidence for platinabenzene or platinabenzvalene intermediates.

Introduction

In our laboratory we have developed a general method for the synthesis of metallabenzenes[1] and their valence isomers starting from *Z*-3-(2-iodoethenyl)cyclopropenes such as **1**.[2−5] Conversion of this compound to its organolithium derivative followed by ligand metathesis with Vaska-type complexes possessing small and/or electron-donating phosphines yields iridabenzvalenes (e.g., **2**) with a σ-bond to the vinyl group of the vinylcyclopropene and π-coordination of the cyclopropene C=C double bond.[3,4] Cyclopropene−vinylalkylidene rearrangement,[6] initiated either through gentle heating or by use of larger phosphines, leads to formation of the corresponding iridabenzenes (e.g., **3**).[2] As part of our efforts to extend this methodology to other metal complexes, we recently reported the first example of a platinabenzene (**4**)[7] in which an (η^5-cyclopentadienyl)Pt(II) unit is part of the metalla-aromatic ring. Interestingly, both the cyclopentadienyl and metalla-aromatic rings in **4** are derived from **1** in its reaction with (1,5-cod)$PtCl_2$.



1 **2** **3** **4**

To extend this chemistry, we decided to investigate the reactions with other Pt(II) precursors. The *cis*-bis(phosphine)platinum(II) unit, *cis*-$(PR_3)_2Pt$, appeared to be a good choice to attempt the synthesis of platinabenzvalenes and -benzenes, as a broad variety of diorgano complexes of this template with a square-planar coordinated d^8 platinum center are known.[8] This template should geometrically be well suited for accommodation of one σ-/π-coordinated vinylcyclopropene precursor **1** as well as for the incorporation in the metalla-aromatic ring of a putative platinabenzene (Scheme 1). However, a systematic approach to complexes with only one vinylcyclopropene ligand bonded to the *cis*-$(PR_3)_2Pt$ unit is required, as straightforward stoichiometric reaction of dihalogeno complexes with organolithium or Grignard compounds often results in complicated mixtures of starting material, mono- and

Scheme 1. Approach to Platinabenzenes and Valence Isomers through *cis*-$(PR_3)_2Pt(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)Y$ Intermediates

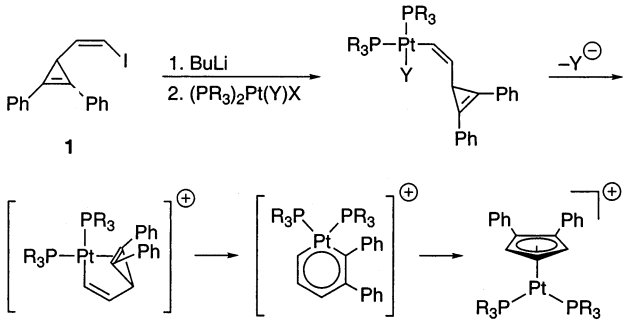


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Table 1. NMR Spectroscopic Data of Compounds 5, 6, and 7·O_2COCF_3[a]

	^{1}H NMR						^{13}C NMR						^{31}P NMR[b]
	Ph group		vinylcyclopropene		PEt_3		vinylcyclopropene		Ph group		PEt_3		PEt_3
5 ($CDCl_3$)	7.79	br d, 4H $^3J_{HH}$ = 7.5	7.24	m, 1H, PtC*H*	1.94	m, 6H	153.1	dd, Pt*C*H $^2J_{PC}$ = 115, 16 $^1J_{PtC}$ = 789	131.2	s	16.9	m, CH_2	9.6 (1825) 8.9 (1766) $^2J_{PP}$ = 13.5
	7.45	t, 4H $^3J_{HH}$ =7.5	6.11	m, 1H, C*H*	1.84	m, 6H	134.8	d, *C*H $^3J_{PC}$ = 4	129.5	s	16.1	m, CH_2	
							119.2	br s, *C*Ph					
	7.33	d, 2H $^3J_{HH}$ = 7.5	3.11	br d, 1H, CH_{Cpr} $^3J_{HH}$ = 8.4	1.14	m, 18H	28.3	d, CH_{Cpr} $^4J_{PC}$ = 6 $^3J_{PtC}$ = 110	128.7	s	8.6	d, CH_3 $^2J_{PC}$ = 6	
			−0.84	dd, 3H, CH_3 $^3J_{PH}$ = 91.2, 7.0 $^2J_{PtH}$ = 574			0.4	dd, CH_3 $^2J_{PC}$ = 100, 17 $^1J_{PtC}$ = 566	127.9	s			
6 ($CDCl_3$)	7.90	br s, 4H	6.64	ddd, 1H, PtC*H* $^3J_{HH}$ = 10.2, 9.0 $^3J_{PH}$ = 22	2.00	m, 12H	142.2	dd, Pt*C*H $^2J_{PC}$ = 107, 11, $^1J_{PtC}$ = 544	130.9	br s	17.3	m, CH_2	14.6 (1671) 7.6 (4147) $^2J_{PP}$ = 14.3
	7.46	t, 4H $^3J_{HH}$ = 7.5	6.14	ddd, 1H, C*H* $^3J_{HH}$ = 10.2, $^4J_{PH}$ = 6, 4.5, $^3J_{PtH}$ = 78	1.12	m, 18H	139.1 118.0	s, *C*H br s, *C*Ph	130.1 128.8	br s br s	15.8	m, CH_2	
	7.32	d, 2H $^3J_{HH}$ = 7.5	3.32	br d, 1H, CH_{Cpr} $^3J_{HH}$ = 9.0			27.9	d, CH_{Cpr} $^4J_{PC}$ = 6 $^3J_{PtC}$ = 70	128.1	s	8.7	d, CH_3 $^2J_{PC}$ = 7	
7·O_2CCF_3 (CD_2Cl_2)	7.41	m, 4H	6.25	t, 1H, C$H_{Cp'}$ $^3J_{HH}$ = 3.0 $^2J_{PtH}$ = 37	1.73	m, 12H	122.4 96.1	s, $CPh_{Cp'}$ s, $CH_{Cp'}$	132.7 129.4	s s	19.6	m, CH_2	1.1 (4229)
	7.27	m, 6H	5.76	br d, 2H, C$H_{Cp'}$ $^3J_{HH}$ = 3.0	0.96	m, 18H	91.1	t, $CH_{Cp'}$ $^2J_{PC}$ = 4	128.9 128.6	s s	8.2	br s, CH_3 $^3J_{PtC}$ = 22	

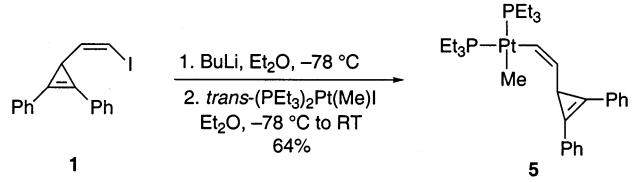
[a] Coupling constants in Hz; data for **7**·BF_4 and **7**·PF_6 are given in the Experimental Section. [b] $^1J_{PtP}$ values in parentheses.

disubstituted products, and low yields.[9,10] One possible route starts with "asymmetric" $(PR_3)_2Pt(X)Y$ (Scheme 1). Only one of the ligands, X, will be substituted for a vinylcyclopropene unit while Y remains unchanged. In the following step Y^- is cleaved from the σ-vinyl compound $(PR_3)_2Pt(Y)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$, allowing for coordination of the cyclopropene double bond. Depending on its stability either this cationic platinabenzvalene or rearranged products such as a platinabenzene or a cyclopentadienyl platinum compound will be isolated. Use of the $(PEt_3)_2Pt$ template and a halogeno ligand as primary leaving group X allows for employing Y = Me as the secondary anionic leaving group. This unexpected choice is based on the high degree of selectivity reported for protonolysis of the chemically different platinum−carbon bonds in $(PEt_3)_2Pt(alkyl)aryl$ compounds.[11,12] We report herein our investigations utilizing the strategy outlined above.

Results and Discussion

Lithiation of vinylcyclopropene **1** with BuLi followed by reaction with *trans*-$(PEt_3)_2Pt(Me)I$[13] yielded *cis*-$(PEt_3)_2Pt(Me)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$, **5** (Scheme 2). While attempts to purify the product by chromatography

Scheme 2



were accompanied by considerable decomposition,[9] **5** was isolated by crystallization from Et_2O/hexanes in 64% yield. In the ^{31}P NMR spectrum ($CDCl_3$) two doublets with nearly identical chemical shifts and $^1J_{PtP}$ coupling constants support the *cis*-$(PEt_3)_2Pt$ configuration in **5** (Table 1). In the ^{1}H NMR spectrum multiplet signals for the vinylic protons are found at δ 7.24 and 6.11. The signal for the cyclopropene sp^3 proton is a broad doublet (δ 3.11), different from the broad, shapeless signal typical for metallabenzvalenes.[3−5] Four signals attributable to the carbon atoms of the σ-coordinated C_5 precursor are found in the ^{13}C NMR spectrum of **5**, along with signals for the aromatic carbons, ethyl groups, and the Pt-bonded methyl group.

Synthesis of **5** provided the desired starting material in which the *cis*-$(PEt_3)_2Pt$ moiety is affixed to one σ-bonded vinylcyclopropene. Selective removal of the secondary leaving group Y = Me was attempted by treatment with an equimolar amount of Bronsted acid. To accomplish this in **5**, however, required discrimination between the Pt−Me bond and the Pt−C(sp^2) bond to the vinylcyclopropene ligand instead of a Pt−C(sp^2) bond to the aryl ligand in $(PEt_3)_2Pt(alkyl)aryl$ compounds.[11,12] After successful cleavage of the Pt−Me bond, products can result from coordination of either the cyclopropene double bond (noncoordinating acid anion case, e.g. BF_4^-) or the acid anion A^- (e.g. Cl^-) by the Pt center. The latter case has the systematic

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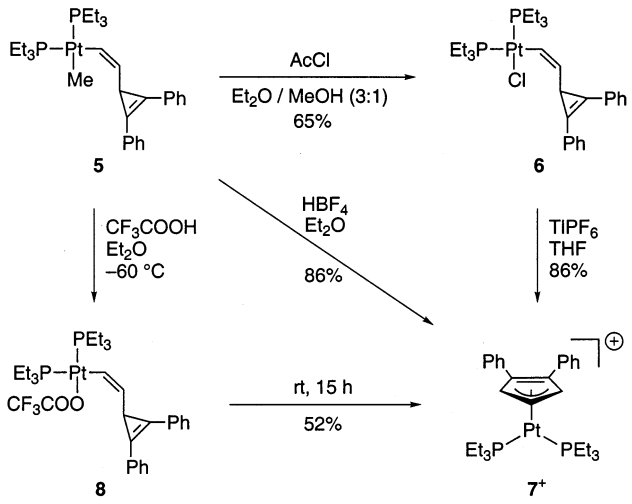
Scheme 3. Reaction of 5 with Bronsted Acid Reagents



advantage that it may allow for the isolation of an intermediate *cis*-$(PEt_3)_2Pt(A)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$. Removal of the anionic leaving group A^- can be performed in a separate second step in the absence of protons, which the desired platinabenzenes and -benzvalenes might well be sensitive toward.

A method for the replacement of methyl for chloride ligands at a Pt(II) center has been introduced by Clark and Manzer.[14] Their in situ generation of hydrochloric acid proved convenient for the conversion of **5** into **6** (Scheme 3). Treatment of a solution of **5** in Et_2O/MeOH (3:1) with an equimolar amount of acetyl chloride led to formation of *cis*-$(PEt_3)_2Pt(Cl)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$, **6**. The compound precipitated from the reaction solution and was isolated in good yield. Small amounts of 1,2-diphenyl-3-vinylcyclopropene and *trans*-$(PEt_3)_2Pt(Me)Cl$, derived from protonolysis of the $Pt{-}C(sp^2)$ bond, as well as *cis*-$(PEt_3)_2PtCl_2$, were formed as byproducts. The ^{31}P NMR spectrum of **6** ($CDCl_3$) shows two doublets with strongly different $^1J_{PtP}$ coupling constants (Table 1); the signal at δ 7.6 is assigned to the phosphorus nucleus trans to the hydrocarbon ligand. Multiplets for the vinyl protons and a doublet signal for the cyclopropenyl proton are observed in the ^1H NMR spectrum, along with the ethyl groups and aromatic protons. The signal of the *ortho* phenyl protons at δ 7.90, however, does not display the expected doublet shape but is extremely broadened. This is mirrored in the ^{13}C NMR spectrum by the *ortho* and *ipso* phenyl carbons as well as by the quaternary carbon atoms of the cyclopropene ring, which give rise to similarly broadened signals. This observation can be attributed to a possible influence of the Pt center on the tethered cyclopropene moiety in close proximity. NMR data for **5** and **6**, however, differ from those of iridabenzvalenes (e.g. **2**), excluding the existence of five-coordinate Pt species in solution.

Crystals suitable for X-ray crystallography were obtained both for the methyl derivative **5** (pentane, 0 °C) and the chloro derivative **6** (Et_2O, 0 °C). Both compounds crystallize without inclusion of solvent molecules, yet in different crystal systems and space

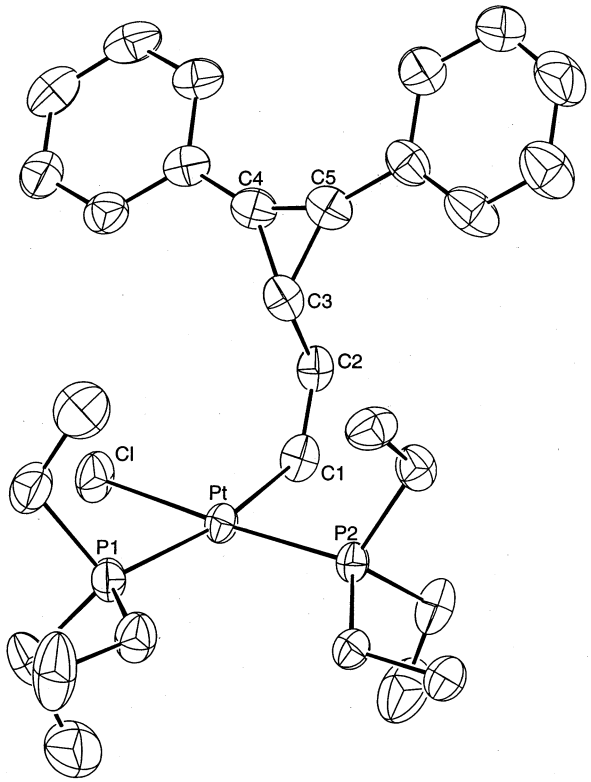


Figure 1. Molecular structure of **6**; ellipsoids are drawn at the 30% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in Compounds 5 and 6

	5 (Y = Me)	**6** (Y = Cl)
Pt−P1	2.305(3)	2.356(2)
Pt−P2	2.290(3)	2.224(2)
Pt−Y	2.119(12)	2.399(2)
Pt−C1	2.043(9)	2.043(8)
C1−C2	1.318(14)	1.334(11)
C2−C3	1.473(15)	1.480(12)
C3−C4	1.535(15)	1.486(12)
C3−C5	1.519(20)	1.495(12)
C4−C5	1.297(21)	1.304(11)
P1−Pt−P2	100.73(9)	105.53(7)
P1−Pt−Y	86.3(3)	84.99(7)
P2−Pt−C1	90.2(3)	84.2(2)
Y−Pt−C1	83.0(4)	85.5(2)
P1−Pt−C1	167.7(3)	169.5(2)
P2−Pt−Y	172.8(3)	169.00(7)
Pt−C1−C2	132.1(8)	125.5(6)
C1−C2−C3	126.2(9)	127.8(7)

groups. The overall features of the solid state structures are very similar (Table 2); therefore, only the structure of **6** is depicted in Figure 1. The vinylcyclopropene moiety is σ-bonded to a square-planar coordinated Pt(II) center. The $Pt{-}C(sp^2)$ bond (2.043 Å) is of the same length in **5** and **6** and significantly shorter than the Pt−Me bond (2.119 Å) in **5**.[15] As expected, the Pt−P bond lengths in **5** are nearly identical, while in **6** the Pt−P1 bond trans to the hydrocarbon ligand is distinctly longer than Pt−P2 trans to the chloro ligand owing to different trans influences (2.356 Å vs 2.224 Å). The angles around the Pt(II) center show a pattern dominated by the steric bulk of the ligands. The *Z*-configuration of the vinylic C=C double bond is retained throughout the complete

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reaction sequence leading from **1** to **6**. The fact that the tethered cyclopropene double bond, which could easily move into a favorable position for η^2-coordination by rotation about the C3−C4 bond (Figure 1), is bent away from the metal center can be attributed to the propensity of Pt(II) for square-planar geometry. Therefore, a well-defined Pt−cyclopropene bonding interaction in solution cannot account for the observed signal broadening in the ^{1}H and ^{13}C NMR spectra of **5** and **6**.

A change in product composition is observed when CF_3CO_2H with the less well coordinating trifluoroacetate anion is used as the proton source (Scheme 3). Addition of 1 equiv of CF_3CO_2H to a light yellow solution of **5** in Et_2O results in a color change to orange-yellow. After the reaction mixture was stirred overnight, **7**·O_2CCF_3 precipitated and was isolated by filtration as an orange solid in 52% yield. Two signals at δ 5.76 and 6.25 (ratio 2:1, Table 1) in the ^{1}H NMR spectrum of this compound show that Pt-mediated rearrangement[16] of the C_5-vinylcyclopropene precursor, presumably through the stages of an intermediate platinabenzvalene and -benzene, which undergoes metal extrusion followed by ring closure,[4,7] to the 1,2-diphenylcyclopentadienyl ligand[17] has taken place. Comparison with the corresponding signals of **4**, in which the 1,2-diphenylcyclopentadienyl ligand is η^5-coordinated to a Pt(II) center (δ 5.09 (1H) and 5.36 (2H); $^2J_{PtH}$ not resolved),[7] shows two differences: (1) a coupling $^2J_{PtH} = 37$ Hz is observed for the signal of the single proton in **7**·O_2CCF_3, and (2) the sequence of chemical shifts is reversed, so that this signal appears downfield of the doublet for the two protons. These two findings advocate allylic η^3- rather than η^5-coordination of the 1,2-diphenylcyclopentadienyl ligand of $\mathbf{7}^+$ in solution.[18,19] To identify possible intermediates, the protonolysis reaction was carried out at −60 °C and monitored by ^{1}H and ^{31}P NMR spectroscopy; *cis*-$(PEt_3)_2Pt(OCOCF_3)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (**8**) formed exclusively as the initial product. While this compound was stable in solution at low temperature, warming resulted in formation of **7**·O_2CCF_3 and of isomerized *trans*-$(PEt_3)_2Pt(OCOCF_3)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ in a ratio of 3:2 after equilibration at room temperature for 15 h. The ^{1}H NMR spectra, however, do not provide any evidence for postulated platinabenzvalene or platinabenzene intermediates in the vinylcyclopropene−cyclopentadienyl rearrangement.

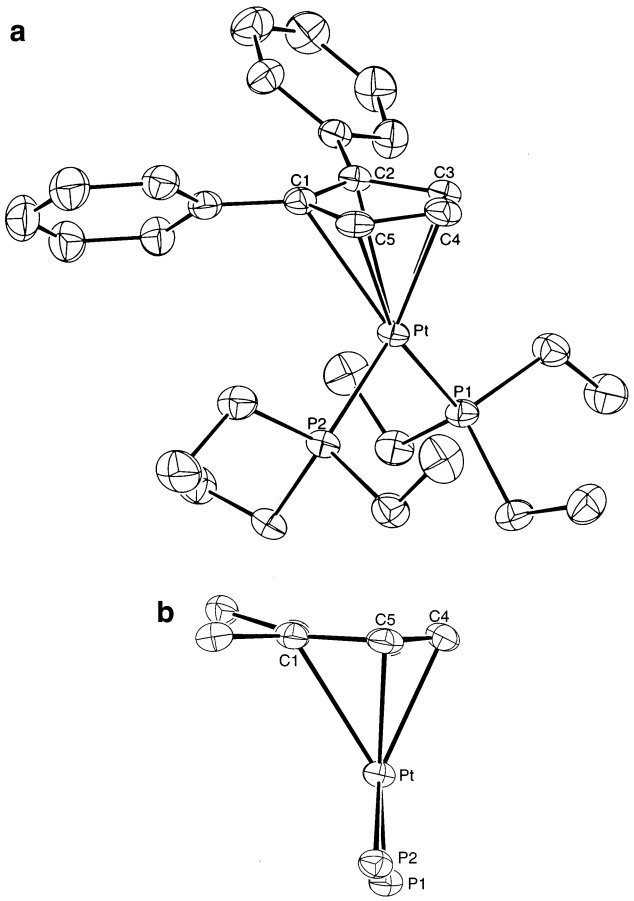

Figure 2. Molecular structure of **7**·O_2CCF_3; ellipsoids are drawn at the 30% probability level. Left: Cation $\mathbf{7}^+$. Right: Reduced view of $\mathbf{7}^+$ parallel to the cyclopentadienyl plain (ethyl and phenyl carbon atoms are omitted for clarity; C2 and C3 are eclipsed by C1 and C5, respectively).

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Cation Portion of 7·O_2CCF_3

Pt−C1	2.508(3)	C1−C2	1.405(4)
Pt−C2	2.587(3)	C2−C3	1.461(4)
Pt−C3	2.319(3)	C1−C5	1.451(4)
Pt−C4	2.258(3)	C3−C4	1.413(5)
Pt−C5	2.252(3)	C4−C5	1.400(5)
Pt−P1	2.255(1)	P1−Pt−P2	97.59(3)
Pt−P2	2.253(1)		

X-ray structure analysis of **7**·O_2CCF_3 was performed on red crystals grown by vapor-phase diffusion of Et_2O into a CH_2Cl_2 solution of the compound. In the solid state the $(PEt_3)_2Pt$ moiety is coordinated to a 1,2-diphenylcyclopentadienyl (Cp′) ligand (Figure 2) with noncoordinated trifluoroacetate serving as the counterion (not shown). Since the $Pt(CH)_{Cp'}$ distances are distinctly shorter than the $Pt(CPh)_{Cp'}$ distances (Table 3), the 1,2-diphenylcyclopentadienyl ligand has to be regarded as η^3-coordinated. Nothing comparable was observed for the structure of **4**[7] or $[CpPt(dppe)]SO_3CF_3$,[20] where all Pt−C distances are of essentially equal length; thus, the authors claim η^5-coordination in both cases. No steric interactions that would force ring-

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slipping are apparent in either case. The distances $CH_{Cp'}-CH_{Cp'}$ and $CPh_{Cp'}-CPh_{Cp'}$ are significantly shorter than $CH_{Cp'}-CPh_{Cp'}$, so that the 1,2-diphenylcyclopentadienyl ligand in $\mathbf{7}^+$ is bisected into the coordinating C_3H_3- and the more distant CPh=CPh unit. Comparison of the η^3-coordinated allyl unit in $\mathbf{7}^+$ with structural data for $[(\eta^3\text{-}C_3H_5)Pt(PCy_3)_2]^+$[21] consequently reveals distinct similarities. Again, the results of solid-state structural analysis are in agreement with NMR data obtained for solutions of $\mathbf{7}^+$, thus excluding that the observed ring-slipping could be regarded as exclusively attributable to crystal packing effects.

Use of HBF_4 with the very poorly coordinating tetrafluoroborate anion did not lead to the product mixture observed with CF_3CO_2H. Addition of 1 equiv of ethereal HBF_4 solution to a solution of **5** in Et_2O cooled to −60 °C was followed by immediate gas evolution and formation of a light yellow precipitate, which turned orange above −30 °C. After the solution was warmed to room temperature and filtered, orange $\mathbf{7}\cdot BF_4$ was isolated in a yield of 86%. Comparison of the NMR spectra of $\mathbf{7}\cdot BF_4$ and $\mathbf{7}\cdot O_2CCF_3$ shows identical chemical shifts and coupling parameters; therefore, the coordination mode of the cyclopentadienyl ligand in $\mathbf{7}^+$ does not depend on the counterion present. Protonolysis with HBF_4 was carried out as a low-temperature NMR experiment in the manner described for the reaction of **5** with CF_3CO_2H, using CD_2Cl_2 as the solvent for reasons of solubility. In this case the reaction led to immediate and exclusive formation of the cyclopentadienyl compound $\mathbf{7}\cdot BF_4$ at −60 °C. Again, no signals attributable to postulated platinabenzvalene and platinabenzene intermediates were found in the ^{1}H NMR spectra.

In compound **6**, the methyl moiety introduced to direct reactivity toward monosubstitution in the synthesis of **5** is replaced by the "conventional" anionic leaving group Y = Cl. Abstraction of this ligand can be effected by a variety of reagents, $TlPF_6$ being one representative example. Reaction of **6** with an equimolar amount of $TlPF_6$ in THF results in immediate formation of cyclopentadienyl complex $\mathbf{7}\cdot PF_6$, indicated by a change of color to red. ^{31}P and ^{1}H NMR spectra of the CD_2Cl_2 extract show that the reaction proceeds cleanly without considerable formation of byproducts.

Studies on the isomerization of *cis*-$(PEt_3)_2Pt(Cl)R$ to the corresponding trans complexes[22] in protic solvents capable of stabilizing chloride anions by solvation postulate a dissociative mechanism involving 14-electron intermediates $[(PEt_3)_2PtR]^+$. Solvolysis should therefore provide a way to open the coordination site occupied by the chloride and avoid use of both Lewis and Bronsted acids stronger than the solvent. The cyclopropene double bond in **6** should be preorganized in an extremely favorable position to trap such an unsaturated intermediate intramolecularly by coordination, leading to ligand exchange rather than cis−trans rearrangement.

Dissolving colorless **6** in CD_3OD at room temperature resulted in an orange solution. Investigation by ^{31}P NMR spectroscopy showed that the starting material, *cis*-$(PEt_3)_2Pt(Cl)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$, was completely converted into two new compounds displaying singlet signals at δ =1.0 (4236 Hz) and 16.1 (2742 Hz). Assignment of the first signal to the cation $\mathbf{7}^+$ is supported by the corresponding cyclopentadienyl resonances in the ^{1}H NMR spectrum. The latter signal belongs to the rearranged complex *trans*-$(PEt_3)_2Pt(Cl)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$. Resonances for the protons of the σ-coordinated vinylcyclopropene ligand of this compound are also present. These results are in good agreement with observations in the low-temperature CF_3CO_2H protonolysis of **5**. They can be interpreted toward competition between the two irreversible processes of cis−trans isomerization and ligand exchange/vinylcyclopropene−cyclopentadienyl rearrangement. No evidence for platinabenzvalene or -benzene intermediates is found even when these mild reaction conditions are applied.

Conclusions

The platinum(II) center in *cis*-$(PEt_3)_2Pt(Me)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (**5**) displays square-planar coordination and does not interact with the C=C double bond of the cyclopropene ring. Protonolysis of **5** with different Bronsted acids shows distinct similarities with corresponding methyl (aryl) compounds in that the Pt−Me bond is cleaved selectively.[12] The observed dependence of the product composition from the acid anion is in accord with the reported influence of anion coordination propensity on the mechanism of this type of reaction.[12] While in the case of poorly coordinating counterions (BF_4^-) salts of cation $\mathbf{7}^+$ were formed exclusively, the main product of protonolysis with hydrochloric acid was complex **6** containing a σ-bonded vinylcyclopropene and coordinated chloride. Reaction of **5** with CF_3CO_2H gave $\mathbf{7}\cdot O_2CCF_3$ as the main product; however, *trans*-$(PEt_3)_2Pt(OCOCF_3)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ was generated as an additional product.

The formation of the $(\eta^3$-1,2-diphenylcyclopentadienyl$)Pt(PEt_3)_2$ cation $\mathbf{7}^+$ is best explained by Pt-mediated rearrangement of the coordinated vinylcyclopropene,[7] presumably passing through the stages of a highly reactive platinabenzvalene and/or platinabenzene (Scheme 1). The role of the Pt center in this process has been established by chloride abstraction from **6** working in the absence of reactants more acidic than methanol, thus excluding mere acid catalysis. Platinabenzvalene or -benzene intermediates could be observed in none of the investigated cases; consequently, the *cis*-$(PEt_3)_2Pt$ unit is not capable of stabilizing a platinabenzene moiety in a way comparable to that of the $(\eta^5$-cyclopentadienyl$)Pt$ unit in **4**.[7] The known examples of square-planar bis(phosphine)platinum complexes with simultaneous coordination of σ-alkyl and carbene ligands, requisite for platinabenzene formation, have the trans configuration.[23] Stabilization through formation of the metalla-aromatic ring system is obviously not sufficient to compensate for adopting the less favorable cis con-

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figuration as metal extrusion with concomitant ring closure to form the cyclopentadienyl ligand occurs instead.

Experimental Section

General. Reactions were carried out using standard Schlenk technique in an inert atmosphere (dry Ar or N_2) when necessary. THF and Et_2O were distilled from Na/benzophenone under nitrogen prior to use. Unless stated otherwise solvents and reagents were purchased commercially and used as received. *Z*-1,2-Diphenyl-3-(2-iodoethenyl)cyclopropene (**1**)[2] and *trans*-$(PEt_3)_2Pt(Me)I$[12] were prepared by literature methods. ^1H (299.94 MHz), ^{13}C (75.43 MHz), and ^{31}P (121.42 MHz) NMR spectra were recorded using a Varian Inova 300 NMR spectrometer. Chemical shifts are expressed in ppm downfield from tetramethylsilane using the residual solvent as internal standard ($CDCl_3$, ^1H 7.27 ppm and ^{13}C 77.2 ppm; CD_2Cl_2, ^1H 5.32 ppm and ^{13}C 54.0 ppm; CD_3OD, ^1H 4.87 and 3.31 ppm and ^{13}C 49.2 ppm; C_4D_8O, ^1H 3.57 and 1.72 ppm and ^{13}C 67.4 and 25.3 ppm). ^{31}P NMR shifts are expressed in ppm downfield to 85% H_3PO_4/H_2O as external standard. Coupling constants are expressed in Hz. IR spectra were recorded using a Nicolet Magna-FTIR 550 spectrometer. UV/vis spectra were recorded in CH_2Cl_2 using a Hewlett-Packard 8453 UV−vis spectrophotometer. Mass spectra were recorded using an Agilent 1100 Series LC/MSD spectrometer (API-ES, APCI). Melting points were determined on a Meltemp II apparatus and are uncorrected. Elemental analyses were performed by Robertson Microlit Laboratories, Inc.

***cis*-$(PEt_3)_2Pt(Me)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (5).** Cyclopropene **1** (546 mg, 1.59 mmol) was dissolved in dry Et_2O (20 mL) under Ar and cooled to −78 °C. BuLi (0.635 mL, 2.5 M in hexanes, 1.60 mmol) was added dropwise and the resulting yellow solution was stirred for 15 min. The cooled lithiate solution was transferred via cannula into a Schlenk flask charged with *trans*-$(PEt_3)_2Pt(Me)I$ (867 mg, 1.51 mmol). The mixture was allowed to warm to room temperature and stirred for 12 h before quenching with a few drops of H_2O and filtration through a thin pad of silica. The yellow filtrate was evaporated to ca. 1 mL, layered with hexanes (5 mL), and stored at 0 °C overnight to yield pale yellow crystals of **5** (550 mg, 55%). A second crop of crystals (93 mg, 9%) was obtained from the mother liquor upon concentration and cooling, for an overall yield of 64%. Crystals suitable for X-ray analysis were obtained by cooling a saturated pentane solution of **5** to 0 °C; mp 109 °C dec. IR (KBr) ν 1811 (m) cm^{-1}. MS (ESI-Pos, MeOH) *m*/*z* 648 (100, M^+ − Me), 663 (32, M^+ − H), 678 (55, M^+ + Me). Anal. Calcd for $C_{30}H_{46}P_2Pt$ (663.71): C, 54.29; H, 6.99; P, 9.33. Found: C, 54.06; H, 6.86; P, 8.89.

***cis*-$(PEt_3)_2Pt(Cl)(Z\text{-}CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (6).** Complex **5** (128 mg, 0.193 mmol) was dissolved in Et_2O/MeOH (3:1, 3 mL) and cooled to −60 °C. Acetyl chloride (0.014 mL, 0.196 mmol) was added dropwise. The resulting yellow solution was stirred at −60 °C for 5 min and then allowed to warm to room temperature. A light-yellow precipitate of **6** formed, which was isolated by filtration after concentration of the mixture to ca. 1 mL. The product was washed with MeOH (0.5 mL) and pentane (1 mL) and dried in vacuo (86 mg, 65%). Colorless crystals suitable for X-ray analysis were obtained by cooling saturated Et_2O solutions of **6** to 0 °C; mp 116 °C dec. IR (KBr) ν 1811 (m) cm^{-1}. MS (ESI-−Pos, MeOH) *m*/*z* 648 (100, M^+ − Cl). Anal. Calcd for $C_{29}H_{43}P_2ClPt$ (684.13): C, 50.91; H, 6.35; P, 9.05. Found: C, 50.86; H, 6.34; P, 9.03.

$[(\eta^3\text{-}C_5H_3Ph_2)Pt(PEt_3)_2]O_2CCF_3$ (7·O_2CCF_3). Complex **5** (134 mg, 0.202 mmol) was dissolved in Et_2O (3 mL) and cooled to −60 °C. CF_3CO_2H (0.016 mL, 0.207 mmol) was added dropwise and the orange solution was stirred at −60 °C for 10 min, then allowed to warm to room temperature. Stirring overnight at room temperature led to formation of a red solution containing an orange precipitate of **7**·O_2CCF_3, which was isolated by filtration, washed with Et_2O (1 mL), and dried in vacuo (61 mg, 40%). A second crop of product (18 mg, 12%) was isolated from the ether filtrate after an additional 24 h of stirring. Compound **7**·O_2CCF_3 crystallized from CH_2Cl_2/Et_2O in red blocks suitable for X-ray structural analysis. IR (KBr) ν 1685 (vs), 1196 (s), 1154 (s), 1116 (s) cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} (ϵ) 460 nm (750). MS (ESI-Pos, MeOH) *m*/*z* 648 (100, M^+ − O_2CCF_3). Anal. Calcd for $C_{31}H_{43}F_3O_2P_2Pt{\cdot}CH_2Cl_2$ (858.64): C, 46.16; H, 5.28. Found: C 46.37, H 5.69.

Protonolysis of 5 with CF_3CO_2H at −60 °C. Complex **5** (20.6 mg, 0.031 mmol) was suspended in THF-d^8 (0.5 mL) in an NMR tube and cooled to −60 °C. CF_3CO_2H (3 μL, 0.039 mmol) was added via syringe. The sample was transferred into the pre-cooled spectrometer and investigated by ^1H and ^{31}P NMR spectroscopy at −60 °C, which revealed exclusive formation of *cis*-$(PEt_3)_2Pt(OCOCF_3)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ (**8**): ^1H NMR (C_4D_8O, 213 K) δ 7.78 (d, 4H, CH_{arom}, $^3J_{HH}$ = 7.0 Hz), 7.41 (pt, 4H, CH_{arom}, $^3J_{HH}$ = 7.3 Hz), 7.28 (t, 2H, CH_{arom}, $^3J_{HH}$ = 7.3 Hz), 6.76 (m, 1H, PtC*H*), 5.92 (ddd, 1H, C*H*, $^3J_{HH}$ = 8.8, 10.5 Hz, $^4J_{PH}$ = 21.1 Hz), 3.41 (d, 1H, CH_{Cpr}, $^3J_{HH}$ = 8.8 Hz), 2.06 (m, 6H, CH_2), 1.81 (m, 6H, CH_2), 1.21 (m, 18H, CH_3). ^{31}P NMR (C_4D_8O, 213 K) δ 2.9 (d, $^2J_{PP}$ = 12 Hz, $^1J_{PtP}$ = 4412 Hz), 19.8 (d, $^2J_{PP}$ = 12 Hz, $^1J_{PtP}$ = 1774 Hz).

The yellow solution turned orange upon warming to room temperature. Additional NMR spectra were taken, showing the complete disappearance of **8** after 15 h and formation of compounds **7**·O_2CCF_3 and *trans*-$(PEt_3)_2Pt(OCOCF_3)(CH{=}CH\text{-}cyclo\text{-}C_3HPh_2)$ in ca. 3:2 ratio. **7**·O_2CCF_3: ^1H NMR (C_4D_8O) δ 6.39 (t, 1H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz, $^2J_{PtH}$ = 37 Hz), 6.02 (br d, 2H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz), 0.98 (m, 18H, CH_3), aromatic C*H* and ethyl CH_2 resonances not assigned. ^{31}P NMR (C_4D_8O) δ 1.5 (s, $^1J_{PtP}$ = 4265 Hz). *trans*-**8**: ^1H NMR (C_4D_8O) δ 6.84 (dt, 1H, PtC*H*, $^3J_{HH}$ = 10.0, $^3J_{PH}$ = 3.0 Hz), 5.57 (t, 1H, C*H*, $^3J_{HH}$ = 10.0 Hz, $^3J_{PtH}$ = 136 Hz), 3.26 (d, 1H, CH_{Cpr}, $^3J_{HH}$ = 10.0 Hz), 1.20 (m, 18H, CH_3), aromatic C*H* and ethyl CH_2 resonances not assigned. ^{31}P NMR (C_4D_8O) δ 19.4 (s, $^1J_{PtP}$ = 2864 Hz).

$[(\eta^3\text{-}C_5H_3Ph_2)Pt(PEt_3)_2]BF_4$ (7·BF_4). Complex **5** (68 mg, 0.102 mmol) was dissolved in Et_2O (3 mL) and cooled to −60 °C. HBF_4 (0.014 mL, 54% in Et_2O, 0.101 mmol) was added dropwise. The resulting yellow suspension was stirred at −60 °C for 15 min, then allowed to warm. At −30 °C the color of the precipitate changed from light yellow to orange. After the mixture was stirred for 2 h at room temperature the orange precipitate of **7**·BF_4 was collected by filtration, washed with Et_2O (2 mL), and dried in vacuo (64 mg, 86%). Compound **7**·BF_4 crystallizes from CH_2Cl_2/Et_2O as red blocks. ^1H NMR (CD_2Cl_2) δ 7.47 (m, 4H), 7.36 (m, 4H), 7.33 (m, 2H), 6.31 (t, 1H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz, $^2J_{PtH}$ = 37 Hz), 5.80 (br d, 2H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz), 1.79 (m, 12H, CH_2), 1.04 (m, 18H, CH_3). ^{13}C NMR (CD_2Cl_2) δ 132.7 (s), 129.4 (s), 128.9 (s), 128.6 (s), 122.5 (s), 96.0 (s), 91.1 (t, $^2J_{PC}$ = 4.0 Hz), 19.7 (m), 8.2 (br s, $^3J_{PtC}$ = 22.0 Hz). ^{31}P NMR (CD_2Cl_2) δ 1.1 (s, $^1J_{PtP}$ = 4229 Hz). IR (KBr) ν 1084 (vs), 1058 (vs) cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} (ϵ) 457 (715) nm. MS (ESI-Pos, MeOH) *m*/*z* 648 (100, M^+ − BF_4). Anal. Calcd for $C_{29}H_{43}BF_4P_2Pt$ (735.48): C, 47.36; H, 5.90; P, 8.42. Found: C, 47.11; H, 5.91; P, 8.41.

$[(\eta^3\text{-}C_5H_3Ph_2)Pt(PEt_3)_2]PF_6$ (7·PF_6). Solid $TlPF_6$ (52 mg, 0.15 mmol) was added to a solution of **6** (96 mg, 0.14 mmol) in THF (3 mL) at room temperature. The mixture turned into an orange suspension immediately. After the mixture was stirred for 15 min the solvent was evaporated and the residue filtered through Celite with CH_2Cl_2 (5 mL). The filtrate was evaporated, washed with Et_2O (10 mL), and dried in vacuo, giving **7**·PF_6 (95 mg, 86%) as a red-orange solid. The compound was crystallized from CH_2Cl_2/Et_2O as red plates. ^1H NMR (CD_2Cl_2) δ 7.47 (m, 4H), 7.33 (m, 6H), 6.32 (t, 1H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz, $^2J_{PtH}$ = 37 Hz), 5.82 (br d, 2H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz), 1.81 (m, 12H, CH_2), 1.04 (m, 18H, CH_3). ^{13}C NMR (CD_2Cl_2) δ 132.4 (s), 129.4 (s), 128.9 (s), 128.6 (s), 122.4 (s), 96.1 (s), 91.1 (t, $^2J_{PC}$ = 6 Hz), 19.7 (m), 8.2 (br s, $^3J_{PtC}$ = 22 Hz). ^{31}P NMR

Table 4. Crystal Data for Complexes 5, 6, and 7·O_2CCF_3

	5	6	7·O_2CCF_3
mol formula	$C_{30}H_{46}P_2Pt$	$C_{29}H_{43}ClP_2Pt$	$C_{31}H_{43}F_3O_2P_2Pt$
mol wt	663.7	684.2	761.7
crystal dimens (mm)	0.11 × 0.13 × 0.32	0.33 × 0.40 × 0.43	0.23 × 0.27 × 0.29
cryst syst	monoclinic	orthorhombic	triclinic
space group	$P2_1$	$P2_12_12_1$	$P\bar{1}$
Z	2	4	2
a (Å)	9.466(2)	10.423(2)	8.4097(6)
b (Å)	16.583(2)	14.476(2)	10.9877(6)
c (Å)	9.8661(13)	20.385(3)	17.8086(11)
α (deg)	90	90	103.727(5)
β (deg)	92.97(2)	90	90.644(6)
γ (deg)	90	90	94.374(5)
V (Å^3)	1546.6(5)	3075.7(9)	1593.2(2)
ρ_{calcd} (g cm^{-3})	1.425	1.477	1.588
μ (cm^{-1})	46.4	47.5	45.3
$2\theta_{max}$ (deg)	54	52	52
scan speed (deg min^{-1})	0.9−4.1	1.0−5.5	1.1−5.5
no. of reflns			
independent	3319	3413	6252
obsd [$I \geq \sigma(I)$]	2712	3386	5904
used in refinement[a]	3258	2995	6252(all)
F_{000}	668	1368	760
rel corr factors	0.824−1.000	0.683−1.000	0.798−1.000
no. of refined parameters	297	299	353
$R(F)/wR$ [$I \geq \sigma(I)$]	0.033/0.034	0.025/0.028	0.022/0.028
$R(F^2)/wR$ (F^2) (all)	0.053/0.070	0.042/0.065	0.036/0.055
residual electron density [e Å^{-3}]	1.77 (near Pt)/−1.73	1.11 (near Pt)/−0.77	0.77 (near Pt)/−0.58

[a] Based on (F^2); all reflections not systematically absent.

(CD_2Cl_2) δ 0.9 (s, $^1J_{PtP}$ = 4236 Hz), −143.4 (sept, PF_6^-, $^1J_{PF}$ = 703 Hz). IR (KBr) ν 841 (vs) cm^{-1}. UV/vis (CH_2Cl_2) λ_{max} (ϵ) 458 (670) nm. MS (ESI-Pos, MeOH) m/z 648 (100, $M^+ - PF_6$). Anal. Calcd for $C_{29}H_{43}F_6P_3Pt$ (793.65): C, 43.89; H, 5.45. Found: C, 44.03; H, 5.21.

Isomerization of 6 in CD_3OD. Complex **6** (7 mg, 0.010 mmol) was suspended in CD_3OD (1 mL) in an NMR tube and sonicated for 30 min. The clear orange solution was investigated by ^{1}H and ^{31}P NMR spectroscopy. **7**·Cl: ^{1}H NMR (CD_3OD) δ 6.39 (t, 1H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz, $^2J_{PtH}$ = 37 Hz), 6.06 (br d, 2H, C$H_{Cp'}$, $^3J_{HH}$ = 3.0 Hz), 1.86 (m, 12H, CH_2), 1.04 (m, 18H, CH_3), aromatic CH resonances not assigned. ^{31}P NMR (CD_3OD) δ 1.0 (s, $^1J_{PtP}$ = 4236 Hz). *trans*-**6**: ^{1}H NMR (CD_3OD) δ 6.89 (dt, 1H, Pt−CH, $^3J_{HH}$ = 10.0, $^3J_{PH}$ = 2.8 Hz), 5.70 (t, 1H, CH, $^3J_{HH}$ = 10.0 Hz, $^3J_{PtH}$ = 143 Hz), 3.20 (d, 1H, CH_{Cpr}, $^3J_{HH}$ = 10.0 Hz), 2.05 (m, 12H, CH_2), 1.24 (m, 18H, CH_3), aromatic CH resonances not assigned. ^{31}P NMR (CD_3OD) δ 16.1 (s, $^1J_{PtP}$ = 2742 Hz).

X-ray Structures of 5, 6, and 7·O_2CCF_3. Data (Table 4) were obtained on an Enraf-Nonius CAD-4 Turbo diffractometer, Mo $K\alpha$ radiation, λ = 0.71073 Å; graphite monochromator; T = 298 K; scan mode $\omega-2\theta$. Structure refinement (C atoms anisotropic, H atoms riding) was accomplished with the teXsan program suite (version 1.7 for SGI workstations).

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Supporting Information Available: X-ray structures of **5**, **6**, and **7**·O_2CCF_3, structure refinement details, and tables of atomic coordinates, thermal parameters, bond lengths, bond angles, torsion angles, and mean planes. This material is available free of charge via the Internet at http://pubs.acs.org.

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