Unprecedented Reactivity of 1-Alkynes with 2-Chloroethanol Promoted by Cationic Solvento(trifluoromethyl)platinum(II) Complexes. Synthesis of β -Alkoxyalkenyl Derivatives and X-ray Structure of *trans*- $[Pt{C(H)=C(Ph)OCH_2CH_2Cl}(CO)(PPh_3)_2][BF_4]\cdot Et_2O^{\dagger}$

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Reactions at ambient temperature of the solvento cationic trifluoromethyl complex *trans*- $[Pt(CF_3)(PPh_3)_2(solv)][BF_4]$ with 1.5 equiv of 1-alkynes RC=CH (R = Ph, p-tolyl) and 2-chloroethanol afford in high yield the β -alkoxyalkenyl complexes *trans*-[Pt{C(H)=C(R)- $OCH_2CH_2Cl_2(CO)(PPh_3)_2[BF_4]$ (R = Ph (1), p-tolyl (2)). In these reactions the CF₃ group is also converted to a CO ligand. Complexes 1 and 2 were characterized by spectroscopic techniques and 1 also by an X-ray diffraction analysis. Reaction of the alkynyl complex *trans*-[Pt(CF₃)(C \equiv C-*p*-tolyl)(PPh₃)₂] with 2-chloroethanol and 1 equiv of HBF₄ gives the acetylide-carbonyl derivative trans- $[Pt(C \equiv C-p-tolyl)(CO)(PPh_3)_2][BF_4]$ (3), which was also formed by reaction of *trans*- $[Pt(CF_3)(C = C-p-tolyl)(PPh_3)_2]$ with aqueous HBF₄. Possible mechanisms of these reactions are discussed.

Introduction

We have previously reported that unsaturated ligands such as CO,¹ RNC,² and RCN³ in carbonyl, isocyanide, and nitrile complexes of various transition metals undergo cyclization reactions with 2-chloroethanol or oxirane to form five-membered dioxy-, aminooxy-, and N-coordinated 2-oxazoline derivatives, respectively. Recently, this reaction chemistry has been extended to Pt^{II}-alkyne and -alkynyl complexes. Thus, it has been shown for instance that the reaction of PhC≡CH in 2-chloroethanol with the solvento cationic complex *trans*-[Pt(Me)(PPh₃)₂(solv)][BF₄] (eq 1) or the reactions

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$\begin{bmatrix} PPh_3 \\ I \\ CH_3 - Pt - solv \\ I \\ PPh_3 \end{bmatrix}$	BF ₄ PhC=CH, +n-BuLi 2-chloroethanol, RT, 15 min		
	$\begin{bmatrix} PPh_{3} & CH_{2}Ph \\ I & CH_{3}-Pt = C \\ I & O(CH_{2})_{2}CI \end{bmatrix}$	BF ₄	(1)

of the halo alcohols $HO(CH_2)_nCl$ (n = 2,3) in the presence of 1 equiv of HBF₄ with the acetylides trans- $[Pt(CH_3)(C \equiv CR)(PPh_3)_2]$ (R = Ph, *p*-tolyl) (eq 2) afforded

$$CH_{3} - \Pr_{l} - C \equiv C - R \xrightarrow{+ HO - (CH_{2})_{n} - Cl, + HBF_{4}(Et_{2}O) \atop benzene, RT, overnight} + BF_{4}(Et_{2}O) \xrightarrow{+ HBF_{4}(Et_{2}O) \atop benzene, RT, overnight} \left[\begin{array}{c} PPh_{3} & CH_{2}R \\ CH_{3} - Pt = C \\ Ph_{3} & O(CH_{2})_{n}Cl \end{array} \right] BF_{4} (2)$$

alkylalkoxycarbene complexes, formally originating from the addition of the halo alcohol at the α -carbon atom of the alkyne or the alkynyl, with no evidence of cyclization reaction products as found for other C- or N-unsaturated

[†] Dedicated to Professor Warren R. Roper on the occasion of his 60th birthday.

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ligands.⁴ In this respect the reactions of halo alcohols with Pt^{II} -alkynyl and –alkyne complexes parallel those reported in the literature with MeOH.⁵ On the other hand, similar reactions with oxirane gave cyclic oxy-carbene complexes, as illustrated in eq 3.⁶

$$CH_{3} - \underbrace{PPh_{3}}_{Pt} - C \equiv C - R \xrightarrow{HBF_{4}, O \swarrow}_{0 \circ C, 3 h}$$

$$\begin{bmatrix} PPh_{3} & H & R \\ PPh_{3} & H & R \\ CH_{3} - Pt = C & H & H & H \\ PPh_{3} & H & H & H \\ PPh_{3} & H & H & H \\ (H_{3} - Pt = C) & H & H & H \\ (H_{3} - Pt = C) & H & H & H \\ (H_{3} - Pt = C) & H & H \\ PPh_{3} & H & H \\ (R = p-tolyl) &$$

During these investigations, we found that the reactions of unsaturated cationic trifluoromethyl complexes of Pt(II) of the type *trans*-[Pt(CF₃)(PPh₃)₂(solv)][BF₄] with 1-alkynes (RC=CH, R = Ph, *p*-tolyl) and 2-chloroethanol proceed differently from those of the parent CH₃ derivatives (eq 1), since Pt(II) complexes containing a β -alkoxyalkenyl (or vinyl ether) ligand, $-C(H)=C(OCH_2-CH_2Cl)R$, formally originating from the addition of the halo alcohol at the β -carbon atom of the alkyne ligand, are formed. Also, the reaction of the acetylide complex *trans*-[Pt(CF₃)(C=C-R)(PPh₃)₂] (R = *p*-tolyl) with 2chloroethanol in the presence of HBF₄ proceeds differently from that of the parent CH₃ derivative (eq 2). The results of this study are reported herein.

Experimental Section

General Procedures and Materials. All reactions were carried out under an N₂ atmosphere. The solvents were of reagent grade and were used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer (abbreviations: s = strong, m = medium). Proton and carbon-13 NMR spectra were obtained on a Bruker AC-200 spectrometer. ¹H NMR shifts were recorded relative to residual ¹H resonance in the deuterated solvent: CDCl₃, δ 7.23. The ¹³C{¹H} NMR shifts are given relative to the solvent resonance: CDCl₃, δ 77.0. The ³¹P{¹H} NMR spectra (CDCl₃) were run on a Varian FT 80-A spectrometer; the chemical shift is referenced to external 85% H₃PO₄ with the downfield value taken as positive. The ¹⁹F NMR spectrum (CDCl₃) was run on a Varian FT 80-A spectrometer, with CFCl₃ as internal reference. In all the NMR spectra chemical shifts are in ppm and J values are in Hz (abbreviations used: s = singlet, t =triplet, q = quartet). The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected. Phenylacetylene and *p*-tolylacetylene were commercially available products and were used as received.

The complex *trans*- $[Pt(CF_3)Br(PPh_3)_2]^7$ was prepared according to the literature procedure, while *trans*- $[Pt(CF_3)-(C\equiv C-p-tolyl)(PPh_3)_2]$ was prepared as follows. A suspension of *trans*- $[Pt(CF_3)Br(PPh_3)_2]$ (302 mg, 0.348 mmol) in acetone (50 mL) at room temperature was treated with a 0.244 M

solution of AgBF₄ (1.56 mL, 0.348 mmol) in acetone. The reaction mixture was stirred for 1 h; then the precipitate of AgCl was filtered off and the solution was treated with NEt₃ (73 μ L, 0.522 mmol) and *p*-tolylacetylene (132 μ L, 1.044 mmol). The reaction mixture was stirred overnight to give a brown precipitate. After filtration, the solid residue was treated with CH₂Cl₂ (25 mL) and the resulting filtered solution was reduced to a small volume under reduced pressure. Addition of *n*-pentane (15 mL) gave a white solid, which was filtered, washed with *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 110 mg (35%). Mp: 209–211 °C dec. Anal. Calcd for C₄₆H₃₇F₃P₂Pt·CH₂Cl₂: C, 57.09; H, 3.98. Found: C, 58.06; H, 4.00. IR (Nujol, cm⁻¹): ν (C=C) 2113 (s). ¹H NMR: 2.11 [s, 3H, CH₃]. ¹⁹F NMR: -16.33 [t, ²*J*(FPt) 469, ³*J*(FP) 14.6, CF₃]. ³¹P{¹H} NMR: 21.80 [q, ¹*J*(PPt) 2898, ³*J*(PF) 14.62].

The same complex can also be prepared using *n*-BuLi instead of NEt₃. The cationic solvento complex *trans*-[Pt(CF₃)-(PPh₃)₂(solv)][BF₄], obtained from *trans*-[Pt(CF₃)Cl(PPh₃)₂]⁷ (750 mg, 0.91 mmol) and a 0.46 M solution of AgBF₄ (2 mL, 0.91 mmol) in acetone (40 mL), was dissolved in 30 mL of THF, and the suspension was treated with *n*-BuLi (0.85 mL, 1.365 mmol) and *p*-tolylacetylene (0.346 mL, 2.73 mmol). The solution became pale yellow and was stirred for 2 h at room temperature. During this time a precipitate formed. After filtration, the solid residue was treated with CH₂Cl₂ (20 mL) and the resulting filtered solution was reduced to a small volume under reduced pressure. Addition of *n*-pentane (20 mL) gave a white solid, which was filtered, washed with *n*-pentane (3 × 5 mL), and dried under vacuum. Yield: 0.386 g (47%).

Synthesis of trans-[Pt{C(H)=C(Ph)OCH2CH2Cl}(CO)-(PPh₃)₂][BF₄] (1). A 0.95 M acetone solution of AgBF₄ (0.363 mL, 0.345 mmol) was added to a suspension of trans-[Pt(CF₃)Br(PPh₃)₂] (300 mg, 0.345 mmol) in 50 mL of CH₂Cl₂. The reaction mixture was stirred for 40 min at room temperature; then the precipitate of AgBr was filtered off and the yellow solution was concentrated under reduced pressure to ca. 15 mL. Diethyl ether (100 mL) was added, and the resulting white precipitate of the cationic complex trans-[Pt(CF₃)(PPh₃)₂(solv)][BF₄] was collected by filtration and dried under vacuum. The cationic solvento complex was dissolved in 30 mL of THF, and the solution was treated with 2-chloroethanol (2 mL) and phenylacetylene (57 μ L, 0.518 mmol). The reaction mixture was stirred for 1 h at room temperature and then taken to dryness. The solid residue was dissolved in CH₂Cl₂ (5 mL), and upon addition of diethyl ether (15 mL) and *n*-hexane (15 mL) a white solid precipitated which was filtered, washed with *n*-hexane (3 \times 5 mL), and dried under vacuum. Yield: 0.251 g (80.5%). Mp: 170-172 °C dec. Anal. Calcd for C47H40O2ClBF4P2Pt: C, 55.56; H, 3.97. Found: C, 55.05; H, 4.05. IR (Nujol, cm⁻¹): v(CO) 2103 (s); v(C=C) 1590 cm⁻¹ (m-w). ¹H NMR: 4.88 [t, ³J(HP) 4.98, ²J(HPt) 37.2, 1H, CH=], 3.42 [t, ³J(HH) 5.41, 2H, OCH₂], 2.99 [t, ³J(HH) 5.41, 2H, CH₂Cl]. ³¹P{¹H} NMR: 14.4 [s, ¹J(PPt) 2553].

Synthesis of *trans*-[Pt{C(H)=C(p-tolyl)OCH₂CH₂Cl}-(CO)(PPh₃)₂][BF₄] (2). This compound was prepared by treating *trans*-[Pt(CF₃)Br(PPh₃)₂] (212 mg, 0.244 mmol) in 20 mL of CH₂Cl₂ at room temperature with a 0.46 M acetone solution of AgBF₄ (0.53 mL, 0.244 mmol). After the solid AgBr was removed, the solution was taken to dryness and the cationic solvento complex was dissolved in 20 mL of 2-chloroethanol and then p-tolylacetylene (46 µL, 0.366 mmol) was added. The colorless solution became immediately dark red. The reaction mixture was stirred for 1.5 h at room temperature and then taken to dryness. The solid residue was dissolved in acetone (5 mL), and upon addition of diethyl ether (20 mL) a white solid precipitated which was filtered, washed with diethyl ether (3 \times 5 mL), and dried under vacuum. Yield: 182.2 mg (72.5%). Mp: 134-136 °C dec. Anal. Calcd for $C_{48}H_{42}O_2ClBF_4P_2Pt: \ \bar{C},\ 55.97;\ H,\ 4.11.$ Found: C, 55.57; H, 3.97. IR (Nujol, cm⁻¹): v(CO) 2099 (s); v(C=C) 1588 cm⁻¹ (m-

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Table 1. Crystal Data for Compound 1

formula	$[C_{47}H_{40}ClO_2P_2Pt][BF_4]\cdot(C_2H_5)_2O$
fw	1090.1
cryst dimens, mm	0.10 imes 0.15 imes 0.25
cryst syst	orthorhombic
<i>a</i> , Å	19.141(3)
<i>b</i> , Å	20.113(3)
<i>c</i> , Å	23.768(4)
<i>V</i> , Å ³	9150(2)
space group	Pbca
ρ (calcd), g cm ⁻³	1.583
Z	8
<i>F</i> (000)	4368
λ(Μο Κα), Å	0.710 73
μ (Mo K α), cm ⁻¹	32
no. of rflns measd	5979
scan method	$\omega - 2\theta$
$2\theta_{\rm max}$, deg	45
no. of obsd rflns $[I > 2\sigma(I)]$	4251
final $R(F)^a$	0.069
$R_{\rm w}(F^2)^b$	0.187
no. of params refined	286
GOF ^c	1.43

^a $R(F) = ||F_0| - |F_c||/\Sigma|F_0|$. ^b $R_w(F^2) = [\Sigma(w(|F_0|^2 - |F_c|^2)^2)/ \Sigma w(|F_0|^2)]^{1/2}$. ^c GOF = $[\Sigma(w(|F_0|^2 - |F_c|^2)^2)/(n-p)]^{1/2}$.

w). ¹H NMR: 4.80 [t, ³*J*(HP) 4.84, ²*J*(HPt) 35.07, 1H, CH], 2.98 [t, ³*J*(HH) 5.47, 2H, CH₂Cl], 3.45 [t, ³*J*(HH) 5.47, 2H, OCH₂], 2.28 [s, 3H, CH₃-*p*-C₆H₄]. ³¹P{¹H} NMR: 15.36 [s, ¹*J*(PPt) 2557]. ¹³C{¹H} NMR: 175.74 (s, CO), 154.01 [t, ²*J*(CP) 25.0, ¹⁹⁵Pt satellites too weak to be observed, CH], 104.04 [t, ²*J*(CPt) 213.62, ³*J*(CP) 10.77, C-C₆H₄-*p*-Me], 66.43 [s, OCH₂], 42.80 [s, CH₂Cl], 21.11 [CH₃].

Synthesis of trans-[Pt(C=C-p-tolyl)(CO)(PPh₃)₂][BF₄] (3). To a solution of *trans*- $[Pt(CF_3)(C \equiv C-p-tolyl)(PPh_3)_2]$ (151) mg, 0.167 mmol) in benzene (30 mL) at 0 °C was added a 54% solution of HBF4 in Et2O (13 µL, 0.184 mmol) and ClCH2CH2-OH (0.2 mL, 2.98 mmol). After the ice-water bath was removed, the reaction mixture was stirred for a few hours at room temperature. The pale yellow solution was then concentrated under reduced pressure to ca. 5 mL, and upon addition of diethyl ether (10 mL) a white solid precipitated. After filtration the solid obtained was washed with *n*-pentane $(3 \times 5 \text{ mL})$, and dried under vacuum. Yield: 70 mg (44%). Mp: 286-288 °C dec. Anal. Calcd for C46H37BF4OP2Pt: C, 58.18; H, 3.93. Found: C, 58.08; H, 3.80. IR (Nujol, cm⁻¹): ν (CO) and ν (C=C) 2129 cm⁻¹ (s) partially overlapped. ¹H NMR: 2.12 [s, 3H, CH₃]. ³¹P{¹H} NMR: 16.01 [s, ¹J(PPt) 2161]. Complex 3 was also obtained by reaction of trans-[Pt(CF₃)(C≡C-*p*-tolyl)(PPh₃)₂] (115 mg, 0.123 mmol) with a 48% aqueous solution of HBF₄ (3 drops). The suspension was stirred for 24 h at room temperature. Then the solid was filtered, washed with *n*-pentane $(3 \times 5 \text{ mL})$, and dried under vacuum. Yield: 0.053 g (45%).

Crystal Structure Determination. Crystal data and summary of data collection and structure refinement details for 1 are collected in Table 1. Crystals were grown by slow diffusion of Et₂O into a CH₂Cl₂ solution of 1. A yellow crystal was mounted on a glass fiber with epoxy, and all measurements were made on a Nicolet Siemens R3m/V four-circle diffractometer. Cell constants were obtained from a leastsquares refinement, using the setting angles of 50 reflections with $2\theta > 20^\circ$. Three reflections were measured every 200 reflections as orientation and intensity control, and significant intensity decay (up to 15%) was observed. Decay, Lorentz, and polarization, but no absorption, corrections were made. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least squares against F^2 with application of anisotropy only to Pt, P, and Cl atoms. Difference maps showed that the ether molecule was disordered into, at least, two positions and in addition the BF₄⁻ anion showed signs of the usual rotational disorder. Occupancies of the disordered Et₂O solvate molecule were estimated

 Table 2. Selected Bond Distances (Å) and Angles (deg) for Compound 1

(8		
2.353(4)	C(1)-C(2)	1.31(2)
2.345(4)	C(2) - O(1)	1.46(2)
2.02(2)	C(3) - O(1)	1.41(2)
1.91(2)	C(3)-C(4)	1.46(2)
1.14(2)	Cl-C(4)	1.76(2)
174.1(1)	Pt-C(5)-O(2)	177(1)
88.3(4)	Pt-C(1)-C(2)	131(2)
91.5(4)	C(1) - C(2) - O(1)	120(2)
87.9(4)	C(2) - O(1) - C(3)	121(2)
92.3(4)	Cl - C(4) - C(3)	107(2)
179.3(6)		
	2.353(4) 2.345(4) 2.02(2) 1.91(2) 1.14(2) 174.1(1) 88.3(4) 91.5(4) 87.9(4) 92.3(4) 179.3(6)	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

from electron density calculations and introduced in a sequence of cycles where occupancies and isotropic thermal coefficients were refined alternatively. They were maintained constant during the rest of the structure refinement; nevertheless, such a treatment of the disorder led to unreasonable bond distances and no other attempt was made to solve this disorder. The largest shift/error ratio in the final cycle was 0.05 in the cation and, although a difference peak with a magnitude of about 1 e Å⁻³ was seen at about 1 Å from the Pt atom, no significant electron density was observed at chemically reasonable distances from the other atoms. Selected bond distances and angles are given in Table 2. Structure determination and refinement were performed with the SHELXTL/ PC and SHELXTL-93 program packages.⁸

Results

Synthesis of β **-Alkoxyalkenyl Complexes.** The reactions leading to **1** and **2** are summarized in eq 4.



 $R = Ph (1), p-tolyl (2); solv = CH_2Cl_2, Et_2O$

Treatment in CH₂Cl₂ of *trans*-[Pt(CF₃)(Br)(PPh₃)₂] with 1 equiv of an acetone solution of AgBF₄ at ambient temperature affords, after filtration of AgBr, in almost quantitative yield the cationic solvento complex *trans*-[Pt(CF₃)(PPh₃)₂(solv)][BF₄], which can be isolated as a white crystalline product upon addition of Et₂O to the dichloromethane solution.⁹ This latter complex was then dissolved in 2-chloroethanol and treated with ca. 1.5 equiv of the terminal acetylene to give a dark red solution, which was stirred for ca. 1–1.5 h at room temperature. After this time, workup of the reaction mixture afforded **1** and **2** in ca. 80 and 72% yield, respectively, as the only isolated reaction products.

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Figure 1. (a, left) ORTEP drawing of *trans*- $[Pt{C(H)=C(Ph)OCH_2CH_2Cl}(CO)(PPh_3)_2]^+$ (cation of **1**). Thermal ellipsoids for Pt, P, and Cl atoms are shown at 40% probability. The solvate molecule and the BF₄⁻ anion have been omitted for clarity. (b, right) Drawing of the cation viewed down the P(1)···P(2) axis, showing the phenyl ring arrangement. The atoms are shown as arbitrarily sized uniform circles.

The structures of **1** and **2** were assigned on the basis of microanalytical, IR, and multinuclear (¹H, ³¹P, ¹³C) NMR data and also by an X-ray structural determination carried out for **1** (see below). The IR spectra (Nujol mulls) show a strong absorption at ca. 2100 cm⁻¹ due to the carbonyl ligand and also a weak-medium band at ca. 1600 cm⁻¹, which can be assigned to the C=C stretching of the vinyl group. The strong absorption at ca. 1050 cm⁻¹ is due to the BF₄⁻ ion.

The trans geometry of 1 and 2 is clearly determined by the ${}^{31}P{}^{1}H$ NMR spectra, which show a singlet for the magnetically equivalent trans PPh₃ ligands, accompanied by ¹⁹⁵Pt satellites (see Experimental Section). The ¹H NMR spectra of **1** and **2** show, in particular, the vinyl proton (δ 4.74–4.98) as a triplet due to coupling with the two P atoms (${}^{3}J_{\rm HP}$ ca. 4.9), flanked by ${}^{195}{\rm Pt}$ satellites (${}^{2}J_{\text{HPt}}$ ca. 35–37). Two triplets at ca. δ 3.4 and 2.9 are also observed, which have been assigned to the -OCH₂- and -CH₂Cl methylene protons, respectively, of the alkoxy substituent (${}^{3}J_{HH}$ ca. 5.4). The ¹³C{¹H} NMR spectrum carried out for **2** shows the α -vinyl carbon at δ 154.0 as a triplet due to coupling with the two cis P atoms (${}^{2}J_{CP}$ 25.0), while the ${}^{195}Pt$ satellites were too weak to be observed. The carbonyl carbon resonance appears as a singlet at δ 175.7.

X-ray Crystal Structure of 1. Figure 1 illustrates the molecular geometry of the cation complex. As can be seen from the esd's, the structure is not a particularly accurate one (see Experimental Section), but it does answer a chemical question and the model provides an adequate conclusion about binding/stereochemistry fea-

tures. In the cation the Pt atom has C_2P_2 roughly square planar (within 0.05(2) Å) coordination (Figure 1a) and deviates by 0.04 Å from the mean plane of the four donors. There is some deformation from the ideal square with the internal angles in the range 87.9–92.3° and P(1)-Pt-P(2) and C(1)-Pt-C(5) angles of 174.1 and 179.3°, respectively. The phenyl ring of the organic ligand is virtually perpendicular to the platinum coordination plane, the dihedral angle being 87.6°, while the C(1)=C(2)-O(1) portion makes a dihedral angle of 85.1° with the same plane. The $P(1)\cdots P(2)$ axis is perpendicular to the $C(1)\cdots C(5)$ (angle of 90.6°) and to the $C(1A)\cdots C(4A)$ line (angle of 88.9°). The phenyl rings C(1B)/C(1F), C(1C)/C(1E), and C(1D)/C(1G) are inclined to one another by 35.2, 21.0, and 38.7°, respectively (Figure 1b). Comparison of the bond distances with the data reported in a survey,¹⁰ covering inter alia the mononuclear Pt(II) complexes, and completed by the recent entries from the Cambridge Structural Database (CSD), shows a somewhat lengthened Pt-PPh₃ bond (mean 2.349 Å compared to a reference value of 2.30 Å), accompanied by a shortening of the Pt-CO bond (1.91 vs 2.04 Å), while the Pt-C(1) bond length compares well with those found for similar complexes (2.02 vs 2.05 Å). The relatively short $O(2)\cdots O(2)$ (at 1 - x, -y, -z) contact of 2.93 Å represents the only separation at van der Waals contact distances.

Discussion

Formation of β -alkoxyalkenyl complexes by nucleophilic attack of alcohols on alkynes activated by coordination to an electron-withdrawing transition-metal center has been reported for internal alkynes, RC=CR,⁵

⁽⁹⁾ The cationic solvento complex *trans*-[Pt(CF₃)(PPh₃)₂(solv)][BF₄] so prepared appears, on the basis of NMR data, to be a mixture of two species, likely due to two different coordinated solvent molecules, e.g. Et₂O and CH₂Cl₂, while the presence of coordinated acetone can be ruled out on the basis of IR data. ³¹P{¹H} NMR (CDCl₃): δ 26.11 (q, ¹J_{PPt} 3040, ³J_{PF} 20.2), 26.52 (q, ¹J_{PPt} 3050, ³J_{PF} 20.9). ¹⁹F NMR (CDCl₃): -9.18 (t, ²J_{PtF} 768, ³J_{PF} 20.2 Hz), -8.91 (t, ²J_{PtF} 802, ³J_{PF} 20.9). In CD₃COCD₃ the ³¹P NMR spectrum shows the presence of only one species at δ 32.08 (q, ¹J_{PPt} 3094, ³J_{PF} 20.0).

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while similar reactions with terminal alkynes, RC=CH, lead to the formation of alkylalkoxycarbene derivatives.^{5,11} Thus, for instance, reactions in methanol of *trans*-[Pt(Me)(Cl)L₂] (L = PMe₂Ph, AsMe₂Ph) complexes with the acetylenes RC=CR (R = CO₂Me, CH₂OH, CO₂H) in the presence of a silver salt gave cationic β -alkoxyalkenyl derivatives of the type *trans*-[Pt{C(R)=C-(OMe)R}L₂]^{+,5} which did not show the presence of the methyl group, being eliminated as methane according to the eq 5.

$$trans-[Pt(Me)(Cl)L_2] + R-C=C-R \xrightarrow{+AgPF_6, -AgCl} [Pt\{C(R)=C(OMe)R\}L_2]PF_6 + CH_4$$
(5)

 $L = PMe_2Ph$, $AsMe_2Ph$; $R = CO_2Me$, CO_2H , CH_2OH

Similarly, the cationic 2-butyne complex [Fe(η^{5} -C₅H₅)-(CO)(MeC=CMe)(PPh₃)][BF₄] reacts with a variety of nucleophiles (H⁻, SBu⁻, SPh⁻, OEt⁻, CN⁻, C=CH⁻, Ph⁻, Me⁻), giving the corresponding η^{1} -vinyl complexes formed by trans addition of the nucleophile with respect to the metal.¹² The observed reactivity was explained with the formation of intermediate η^{2} -alkyne species, which could be also isolated for the Fe(II) complexes and also in some cases for the Pt(II) derivatives.

Conversely, as mentioned earlier, nucleophilic attack by alcohols on terminal alkynes coordinated to Pt(II) leads to alkylalkoxycarbene derivatives, as specifically reported for the reactions of a number of cationic species of the type *trans*-[Pt(CH₃)(RC=CH)L₂]⁺ (R = aryl, L = tertiary phosphine or arsine) with R'OH to give *trans*-[Pt(CH₃){=C(CH₂R)OR'}L₂}⁺ (R' = CH₃,⁵ CH₂CH₂Cl⁴). The same products are also formed by reaction of platinum acetylides of the type *trans*-[Pt(CH₃)(C=CR)-L₂] with R'OH in the presence of a strong acid (HBF₄, HPF₆).^{4.5} In both cases, the formation of alkoxyalkylcarbene complexes may be reasonably explained by the intermediacy of a Pt^{II}-vinylidene species^{4,11a,b} (although never isolated or characterized for Pt(II) systems), Pt=C=C(H)R, which then undergoes nucleophilic attack by alcohols at the electrophilic α -carbon atom, as found for several other transition-metal vinylidene complexes. ^11a,b

The unexpected formation of β -alkoxyalkenyl derivatives (eq 4) from terminal alkynes and 2-chloroethanol when the trifluoromethyl cationic complex *trans*-[Pt(CF₃)-(PPh₃)₂(solv)]⁺ is the starting material must be related to a different role of the CF₃ ligand compared to CH₃.

The electronic and chemical properties of the trifluoromethyl group in transition-metal complexes have been extensively investigated.¹³ Late-transition-metal trifluoromethylated compounds are found to be significantly more thermally and oxidatively stable and also to have shorter M-C bond distances than the analogous methylated species. As a consequence, the M-CF₃ metal-carbon bond is less reactive and is stronger than the M-CH₃ metal-carbon bond.¹³ This finding has been rationalized by invoking back-bonding from the filled metal d orbitals to the nominally unoccupied C-F antibonding orbitals, a type of bonding that is not available to M-CH₃ derivatives. This would explain, for instance, the shortening of the Pt-Cl bond length in the perfluoroalkyl complexes *trans*-[Pt(R_F)Cl(PMePh₂)₂] $(R_F = CF_3, C_2F_5)$ compared to that found in the methyl derivative trans-[Pt(CH₃)Cl(PMePh₂)₂].^{13b}

The higher electron-withdrawing properties of the CF₃ group compared to CH₃ would make the cationic complex $[Pt(CF_3)(PPh_3)_2(solv)]^+$ more electrophilic, and this feature may reasonably explain a greater stabilization of the π -alkyne **A** compared to the vinylidene **B** intermediate (Scheme 1).

Nucleophilic attack of 2-chloroethanol at the electrophilic β -carbon atom of the π -alkyne **A** would lead to the trifluoromethyl- β -alkoxyalkenyl intermediate **C** with liberation of H⁺ and then to the final carbonyl- β -alkoxyalkenyl complexes **1** and **2**. The presence of **B** as an intermediate is therefore ruled out because it would be expected to lead to the formation of alkylalkoxycarbene derivatives of type **D**, as otherwise found for similar reactions of Pt(II) complexes with 1-alkynes and alcohols.^{4,11a,b} On the other hand, the intermediacy of the η^2 -alkyne **A** appears to be supported by spectroscopic data, which have been obtained upon following

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reaction 4, but without any 2-chloroethanol added, by ¹⁹F and ³¹P NMR spectroscopy (eq 6).



To the initial solvento complex trans-[Pt(CF₃)(PPh₃)₂-(solv)][BF₄] was added in CDCl₃ 1.5 equiv of *p*-tolylacetylene at room temperature. The ³¹P NMR spectrum of the reaction mixture shows after 30 min the presence of a singlet at 16.04 ppm (${}^{1}J_{PPt}$ 2156), which is assigned to *trans*-[Pt(C=C-p-tolyl)(CO)(PPh₃)₂][BF₄] (complex **3**, see below) and a quartet at 14.91 ppm (${}^{3}J_{\text{FP}}$ 18.6, ${}^{1}J_{PPt}$ 2447), which is attributed to the η^{2} -alkyne complex *trans*-[Pt(CF₃)(PPh₃)₂{ η^2 -C(H)=C(*p*-tolyl)}][BF₄]. The assignment of this latter species appears to be supported by ¹⁹F NMR data. In fact, the same reaction mixture shows in the ¹⁹F NMR spectrum a new triplet, flanked by ^{195}Pt satellites, at -20.89 ppm with $^2J_{FPt}\,618$ and ${}^{3}J_{\text{FP}}$ 18.6; no other resonances were observed. These data may be compared with those obtained in a similar reaction of trans-[Pt(CF₃)(PPh₃)₂(solv)][BF₄] with 1 equiv of CH₃C=CCH₃, which would likely give trans- $[Pt(CF_3)(PPh_3)_2\{\eta^2 - C(CH_3) \equiv C(CH_3)\}][BF_4] (\delta(CF_3) - 20.62]$ (t), ${}^{3}J_{\text{FP}}$ 22.6). This latter complex is formed in a very low concentration, and the ¹⁹F-¹⁹⁵Pt coupling could not be safely assigned; addition of more 2-butyne leads to the formation of a white precipitate likely due to a polymerization process of the alkyne, as previously observed by Chisholm and Clark.⁵

In the reactions reported in Scheme 1, a CF₃ ligand is converted to CO, as shown in the final complexes 1 and **2**. The mechanism of this conversion is currently not known. However, it is likely that this reaction would initially proceed by electrophilic attack of H⁺ on CF₃ to give an intermediate difluorocarbene species. The susceptibility of the C-F bonds in (trifluoromethyl)platinum(II) complexes to undergo electrophilic attack by proton or Lewis acids was previously reported¹⁴ for the trifluoromethyl-hydrido species trans-[Pt(CF₃)(H)-

 $(PPh_3)_2$]. For instance, the reaction with an ethereal solution of HBF₄ affords the highly reactive difluorocarbene intermediate *trans*-[Pt(H)(=CF₂)(PPh₃)₂][BF₄], which then converts to the hydrido-carbonyl derivative *trans*-[Pt(H)(CO)(PPh₃)₂][BF₄] in the presence of adventitious water in the reaction mixture. The rapid hydrolysis of metal-bound CF₂ groups to CO has been reported to occur also in certain complexes of Ru and Fe.15

Reaction of *trans*-[Pt(CF₃)(C≡C-*p*-tolyl)(PPh₃)₂] with 2-Chloroethanol and HBF₄. The reaction of the alkynyl complex *trans*- $[Pt(CF_3)(C \equiv C - p - tolyl)(PPh_3)_2]$, HBF₄ (1 equiv), and 2-chloroethanol (Scheme 2, route a), yields trans- $[Pt(C \equiv C - p - tolyl)(CO)(PPh_3)_2][BF_4]$ (3), with no evidence of formation of β -alkoxyalkenyl (eq 4) or carbene complexes (eq 2). Complex 3 was also obtained by reaction of the acetylide with an aqueous solution of HBF₄ (route *b*).

Complex 3 was characterized by microanalysis and multinuclear (¹H, ³¹P) NMR spectroscopy (see Experimental Section). As also discussed earlier, the formation of **3** may be explained by an initial electrophilic attack of HBF₄ on a fluorine atom of the CF₃ group to give the difluorocarbene intermediate $[Pt(=CF_2)(C=C-C-C)]$ p-tolyl)(PPh₃)₂][BF₄], which then rapidly reacts with adventious H₂O to afford the carbonyl derivative. Reaction a of Scheme 2 was followed by ¹⁹F and ³¹P NMR at the probe temperature. To an initial solution of trans- $[Pt(CF_3)(C \equiv C - p - tolyl)(PPh_3)_2]$ in $CDCl_3$ was added 1 equiv of ethereal HBF₄: ³¹P NMR shows the immediate formation of **3** as the major product, together with two small quartets, flanked by ¹⁹⁵Pt satellites, which were assigned on the basis of ¹⁹F NMR data to the solvento species *trans*-[Pt(CF₃)(PPh₃)₂(solv)][BF₄] and the π -alkyne complex *trans*-[Pt(CF₃)(PPh₃)₂{ η^2 -C(H)=C(p-tolyl)}][BF₄], respectively. It is also observed in the ¹⁹F NMR spectrum that the resonance corresponding to the cationic solvento species slowly converts to that attributed to the π -alkyne complex, which then converts to **3** and eventually disappears upon addition of 2-chloroethanol.

Thus, this reaction chemistry indicates that the preferential sites of attack by H⁺ are the fluorine atoms of the CF₃ group rather than the β -carbon atom of the acetylide, which would give a vinylidene intermediate, as proposed for the other Pt^{II}–alkynyl reactions.^{4,11}

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Concluding Remarks

This study has shown that the reactions of terminal alkynes with halo alcohols, and specifically 2-chloroethanol, promoted by cationic Pt(II) solvento complexes of the type *trans*-[Pt(R')(PPh_3)_2(solv)]⁺ appear to be influenced by the electronic properties of the alkyl ligand R'. When R' = CH₃, a strong σ -electron donor, the reactions lead to the formation of acyclic oxycarbene derivatives of type I, while with R' = CF₃, a good electron-withdrawing group, these lead to β -alkoxy-alkenyl derivatives of type II.

The formation of the two different reaction products has been suggested to occur through different reaction intermediates i.e., a Pt(II) vinylidene, Pt=C=C(H)R, in the case of **I** and a π -alkyne, Pt(η^2 -RC=CH), in the case of **II**.



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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles for **1** (7 pages). Ordering information is given on any current masthead page.

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