

Generation of (μ -Ethyndiyl)(methylalkoxycarbene)diplatinum Complexes from Reaction of *cis,trans*-[(OC)(C₆F₅)₂Pt(μ - η^2 -C \equiv CSiMe₃)Pt(C \equiv CSiMe₃)L₂] with ROH (R = Et, Me)

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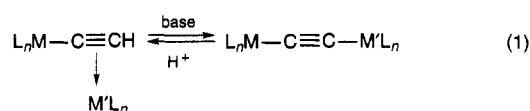
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Reaction of *cis*-[Pt(C₆F₅)₂(CO)(THF)] with *trans*-[Pt(C \equiv CSiMe₃)₂L₂], followed by reaction of the neutral μ - η^2 -monoacetylide-bridged diplatinum intermediates *cis,trans*-[(OC)(C₆F₅)₂Pt(μ - η^2 -C \equiv CSiMe₃)Pt(C \times ba \equiv CSiMe₃)L₂] (L = PPh₃ (**1**), PEt₃ (**2**)) with alcohols (EtOH, MeOH) yields the (μ -ethyndiyl)(methylalkoxycarbene)diplatinum species *cis,trans*-[(OC)(C₆F₅)₂Pt-C \equiv C-Pt{C(Me)OR}L₂] (L = PPh₃, R = Et (**3a**), Me (**3b**); L = PEt₃, R = Et (**4a**), Me (**4b**)), resulting from unexpected rearrangement chemistry involving bridging and terminal (trimethylsilyl)acetylide ligands. The X-ray molecular structure of the complex *cis,trans*-[(OC)(C₆F₅)₂Pt-C \equiv C-Pt{C(Me)OEt}(PEt₃)₂] (**4a**) has been determined. It crystallizes in the monoclinic system, space group *P2₁/c* with *a* = 15.216(3) Å, *b* = 14.197(4) Å, *c* = 18.167(5) Å, β = 107.99(2)°, *V* = 3733(2) Å³, and *Z* = 4. The two coordination planes around the platinum atoms adopt an almost eclipsed arrangement (dihedral angle 6.7°) rather than the staggered form found in similar diplatinum complexes.

Introduction

There is considerable current interest in bimetallic complexes either bridged or connected by an organic group due to their possibly unique role in catalytic processes.¹ Particularly interesting are the ethyndiyl connected complexes [L_{*n*}M-C \equiv C-M'L_{*n*}], which comprise a relatively small but rapidly expanding group of compounds due not only to their potential catalytic activity but also to their role in new areas of electronic and material science.² In general, these types of complexes have been prepared:^{2a,2b} (i) from metal halides or alkyl complexes and alkali-metal acetylides or alkyne

complexes having acidic protons, (ii) from metal alkyls and acetylene, (iii) from dihaloacetylene and carbonylmetalate ions, and (iv) from lithiated metal alkynes and metal halides. Recently, it has been shown that cationic complexes containing μ - η^2 -C \equiv CH bridges can also be easily deprotonated, yielding μ -ethyndiyl compounds^{2b,e,i,g,j} (eq. 1).



Here we wish to report that compounds with two different organometallic platinum fragments linked by a C₂ group can also be prepared from neutral complexes containing a μ - η^2 -C \equiv CSiMe₃ bridging ligand.³

Results and Discussion

As part of our current research on polynuclear platinum complexes with bridging acetylide groups,⁴ we recently reported the synthesis of the unusual zwitterionic complexes [(OC)(C₆F₅)₂Pt⁻(μ - η^2 -C \equiv CR)M⁺L_{*n*}] by reacting *cis*-[Pt(C₆F₅)₂(CO)(THF)] with several metal

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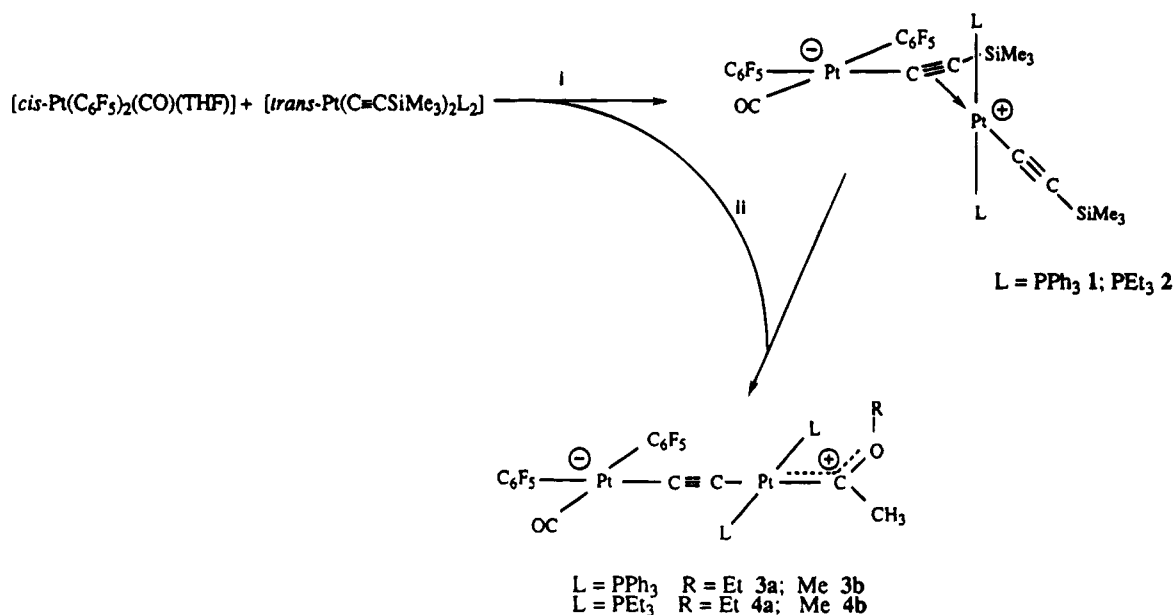
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(3) The complex [Cp'₂Ti(μ - η^2 -C \equiv CSiMe₃)(σ -C \equiv C)Cu]₂ is reported as the product of the reaction of [Cp'₂Ti(C \equiv CSiMe₃)₂] with [Cu(C \equiv CSiMe₃)₂] in ref 14 in: Lang, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 547. However, the reference given is an unpublished work.

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Scheme 1^a

^a Legend: (i) CH₂Cl₂, 1 h; (ii) CH₂Cl₂, 1 h; treatment with ROH (R = Me, Et; 1 h, L = PPh₃; 48 h, L = PEt₃).

alkynyl complexes L_nMC≡CR.^{4e} These species arise from an unexpected alkynylation of the fragment "cis-Pt(C₆F₅)₂(CO)", probably brought about by the enhanced acidity of the metal center in cis-[Pt(C₆F₅)₂(CO)(THF)].^{4e} However, analogous reactions with the silylacetylide complexes rendered very soluble derivatives, which required a very long workup for crystallizing, and some other reactions, which were not explored at that moment, took place depending on the crystallizing solvents. In this paper we report on such processes which render the *cis,trans*-[(OC)(C₆F₅)₂Pt(μ-η²-C≡CSiMe₃)Pt(C≡C-SiMe₃)L₂] (L = PPh₃ (**1**), PEt₃ (**2**)) zwitterionic complexes and upon reaction of these species with alcohols (EtOH or MeOH), which give in moderate yield (μ -ethyndiyl)-(methylalkoxycarbene)diplatinum complexes (Scheme 1).

Reaction of *trans*-[Pt(C≡CSiMe₃)₂L₂] (L = PPh₃, PEt₃) with *cis*-[Pt(C₆F₅)₂(CO)(THF)] in CH₂Cl₂, at room temperature, affords first the expected *cis,trans* zwitterionic complexes **1** (L = PPh₃) and **2** (L = PEt₃), respectively (Scheme 1). Both complexes can be isolated (see Experimental Section) as air-stable microcrystalline white solids in low yields (29%, **1**; 25%, **2**), due to their high solubility in common organic solvents including hexane. Together with **1**, part of the starting material *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] (25%) is also recovered (see Experimental Section). Both compounds **1** and **2** have been characterized by elemental analysis and IR and ¹H, ¹⁹F, and ³¹P NMR spectroscopic data. Thus, their IR spectra show three intense bands (2098, 2070 and 1928 cm⁻¹ for **1** and 2089, 2062, and 1930 cm⁻¹ for **2**) which are respectively assigned to the ν (CO) and terminal and bridging ν (C≡C) vibrations.^{4e} As in previous observations,^{4e} the ν (CO) bands (2098 cm⁻¹ for **1** and 2089 cm⁻¹ for **2**) are substantially lower in energy than that of *cis*-[Pt(C₆F₅)₂(CO)(THF)] (2124 cm⁻¹), suggesting that the formation of the binuclear derivatives results in an increase of the electron density of the carbonyl platinum center (formal alkynylation of "Pt-(C₆F₅)₂(CO)") in accord with the proposed structure. In addition, the shift of the terminal ν (C≡C) from 2041 cm⁻¹ in *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] or 2034 cm⁻¹ in *trans*-[Pt(C≡CSiMe₃)(PEt₃)₂] to 2070 cm⁻¹ in **1** or 2062

cm⁻¹ in **2** is consistent with the expected decrease of the electron density of this platinum center as a consequence of the reaction. Moreover, the ³¹P{¹H} NMR spectra of **1** and **2** show a singlet with platinum satellites consistent with the *trans* arrangement of the [Pt(C≡CSiMe₃)L₂] moiety and their ¹⁹F NMR spectra exhibit two sets of three signals (2:1:2) in accord with the *cis* disposition of the C₆F₅ groups in the *cis*-[Pt-(C₆F₅)₂(CO)] fragment. Finally, two signals for the SiMe₃ protons in the ¹H NMR (δ -0.61 and -0.77 for **1** and δ 0.19 and 0.05 for **2**) support the proposed structure with terminal and bridging C≡CSiMe₃ groups.

When both reactions are monitored in CDCl₃ by ³¹P NMR spectroscopy, it can be detected that the formation of complex **2** is complete in a few minutes (1 or 2 min) and that **2** is the only phosphine-containing compound present in solution. However, when a solution of *cis*-[Pt(C₆F₅)₂(CO)(THF)] is added to a solution of *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂], ³¹P NMR examination of the reaction mixture shows signals due to **1** and to the starting material *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] in a ca. 2:1 molar ratio, plus one small signal at δ 17.9 indicating the presence of another product in very low concentration. Although the identity of the intermediate species remains uncertain due to its relatively low concentration, we tentatively suggest that this signal (δ 17.9 ppm) could be attributed to the initial formation of the binuclear acetylene complex *trans,cis*-[(PPh₃)₂(Me₃-SiC≡C)Pt(μ-C≡CSiMe₃)Pt(C₆F₅)₂(CO)], which rearranges to the final complex **1** through an intramolecular -C≡CSiMe₃ migration between the platinum centers. On standing, this minor product disappears but, surprisingly, after ca. 4 h the ratio of **1** and *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] remains practically unaltered. During our attempts to crystallize **1** with ethanol we observed that a subsequent reaction occurs, leading to the precipitation of a yellow microcrystalline solid. Therefore, we decided to investigate the behavior of the reaction mixtures toward EtOH and MeOH.

Treatment of the reaction mixture containing **2** in CH₂Cl₂ with EtOH and MeOH at room temperature results in the formation of pale yellow solids **4a** and **4b** (see Experimental Section) which according to the

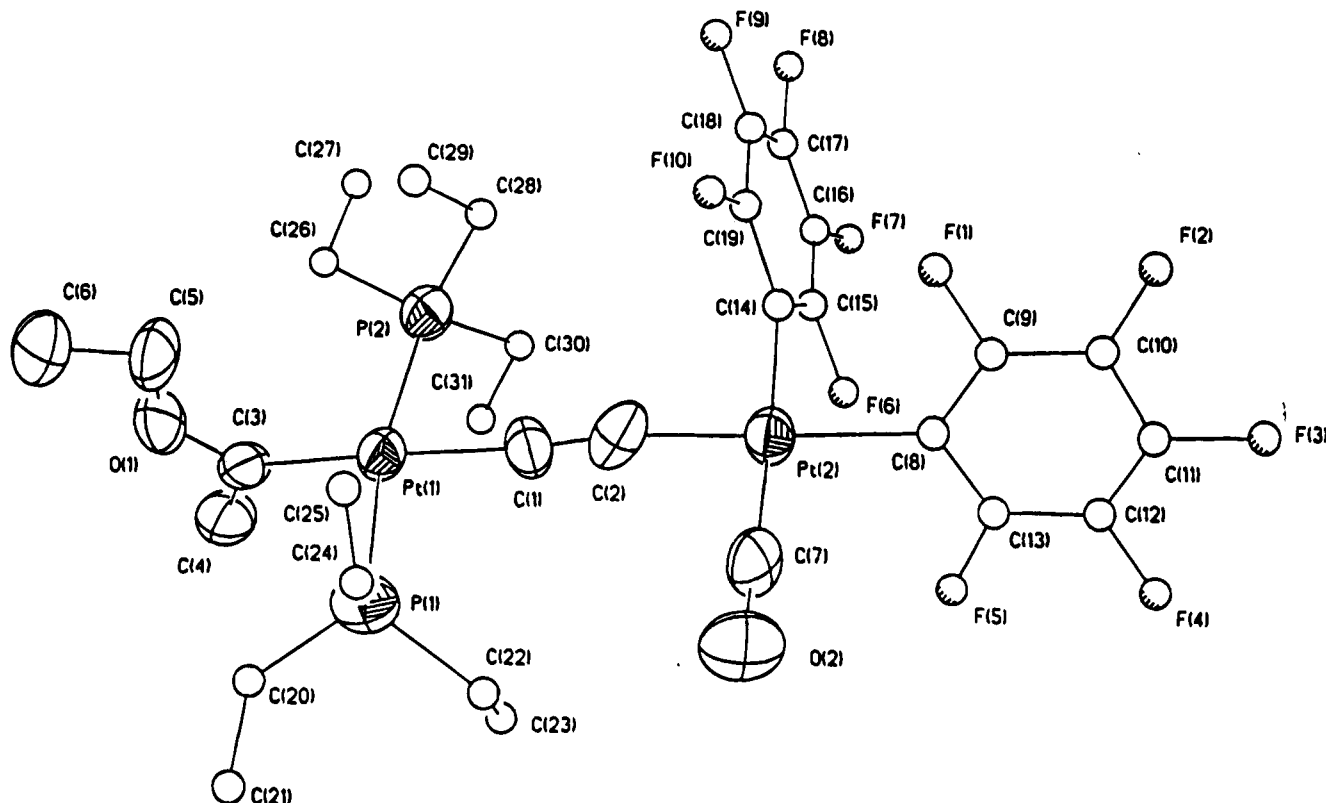


Figure 1. Molecular structure of *cis,trans*-[(OC)(C₆F₅)₂Pt-C≡C-Pt{C(Me)OEt}(PEt₃)₂] (**4a**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **4a**

Pt(1)-P(1)	2.30(1)	Pt(1)-P(2)	2.31(1)
Pt(1)-C(1)	2.02(2)	Pt(1)-C(3)	2.00(3)
Pt(2)-C(2)	2.00(2)	Pt(2)-C(7)	1.83(2)
Pt(2)-C(8)	2.09(2)	Pt(2)-C(14)	2.05(2)
P(1)-C(20)	1.82(3)	P(1)-C(22)	1.89(4)
P(1)-C(24)	1.79(5)	P(2)-C(26)	1.88(3)
P(2)-C(28)	1.81(4)	P(2)-C(30)	1.88(3)
O(1)-C(3)	1.31(3)	O(1)-C(5)	1.47(4)
O(2)-C(7)	1.18(3)	C(1)-C(2)	1.22(3)
C(3)-C(4)	1.46(4)	C(5)-C(6)	1.50(4)
P(1)-Pt(1)-P(2)	169.6(3)	P(1)-Pt(1)-C(1)	86.3(6)
P(2)-Pt(1)-C(1)	83.3(6)	P(1)-Pt(1)-C(3)	94.4(6)
P(2)-Pt(1)-C(3)	96.0(6)	C(1)-Pt(1)-C(3)	175.6(11)
C(2)-Pt(2)-C(7)	88.9(10)	C(2)-Pt(2)-C(8)	177.5(9)
C(7)-Pt(2)-C(8)	93.4(10)	C(2)-Pt(2)-C(14)	87.7(8)
C(7)-Pt(2)-C(14)	176.4(10)	C(8)-Pt(2)-C(14)	90.0(8)
Pt(1)-P(1)-C(20)	116.2(9)	Pt(1)-P(1)-C(22)	115.6(13)
C(20)-P(1)-C(22)	107.4(17)	Pt(1)-P(1)-C(24)	113.1(16)
C(20)-P(1)-C(24)	103.4(25)	C(22)-P(1)-C(24)	99.1(26)
Pt(1)-P(2)-C(26)	113.7(9)	Pt(1)-P(2)-C(28)	114.5(10)
C(26)-P(2)-C(28)	108.2(14)	Pt(1)-P(2)-C(30)	109.9(11)
C(26)-P(2)-C(30)	104.1(13)	C(28)-P(2)-C(30)	105.6(15)
C(3)-O(1)-C(5)	120.1(20)	Pt(1)-C(1)-C(2)	174.6(19)
Pt(2)-C(2)-C(1)	171.7(23)	Pt(1)-C(3)-O(1)	127.2(21)
Pt(1)-C(3)-C(4)	124.9(18)	O(1)-C(3)-C(4)	107.7(22)
O(1)-C(5)-C(6)	108.9(25)	Pt(2)-C(7)-O(2)	178.5(17)
Pt(2)-C(8)-C(9)	125.0(19)	Pt(2)-C(8)-C(13)	121.2(21)
Pt(2)-C(14)-C(15)	123.9(21)	Pt(2)-C(14)-C(19)	125.3(16)

elemental analyses correspond apparently to 1:1 adducts of the desilylated starting material and the alcohols. Similar yellow solids were obtained with the reaction mixture containing **1** and *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)], but in this case the products (**3a,b**) crystallize with solvent, which is supported by elemental analysis and ¹H NMR spectroscopy. The IR and ¹H, ¹⁹F, and ³¹P-¹H NMR spectra of these solids suggest that the complexes obtained from these reactions are the *cis,trans*-(μ -ethynediyl)(methylalkoxycarbene)diplatinum complexes **3** and **4** (Scheme 1).

The IR spectra in Nujol show one strong absorption between 2074 and 2064 cm⁻¹ and a medium band between 2030 and 2019 cm⁻¹ which can be assigned to the ν (CO) and ν (C≡C) frequencies, respectively. Moreover, the two absorptions observed in the 794–778 cm⁻¹ region due to the IR-active vibrations of the x-sensitive modes of the C₆F₅ moiety indicate that both groups are mutually *cis*⁵ (this fact is also confirmed by ¹⁹F NMR spectroscopy).

The absence of silyl groups and the presence of a methylalkoxycarbene ligand is inferred from the ¹H NMR spectra, which do not contain SiMe₃ proton resonances, showing the usual signals attributable to :C(CH₃)OR (R = CH₂CH₃ (**3a**, **4a**), CH₃ (**3b**, **4b**)) ligands (see Experimental Section for data). The ³¹P{¹H} NMR spectra exhibit a singlet with platinum satellites, indicating that the two phosphine ligands are equivalent, the magnitude of ¹J(¹⁹⁵Pt–³¹P) (2357–2669 Hz) being typical of mutually *trans* phosphine groups.⁶

The definitive characterization of **3** and **4** as (μ -ethynediyl)(methylalkoxycarbene)diplatinum compounds came from a single-crystal X-ray diffraction study on complex **4a**. A view of the molecular geometry of this complex is shown in Figure 1. Selected interatomic distances and angles are given in Table 1.

This study confirms the presence of two organometallic moieties "Pt(2)(C₆F₅)₂(CO)" and "Pt(1){C(Me)OEt}-(PEt₃)₂" connected by the ethynediyl group (-C(1)≡C(2)-). The most striking feature of this structure is that the two coordination planes around the platinum atoms are almost coplanar (dihedral angle 6.7°). This fact is in contrast with the staggered geometry found in the only two other (μ -ethynediyl)diplatinum complexes struc-

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turally characterized. In the structure of I(Me₃P)₂-Pt-C≡C-Pt(PMe₃)₂I, reported by Takahashi et al. several years ago,²¹ this angle is 89.8(3)°, and in Cl-(PPh₃)₂Pt-C≡C-Pt(PPh₃)₂Cl, recently reported by Sünkel et al.,^{2c} this angle is 82°. An ideal eclipsed conformation has been also found in the dinuclear (OC)₅-ReC≡CRe(CO)₅ complex.²¹ The Pt(1)-C(1) (2.02(2) Å), Pt(2)-C(2) (2.00(2) Å), and C(1)-C(2) (1.22(3) Å) bond lengths of the fragment Pt(1)-C(1)≡C(2)-Pt(2) are similar to those found in XL₂PtC≡CPtL₂X (X = I, L = PMe₃;²¹ X = Cl, L = PPh₃)^{2c} and compare well with those of other μ -ethyndiyl complexes.^{2b}

The Pt(1)-C(1)-C(2) (174.6(19)°) and C(1)-C(2)-Pt(2) (171.7(23)°) angles indicate, as expected, a nearly linear sp hybridization at C(1) and C(2).

Each of the two moieties also shows the expected structural features. Thus, the Pt(2)-C(pentafluorophenyl) (2.05(2) and 2.09(2) Å) and carbonyl (Pt(2)-C(7) = 1.83(2) Å) distances are similar to those found in *cis*-*trans*-[(OC)(C₆F₅)₂Pt(μ -C≡CPh)Pt(C≡CPh)(PPh₃)₂]^{4e} and the Pt(1)-P distances (2.31(1) and 2.30(1) Å) are similar to those found in the related *trans*-Pt(II) phosphine complexes.^{2c,1} Finally, the structural data of the carbene group formed are typical of platinum(II)-carbene complexes. Thus, the carbene ligand is oriented essentially perpendicular to the local coordination plane of Pt(1) (the dihedral angle formed by the fragment C(3)C(4)O-(1) and the Pt(1) coordination plane is 88.17(2)°), as found in related platinum(II)-carbene complexes.⁷ In addition, the Pt-C(carbene) distance (2.00(3) Å) is comparable to distances found in other platinum carbene complexes.⁷ The high standard deviations in the C-O bond distances in the carbene group preclude any meaningful comparison between them. As is observed in Figure 1, the ethoxy and methyl substituents are anti to one another with the former bent away from Pt(1).

The formation of complexes **3** and **4** can be rationalized according to the mechanism outlined in Scheme 2.

Taking into account that C-Si bonds can easily be cleaved by proton sources⁸ (even with traces of H₂O or alcohol⁹), it seems sensible to assume that the addition of alcohol to **1** or **2** would promote the desilylation of the μ - η^2 -C≡CSiMe₃ group as the first step (i), yielding similar derivatives containing μ - η^2 -ethynyl bridges (**A**). Then, in analogy to the known reactivity of μ - η^2 -C≡CH dinuclear species toward bases^{2b,e,g,i,j,10} and that of terminal acetylide toward acids,¹¹ the resulting intermediates (**A**) could undergo a sequence of two successive steps, deprotonation (ii)/protonation (iii), yielding the zwitterionic μ -ethyndiyl vinylidene species type **C**. Finally, nucleophilic addition of ROH across the vinylidene carbon-carbon double bond, which is a very common process,^{11a-c,12} could produce the resulting (μ -ethyndiyl)(methylalkoxycarbene)diplatinum complexes

3 and **4**. The desilylation of the terminal C≡CSiMe₃ ligand could have taken place at some point during the three initial steps. In favor of the mechanism, we have to point out that Chisholm et al. have previously proposed the formation of similar vinylidene cations or carbocations [Pt-C=CHR]⁺ ↔ [Pt-C⁺=CHR] as intermediates in the formation of cationic alkoxycarbene complexes by treatment of alkynylplatinum compounds with acids in alcohols.¹³

Experimental Section

All manipulations were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures and distilled under dry N₂ before use. The C, H, and N analyses and IR spectra were obtained as described elsewhere.⁴ Proton, ¹³C, ¹⁹F, and ³¹P NMR spectra were recorded on either a Varian Unity 300 or a Bruker ARX 300 spectrometer. Chemical shifts are reported in ppm relative to external standard (SiMe₄, CFC₃, and 85% H₃PO₄). *cis*-[Pt(C₆F₅)₂(CO)(THF)]¹⁴ and *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂]^{4c} were prepared according to literature procedures. *trans*-[Pt(C≡CSiMe₃)₂(PEt₃)₂]¹⁵ was prepared by reacting *cis*-[PtCl₂(PEt₃)₂] with LiC≡CSiMe₃.

***cis,trans*-[(OC)(C₆F₅)₂Pt(μ -C≡CSiMe₃)Pt(C≡CSiMe₃)(PPh₃)₂]** (**1**). To a solution of *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] (0.16 g, 0.17 mmol) in CH₂Cl₂ (15 mL) was added *cis*-[Pt(C₆F₅)₂(CO)(THF)] (0.107 g, 0.17 mmol), and the mixture was stirred at room temperature for 2 h. Evaporation of the resulting yellow solution to dryness and addition of Et₂O (10 mL) cause the precipitation of a white solid, which was identified by IR spectroscopy as the starting material *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] (25% yield).

The resulting filtrate was evaporated to dryness, and after addition of *n*-hexane (4 cm³), compound **1** was obtained as a white solid, yield 29%. Anal. Calcd for C₅₉F₁₀H₄₈O₂Pt₂Si₂: C, 48.16; H, 3.29. Found: C, 47.96; H, 3.38. IR (cm⁻¹): ν (CO) 2098 (s); ν (C≡C) 2070 (s), 1928 (s); ν (C₆F₅)_x-sens 800(s), 787 (s).⁵ ¹H NMR (δ ; CDCl₃): 7.72, 7.41 (m, 30 H, PPh₃); -0.61 (s, 9 H, SiMe₃); -0.77 (s, 9 H, SiMe₃). ¹⁹F NMR (δ ; CDCl₃): -116.8 (dm, F_{ortho}, ³J(Pt-F_{ortho}) = 371 Hz); -117.6 (dm, F_{ortho}, ³J(Pt-F_{ortho}) = 325 Hz); -161.3 (t, F_{para}); -161.6 (t, F_{para}); -164.5 (m, F_{meta}); -165.0 (m, F_{meta}). ³¹P NMR (δ ; CDCl₃): 16.6 (¹J(¹⁹⁵Pt-P) = 2510 Hz).

***cis,trans*-[(OC)(C₆F₅)₂Pt(μ -C≡CSiMe₃)Pt(C≡CSiMe₃)(PEt₃)₂]** (**2**). *cis*-[Pt(C₆F₅)₂(CO)(THF)] (0.15 g, 0.24 mmol) was added to a solution of *trans*-[Pt(C≡CSiMe₃)₂(PEt₃)₂] (0.15 g, 0.24 mmol) in CH₂Cl₂ (8 mL), and the mixture was stirred for

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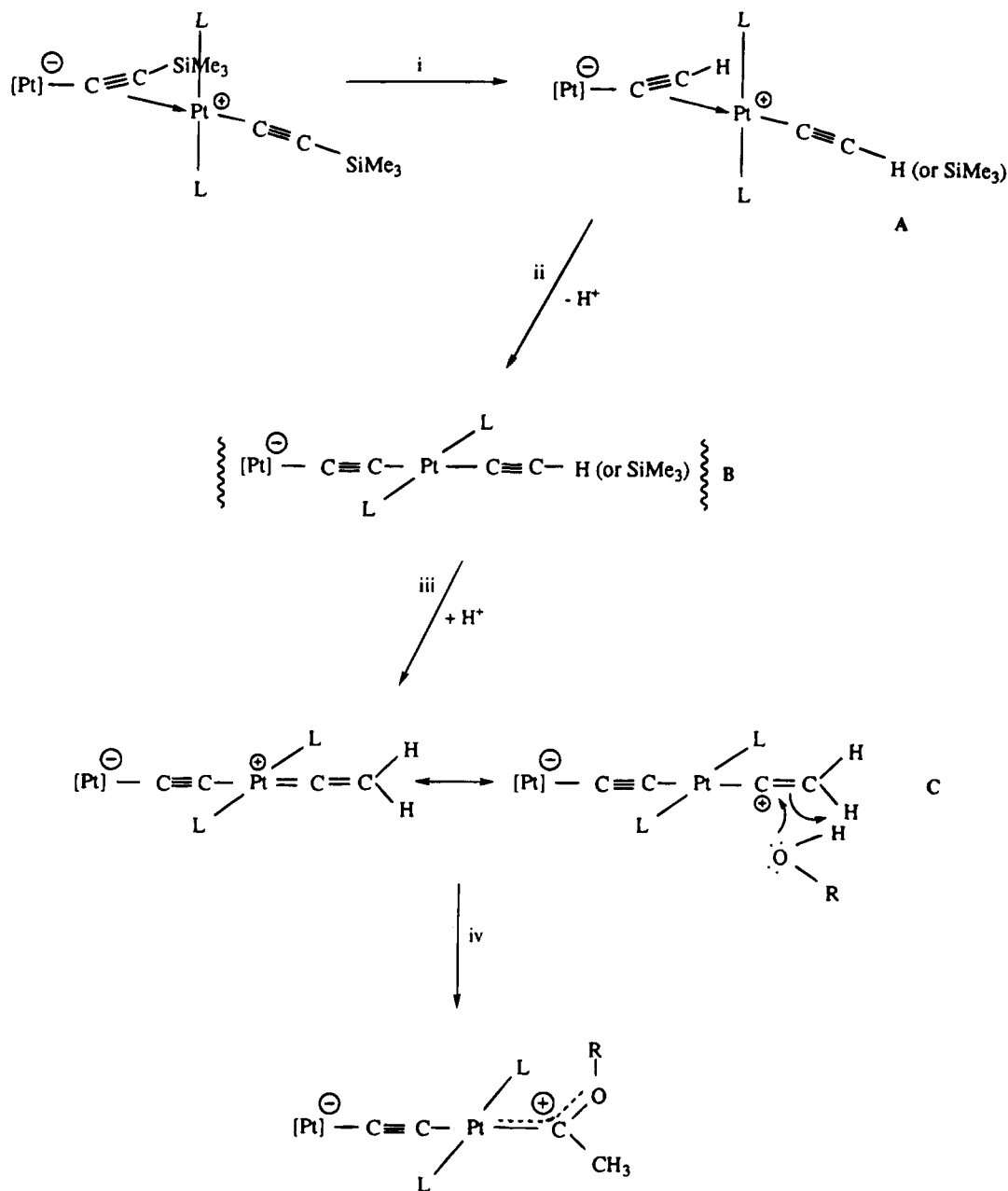
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Scheme 2^a

^a [Pt] = *cis*-Pt(C₆F₅)₂(CO); L = PPh₃, PET₃; ROH = EtOH, MeOH.

1 h. The resulting yellow solution was filtered through Kieselguhr and evaporated to dryness. By addition of *n*-hexane (5 mL) and standing overnight at -30 °C, a white solid, identified as complex **2**, separated; yield 25%. Anal. Calcd for C₃₅F₁₀H₄₈OP₂Pt₂Si₂: C, 35.53; H, 4.1. Found: C, 35.64; H, 3.81. IR (cm⁻¹): ν(CO) 2089 (vs); ν(C≡C) 2062 (vs), 1930 (vs); ν(C₆F₅)_x-sens 799 (s), 787 (s).⁵ ¹H NMR (δ; CDCl₃): 2.03 (m, 12 H, CH₂, PET₃); 1.13 (m, 18 H, CH₃, PET₃); 0.19 (s, 9 H, SiMe₃); 0.05 (s, 9 H, SiMe₃). ¹⁹F NMR (δ; CDCl₃): -117.7 (dd, F_{ortho}, ³J(Pt-F_{ortho}) = 359 Hz); -118.4 (dm, F_{ortho}, ³J(Pt-F_{ortho}) = 358 Hz); -160.2 (t, F_{para}); -161.2 (t, F_{para}); -163.5 (m, F_{meta}); -164.3 (m, F_{meta}). ³¹P NMR (δ; CDCl₃): 11.26 (¹J(¹⁹⁵Pt-P) = 2309 Hz).

***cis,trans*-[(OC)(C₆F₅)₂Pt-C≡C-Pt{C(CH₃)(OEt)}-(PPh₃)₂]₂Me₂CO (3a·2Me₂CO)**. To a CH₂Cl₂ (10 mL) solution of *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] (0.18 g, 0.2 mmol) was added *cis*-[Pt(C₆F₅)₂(CO)(THF)] (0.125 g, 0.2 mmol). The mixture was stirred for 1 h, and the resulting yellow solution was concentrated to ~5 mL. By addition of EtOH (2 mL) and stirring for 2 h, a yellow solid separated. Subsequent recrystallization from Me₂CO-hexane gave complex **3** as a yellow microcrystalline solid. Under these conditions, **3** crystallizes

with two molecules of Me₂CO (observed by ¹H NMR); yield 30%. Anal. Calcd for C₆₁F₁₀H₅₀O₄P₂Pt₂: C, 49.20; H, 3.38. Found: C, 49.36; H, 3.08. IR (cm⁻¹): ν(CO) 2071 (vs); ν(C≡C) 2026 (m); ν(C₆F₅)_x-sens 792 (m), 778 (m).⁵ ¹H NMR (δ; CDCl₃): 7.72, 7.42 (m, 30 H, PPh₃); 4.64 (q, 2H, :CMeOCH₂Me, ³J(H-H) = 7.2 Hz); 2.15 (s, 12 H, CO(CH₃)₂); 1.43 (s, 3H, :C(CH₃)OCH₂Me); 1.10 (t, 3H, :CMeOCH₂CH₃, ³J(H-H) = 7.2 Hz). ¹⁹F NMR (δ; CDCl₃): -116.8 (dd, F_{ortho}, ³J(Pt-F_{ortho}) = 294 Hz); -117.9 (dd, F_{ortho}, ³J(Pt-F_{ortho}) = 412 Hz); -164.3 (t, F_{para}); -166.2 (t, F_{para}); -165.9 (m, F_{meta}); -166.9 (m, F_{meta}). ³¹P (δ; CDCl₃): 14.1 (¹J(¹⁹⁵Pt-P) = 2669 Hz).

***cis,trans*-[(OC)(C₆F₅)₂Pt-C≡C-Pt{C(CH₃)(OMe)}-(PPh₃)₂]₂·2CH₂Cl₂ (3b·2CH₂Cl₂)**. This complex was prepared from *trans*-[Pt(C≡CSiMe₃)₂(PPh₃)₂] (0.16 g, 0.17 mmol) and *cis*-[Pt(C₆F₅)₂(CO)(THF)] (0.11 g, 0.17 mmol) as described for **3a**. Under these conditions, **3b** crystallizes with two molecules of CH₂Cl₂; yield 26%. Anal. Calcd for C₅₆Cl₄F₁₀H₄₀O₂P₂Pt₂: C, 44.00; H, 2.64. Found: C, 44.42; H, 2.60. IR (cm⁻¹): ν(CO) 2068 (vs); ν(C≡C) 2030 (m); ν(C₆F₅)_x-sens 793 (s), 779 (s).⁵ ¹H NMR (δ; CDCl₃): 7.74, 7.45 (m, 30 H, PPh₃); 4.33 (s, 3H, :CMeOCH₃); 1.42 (s, 3H, :C(CH₃)OMe). ¹⁹F NMR (δ; CDCl₃): -116.3 (dd, F_{ortho},

Table 2. Crystallographic Data for Complex 4a

formula	C ₃₁ H ₃₈ O ₂ F ₁₀ P ₂ Pt ₂
fw	1084.7
color	yellow
cryst size, mm	0.17 × 0.28 × 0.30
space group	P2 ₁ /c
a, Å	15.216(3)
b, Å	14.197(4)
c, Å	18.167(5)
β, deg	107.99(2)
V, Å ³	3773(2)
temp, °C	20 ± 1
data collected	±h, ±k, ±l
Z	4
density (calcd), g cm ⁻³	1.93
F(000)	2064
abs coeff, cm ⁻¹	76.47
total no. of rflns collected	4687 + 216 ψ scan
2θ range, deg	3.0–43.0
no. of indep rflns	4295
no. of obsd rflns	2645 (F > 4.0σ(F))
final R indices (obsd data)	R = 0.0504, R _w = 0.0587
weighting scheme	w ⁻¹ = σ ² (F) + 0.0017F ²
largest shift/esd	0.001
largest diff peak, e Å ⁻³	0.77
transmissn factors: min, max	0.468, 1.000
no. of params refined	424

³J(Pt–F_{ortho}) = 310 Hz); –117.3 (dm, F_{ortho}, ³J(Pt–F_{ortho}) = 419 Hz); –164.0 (t, F_{para}); –165.5 (m, overlap of a signal due to a F_{para} and a F_{meta}); –166.3 (m, F_{meta}). ³¹P NMR (δ; CDCl₃): 14.1 (¹J(¹⁹⁵Pt–P) = 2656 Hz, ⁴J(¹⁹⁵Pt–P) = 14.4 Hz).

cis,trans-[(OC)(C₆F₅)₂Pt–C≡C–Pt{C(CH₃)(OEt)}-(PEt₃)₂] (4a). To a solution of *trans*-[Pt(C≡CSiMe₃)₂(PEt₃)₂] (0.156 g, 0.24 mmol) in CH₂Cl₂ (6 mL) was added *cis*-[Pt(C₆F₅)₂(CO)(THF)] (0.15 g, 0.24 mmol), and the mixture was stirred for 30 min. The resulting yellow solution was treated with EtOH (4 mL), stirred for 48 h, and evaporated to dryness. The addition of Et₂O (5 mL) afforded 4a as a pale yellow solid, yield 54%. Anal. Calcd for C₃₁H₃₈O₂F₁₀P₂Pt₂: C, 34.33; H, 3.53. Found: C, 34.41; H, 3.44. IR (cm⁻¹): ν(CO) 2066 (vs); ν(C≡C) 2021 (m); ν(C₆F₅)_{x-sens} 792 (s), 781 (s).⁵ ¹H NMR (δ; CDCl₃): 5.07 (q, 2H, :CMeOCH₂Me, ³J(H–H) = 7.2 Hz); 2.45 (s, 3H, :C(CH₃)OCH₂Me); 1.93 (m, 12 H, CH₂, PEt₃); 1.59 (t, 3H, :CMeOCH₂CH₃, ³J(H–H) = 7.2 Hz); 1.07 (m, 18H, CH₃, PEt₃). ¹³C NMR (δ; CDCl₃): 309.8 (t, ²J(P–C) = 7.3 Hz, Pt=C); 173.3 (t, ²J(P–C) = 4.5 Hz, C=Pt–C≡C); 149–133 (m, C₆F₅); 80.2 (s, ³J(Pt–C) = 77 Hz, OCH₂CH₃); 43.7 (s, ²J(Pt–C) = 98.5 Hz, CH₃C=Pt); 16.0 (¹J(P–C) + ³J(P–C) ≈ ²J(Pt–C) ≈ 37 Hz, PCH₂); 13.9 (s, OCH₂CH₃); 7.94 (s, ³J(Pt–C) = 25 Hz, PCH₂CH₃). ¹⁹F NMR (δ; CDCl₃): –116.1 (d, F_{ortho}, ³J(Pt–F_{ortho}) = 311 Hz); –117.3 (d, F_{ortho}, ³J(Pt–F_{ortho}) = 416 Hz); –163.2 (t, F_{para}); –164.6 (t, F_{para}); –164.9 (m, F_{meta}); –166.0 (m, F_{meta}). ³¹P NMR (δ; CDCl₃): 14.7 (¹J(¹⁹⁵Pt–P) = 2373 Hz).

cis,trans-[(OC)(C₆F₅)₂Pt–C≡C–Pt{C(CH₃)(OMe)}-(PEt₃)₂] (4b). This complex was prepared as a pale yellow solid by a method similar to that for 4a, but MeOH was used instead of EtOH; yield 26%. Anal. Calcd for C₃₀H₃₆O₂F₁₀Pt₂: C, 33.66; H, 3.39. Found: C, 33.57; H, 3.45. IR (cm⁻¹): ν(CO) 2074 (vs); ν(C≡C) 2019 (m); ν(C₆F₅)_{x-sens} 794 (s), 782 (s).⁵ ¹H NMR (δ; CDCl₃): 4.71 (s, 3H, :CMeOCH₃); 2.46 (s, 3H, :C(CH₃)OMe); 1.93 (m, 12 H, CH₂, PEt₃); 1.07 (m, 18H, CH₃, PEt₃). ¹⁹F NMR (δ; CDCl₃): –116.6 (dm, F_{ortho}, ³J(Pt–F_{ortho}) = 310 Hz); –117.8 (dm, F_{ortho}, ³J(Pt–F_{ortho}) = 416 Hz); –163.6 (t, F_{para}); –165.1 (t, F_{para}); –165.4 (m, F_{meta}); –166.5 (m, F_{meta}). ³¹P NMR (δ; CDCl₃): 15.35 (¹J(¹⁹⁵Pt–P) = 2357 Hz).

Crystal Structure Determination of the Complex cis,trans-[(OC)(C₆F₅)₂Pt–C≡C–Pt{C(CH₃)(OEt)}(PEt₃)₂] (4a). Suitable crystals of 4a for X-ray studies were obtained by slow diffusion of *n*-hexane into a THF solution of 4a at –30 °C.

Crystallographic data were collected by Crystalalytics (Lincoln, NE) on a four-circle Nicolet (Siemens) autodiffractometer using graphite-monochromated Mo Kα X-radiation (0.710 731

Table 3. Atomic Coordinates (×10⁴) for Complex 4a

	x	y	z
Pt(1)	2983(1)	1227(1)	2047(1)
Pt(2)	2867(1)	4480(1)	3372(1)
P(1)	4269(5)	894(5)	3075(4)
P(2)	1682(5)	1812(4)	1135(4)
O(1)	2652(13)	–749(11)	1475(10)
O(2)	4616(14)	3874(14)	4585(10)
C(1)	2940(17)	2469(16)	2581(14)
C(2)	2838(18)	3222(16)	2866(13)
C(3)	3072(16)	50(17)	1466(14)
C(4)	3582(18)	–36(18)	910(17)
C(5)	2049(21)	–86(16)	1966(17)
C(6)	1979(23)	–1886(18)	2133(22)
C(7)	3931(20)	4121(16)	4116(14)
C(8)	2866(18)	5818(15)	3854(14)
C(9)	2187(19)	6159(17)	4139(13)
C(10)	2189(21)	7025(21)	4486(14)
C(11)	2940(26)	7594(18)	4513(18)
C(12)	3594(19)	7300(16)	4244(14)
C(13)	3572(19)	6441(18)	3916(13)
F(1)	1463(11)	5570(10)	4120(10)
F(2)	1500(13)	7286(12)	4750(11)
F(3)	2944(13)	8452(11)	4866(13)
F(4)	4321(12)	7892(10)	4312(11)
F(5)	4279(11)	6221(10)	3676(9)
C(14)	1690(17)	4814(14)	2497(12)
C(15)	1673(22)	5394(18)	1894(17)
C(16)	929(30)	5626(22)	1264(21)
C(17)	110(30)	5235(24)	1254(16)
C(18)	23(19)	4684(21)	1810(19)
C(19)	782(15)	4458(16)	2419(15)
F(6)	2510(13)	5794(10)	1886(9)
F(7)	980(16)	6220(14)	723(10)
F(8)	–688(14)	5464(15)	667(11)
F(9)	–801(12)	4289(14)	1807(11)
F(10)	705(11)	3900(11)	2973(9)
C(20)	4950(22)	–113(19)	2960(16)
C(21)	5803(22)	–388(23)	3675(23)
C(22)	5093(26)	1908(31)	3437(28)
C(23)	5416(31)	2242(36)	2868(33)
C(24)	4001(36)	631(53)	3948(21)
C(25)	3197(32)	486(31)	4023(18)
C(26)	1155(21)	973(21)	312(16)
C(27)	345(21)	1391(21)	–296(18)
C(28)	782(22)	2199(20)	1521(18)
C(29)	523(23)	1440(24)	2039(21)
C(30)	1993(25)	2874(20)	651(17)
C(31)	2715(31)	2626(27)	226(22)

Å). Crystallographic details are summarized in Table 2. Cell constants were refined from 2θ values of 15 reflections including Friedel pairs (2θ > 25°). An absorption correction based on ψ scans was applied. Six standard reflections were measured every 300 reflections but showed no decay. The structure was solved by Patterson synthesis and subsequent difference Fourier maps (SHELXTL-PLUS¹⁶). All non-hydrogen atoms were refined anisotropically. All calculations were done on a Local Area VAX Cluster/VMS V.5.5. Positional parameters are given in Table 3.

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Supplementary Material Available: Tables of bond distances, bond angles, and isotropic and anisotropic thermal parameters (5 pages). Ordering information is given on any current masthead page.

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(16) SHELXTL-PLUS, Release 4.21/v; Siemens Analytical X-ray Instruments, Inc., 1990.