ELSEVIER

Inorganica Chimica Acta 275-276 (1998) 515–520

Inorganica Chimica Acta

Reactions of platinum(II)–alkyne and –alkynyl complexes with the hydroxy compounds $HO(CH_2)_2X$ (X = Br, I, OH) [1]

Umberto Belluco, Roberta Bertani, Stefania Fornasiero, Rino A. Michelin *, Mirto Mozzon

Dipartimento dei Processi Chimici dell'Ingegneria and Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Università di Padova, Via F. Marzolo 9, 35131 Padua, Italy

Received 22 July 1997; accepted 2 September 1997

Abstract

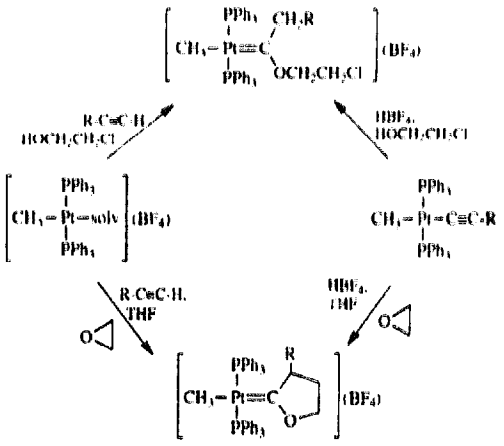
The cationic solvento species *trans*-[Pt(Me)(PPh_3)$_2$(solv)][BF_4] (solv = CH_2Cl_2, Et_2O) reacts with 1.5 equiv. of *p*-tolylacetylene in the presence of a 10-fold excess of the hydroxylated compounds $HOCH_2CH_2X$ (X = Br, I, OH) to give the corresponding (alkoxy)alkyl carbene complexes *trans*-[Pt(Me){=C(OCH_2CH_2X)CH_2(*p*-tolyl)}(PPh_3)$_2$][BF_4] (**1–3**). Complexes **1–3** were also obtained by reaction of the acetylide complex *trans*-[Pt(Me)(C≡CR)(PPh_3)$_2$] (R = *p*-tolyl) in the presence of 1 equiv. of HBF_4 with an excess of $HOCH_2CH_2X$. The carbene complex *trans*-[Pt(Me){=C(OCH_2CH_2Cl)CH_2R}(PPh_3)$_2$][BF_4] (R = *p*-tolyl) can be readily deprotonated by NEt_3 to afford the vinyl complex *trans*-[Pt(Me){C(OCH_2CH_2Cl)=CH(R)}(PPh_3)$_2$] (**4**). A similar behavior is observed also for **1–3** when treated with a base.

Keywords: Platinum complexes; Alkyne complexes; Alkynyl complexes; Carbene complexes

1. Introduction

Terminal alkynes (R–C≡C–H) and alkynyl (R–C≡C:$^-$) ligands coordinated to electron-withdrawing transition metal centers (L_nM), e.g. in medium to high oxidation state, react with protic nucleophiles such as alcohols R'OH to give (alkoxy)alkyl carbene complexes of the type [L_nM{=C(OR')CH_2R}] [1].

We have been recently interested [2–4] in the reactions of Pt(II)–alkyne and –alkynyl complexes with 2-chloroethanol, $HOCH_2CH_2Cl$, and oxirane, $\overline{OCH_2CH_2}$, which have been previously shown to undergo cycloaddition reactions to other isoelectronic unsaturated ligands such as isocyanides [5], carbonyls [6] and nitriles [7] to form C- or N-coordinated heterocycles. On the other hand, as summarized in Scheme 1, the reactions with $HOCH_2CH_2Cl$ of cationic solvento species of the type *trans*-[Pt(Me)(PPh_3)$_2$(solv)][BF_4] in the presence of 1-alkynes or the acetylides *trans*-[Pt(Me)-(C≡CR)(PPh_3)$_2$] in the presence of a strong acid such as HBF_4, afford (alkoxy)alkyl carbene complexes [2] with no evidence of formation of cyclic carbenes.



Scheme 1.

However, similar reactions with oxirane (Scheme 1) lead to oxacyclopentylidene complexes [3]. The nature of the reaction products has suggested that all these reactions might proceed through the intermediacy of a vinylidene species, Pt(II)=C=C(H)R, which has never been isolated for Pt(II), but its occurrence has been proved for other transition metal centers [1].

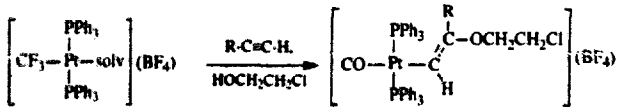
The reactions of the cationic solvento Pt(II) species with R–C≡C–H and $HOCH_2CH_2Cl$ are strongly influenced by the electronic properties of the Pt–alkyl ligand as observed for

* Corresponding author. Tel.: +39-49-827 5522; fax: +39-49-827 5525; e-mail: michelin@ux1.unipd.it

[1] This paper is dedicated to Professor Ivano Bertini for his outstanding contributions to the advancement of the fundamentals of bioinorganic chemistry, organometallic chemistry, and chemical sciences.

0020-1693/98/$19.00
PII S0020-1693(98)00149-2

those involving the trifluoromethyl complex *trans*-[Pt(CF_3)(PPh_3)$_2$(solv)][BF_4] and 1-alkynes in the presence of 2-chloroethanol which proceed differently from those of the parent CH_3 derivatives, since β-alkoxyalkenyl (vinyl ether) complexes are formed [4], together with a concomitant CF_3 to CO conversion (Eq. (1)).



(1)

In this latter case, the more electrophilic nature of the solvento cationic species due to the presence of a strong electron-withdrawing trifluoromethyl group would stabilize a π-alkyne intermediate rather than a vinylidene, which would explain the observed reaction products.

The variety of reactions described in Scheme 1 and Eq. (1), led us to explore and extend the chemistry of Pt(II)–alkyne and –alkynyl complexes with hydroxylated compounds of the type $HOCH_2CH_2X$ (X = Br, I, OH) and also to investigate the reactions of the derived carbene complexes with bases.

2. Experimental

2.1. General procedures

All reactions were carried out under an N_2 atmosphere. THF and CH_2Cl_2 were purified according to standard procedures [8]. All the other solvents were of reagent grade and used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer (abbreviations: s = strong, m = medium). Proton and phosphorus-31 NMR spectra were obtained on a Bruker AC-200 spectrometer. ^{1}H NMR shifts were recorded relative to residual ^{1}H resonance in the deuterated solvent: $CDCl_3$, δ 7.23; the ^{31}P{^{1}H} chemical shifts are referenced to external 85% H_3PO_4 with downfield values taken as positive. In all the NMR spectra *J* are in Hz; abbreviations used: s = singlet, t = triplet, m = multiplet, br = broad. The elemental analyses were performed by the Department of Analytical, Inorganic and Organometallic Chemistry of the University of Padua. The melting points were taken on a hot plate apparatus and are uncorrected.

2.2. Starting compounds

The complexes *trans*-[Pt(Me)Cl(PPh_3)$_2$] [9], *trans*-[Pt(Me)(C≡C(*p*-tolyl))(PPh_3)$_2$] [2] and *trans*-[Pt(Me){=C(OCH_2CH_2Cl)CH_2(*p*-tolyl)}(PPh_3)$_2$][BF_4] [2] were prepared according to literature procedures. *p*-Tolylacetylene and the compounds $HOCH_2CH_2X$ (X = Br, I, OH) were commercially available products and used as received.

2.3. Synthesis of the complexes

2.3.1. Trans-[Pt(Me){=C(OCH_2CH_2Br)CH_2(*p*-tolyl)}(PPh_3)$_2$][BF_4] (1)

Method A. To a solution of *trans*-[Pt(Me)(PPh_3)$_2$Cl] (174 mg, 0.227 mmol) in CH_2Cl_2 (20 ml) at room temperature was added a 0.46 M solution of $AgBF_4$ in acetone (0.54 ml, 0.250 mmol). After it was stirred for 1 h, the suspension was filtered off to remove AgCl, and the solution was taken to dryness under reduced pressure to give a white solid of the solvento complex *trans*-[Pt(Me)(PPh_3)$_2$(solv)][BF_4] (solv = CH_2Cl_2). It was dissolved in benzene (20 ml) and treated at 0°C with *p*-tolylacetylene (0.036 ml, 0.34 mmol) and an excess of $HOCH_2CH_2Br$ (0.6 ml, 2.7 mmol). After 1 h stirring, the reaction mixture was left to reach room temperature and then stirred for an additional 6 h. The solution was then reduced to a small volume (5 ml) and treated with Et_2O to give a white solid, which was filtered off and dried under vacuum. Yield 193 mg (80%). M.p. 153–155°C dec. *Anal.* Calc. for $C_{48}H_{46}OP_2PtBrBF_4$: C, 54.25; H, 4.36. Found: C, 53.83; H, 4.01%. IR (Nujol mull): ν(C–O) 1280 (m) cm^{-1}. ^{1}H NMR (δ, $CDCl_3$): −0.13 [t, 3H, CH_3, ^2J(HPt) 45.2, ^3J(HP) 8.6], 2.33 [s, 3H, CH_3(*p*-tolyl)], 3.28 [t, 2H, CH_2Br, ^3J(HH) 4.5], 3.48 [s, 2H, CH_2(*p*-tolyl)], 5.00 [m, 2H, OCH_2]. ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 24.15 [s, ^1J(PPt) 2902]. On the basis of the ^{31}P NMR data, complex **1** was revealed to be impure due to the carbonyl complex *trans*-[Pt(Me)(PPh_3)$_2$(CO)][BF_4] (~5%).

Method B. To a solution of the acetylide complex *trans*-[Pt(Me)(C≡C(*p*-tolyl))(PPh_3)$_2$] (422 mg, 0.498 mmol) in benzene (20 ml) at 0°C, were added 0.07 ml (0.55 mmol) of a 7.2 M ethereal solution of HBF_4 and an excess of $HOCH_2CH_2Br$ (0.4 ml, 6.0 mmol). After stirring for 1 h, the solution was warmed up to room temperature and stirred for an additional 12 h. It was then reduced to a small volume and treated with Et_2O to give a white solid, which was filtered, washed with n-pentane (3 × 5 ml) and dried under vacuum. On the basis of spectral data, complex **1** prepared by method B was revealed to be impure due to the carbonyl complex *trans*-[Pt(Me)(CO)(PPh_3)$_2$][BF_4] (~2%) (see Section 3). The total yield was 225 mg (42.5%).

2.3.2. Trans-[Pt(Me){=C(OCH_2CH_2I)CH_2(*p*-tolyl)}(PPh_3)$_2$][BF_4] (2)

Method A. To a solution of *trans*-[Pt(Me)(PPh_3)$_2$Cl] (174 mg, 0.227 mmol) in CH_2Cl_2 (20 ml) at room temperature was added a 0.46 M solution of $AgBF_4$ in acetone (0.54 ml, 0.250 mmol). After it had been stirred for 1 h, the suspension was filtered off to remove AgCl, and the solution was taken to dryness under reduced pressure to give a white solid of the solvento complex *trans*-[Pt(Me)(PPh_3)$_2$(solv)][BF_4] (solv = CH_2Cl_2). It was dissolved in benzene (20 ml) and treated at 0°C with *p*-tolylacetylene (0.036 ml, 0.34 mmol) and an excess of $HOCH_2CH_2I$ (1.02 ml, 2.7 mmol). After 1 h stirring at 0°C and 30 min at room temperature, the reaction mixture was taken to dryness. On treating

with Et_2O a white solid formed, which was filtered off, washed with n-pentane (3×5 ml) and dried under vacuum. Yield 207 mg (82.8%). M.p. 164–166°C. *Anal.* Calc. for $C_{48}H_{46}OP_2PtIBF_4$: C, 51.95; H, 4.18. Found: C, 50.89; H, 4.01%. IR (Nujol mull): ν(C–O) 1280 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): −0.13 [t, 3H, CH_3, ^2J(HPt) 45.3, ^3J(HP) 8.6], 2.33 [s, 3H, CH_3(*p*-tolyl)], 3.00 [t, 2H, CH_2I, ^3J(HH) 5.7], 3.49 [s, 2H, CH_2(*p*-tolyl)], 4.99 [t, 2H, OCH_2, ^3J(HH) 5.7]. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 24.20 [s, ^1J(PPt) 2907]. On the basis of NMR data, also complex **2** prepared by this method was revealed to be impure due to the carbonyl complex *trans*-[Pt(Me)(CO)$(PPh_3)_2$][BF_4] (~5%) (see Section 3).

Method B. The procedure is similar to that reported for **1** starting from *trans*-[Pt(Me)(C≡C(*p*-tolyl))$(PPh_3)_2$] (151 mg, 0.178 mmol), 0.015 ml (0.196 mmol) of a 7.2 M ethereal solution of HBF_4 and an excess of $HOCH_2CH_2I$ (2.27 ml, 6.0 mmol). After stirring for 1 h at 0°C and 12 h at room temperature, the solution was taken to dryness to give a brown oil which, upon treatment with Et_2O, gave a white solid. It was filtered off, washed with n-pentane (3×5 ml) and dried under vacuum. On the basis of NMR data, also complex **2** prepared by this method was revealed to be impure due to the carbonyl complex *trans*-[Pt(Me)(CO)$(PPh_3)_2$][BF_4] (~5%) (see Section 3). The total yield was 95 mg (48.1%).

2.3.3. *Trans-[Pt(Me){=C(OCH$_2$CH$_2$OH)CH$_2$(p-tolyl)}(PPh$_3$)$_2$][BF$_4$] (3)*

Method A. The procedure is similar to those reported for **1** and **2**. To a solution of *trans*-[Pt(Me)$(PPh_3)_2$Cl] (156 mg, 0.204 mmol) in CH_2Cl_2 (20 ml) at room temperature was added a 0.46 M solution of $AgBF_4$ in acetone (0.47 ml, 0.220 mmol). After it was stirred for 1 h, the suspension was filtered off to remove AgCl, and the solution was taken to dryness under reduced pressure to give a white solid of the solvento complex *trans*-[Pt(Me)$(PPh_3)_2$(solv)][BF_4] (solv = CH_2Cl_2). It was dissolved in benzene (20 ml) and treated at 0°C with *p*-tolylacetylene (0.029 ml, 0.28 mmol) and an excess of $HOCH_2CH_2OH$ (0.141 ml, 2.04 mmol). After 15 min at 0°C, the reaction mixture was warmed to room temperature, and stirred for 1 h. The solution was reduced to a small volume and, on treating with Et_2O, a pale yellow solid formed, which was filtered off, washed with n-pentane (3×5 ml) and dried under vacuum. Yield 141 mg (69%). M.p. 156–157°C. *Anal.* Calc. for $C_{48}H_{47}P_2O_2PtBF_4$: C, 57.67; H, 4.74. Found: C, 57.25; H, 4.56%. IR (Nujol mull): ν(OH) 3535 (m), ν(C–O) 1280 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): −0.16 [t, 3H, CH_3, ^2J(HPt) 44.9, ^3J(HP) 8.4], 2.34 [s, 3H, CH_3(*p*-tolyl)], 3.14 [t, 1H, OH, ^3J(HH) 6.4], 3.28 [s, 2H, CH_2(*p*-tolyl)], 3.79 [m, 2H, CH_2OH], 4.88 [m, 2H, $=COCH_2$]. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 24.43 [s, ^1J(PPt) 2926]. On the basis of NMR data, also complex **3** prepared by this method was revealed to be impure due to the carbonyl complex *trans*-[Pt(Me)(CO)$(PPh_3)_2$][BF_4] (~5%) (see Section 3).

Method B. The procedure is similar to those reported for **1** and **2** starting from *trans*-[Pt(Me)(C≡C(*p*-tolyl))$(PPh_3)_2$] (144 mg, 0.169 mmol), 0.026 ml (0.186 mmol) of a 7.2 M ethereal solution of HBF_4 and an excess of $HOCH_2CH_2OH$ (0.42 ml, 6.0 mmol). After stirring for 1 h at 0°C and 12 h at room temperature, the solution was taken to dryness to give an oil which, upon treatment with Et_2O, gave a white solid, which was filtered off, washed with n-pentane (3×5 ml) and dried under vacuum. Yield 55 mg (32.6%).

2.3.4. *Trans-[Pt(Me)(PPh$_3$)$_2$(CO)][BF$_4$]*

To a solution of *trans*-[Pt(Me)$(PPh_3)_2$Cl] (197 mg, 0.254 mmol) in CH_2Cl_2 (20 ml) at room temperature was added a 0.46 M solution of $AgBF_4$ in acetone (0.58 ml, 0.270 mmol). After it had been stirred for 1 h, the suspension was filtered off to remove AgCl, and the solution was taken to dryness under reduced pressure to give a white solid of the solvento complex *trans*-[Pt(Me)$(PPh_3)_2$(solv)][BF_4] (solv = CH_2Cl_2). It was dissolved in CH_2Cl_2 (100 ml) and treated overnight at room temperature with CO at 1 atm. Then the solution was concentrated to reduced volume (5 ml) and by adding n-pentane a whitish compound precipitated. Yield 60% (131 mg). IR (Nujol mull): ν(CO) 2097 (m) cm^{-1}. ^1H NMR (δ, $CDCl_3$): 0.47 [t, 3H, CH_3, ^2J(HPt) 61.03, ^3J(HP) 8.4]. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 21.71 [s, ^1J(PPt) 2624].

2.3.5. *Trans-[Pt(Me){C(OCH$_2$CH$_2$Cl)=CH(p-tolyl)}(PPh$_3$)$_2$] (4)*

To a solution of *trans*-[Pt(Me){=C(OCH_2CH_2Cl)CH_2-(*p*-tolyl)}$(PPh_3)_2$][BF_4] (74 mg, 0.073 mmol) in THF at room temperature, an excess of NEt_3 (0.101 ml, 0.726 mmol) was added. The solution turned yellow. After 3 h the solution was taken to dryness. The solid residue was treated with CH_2Cl_2 and the solution filtered off. The product formed was reprecipitated with Et_2O/pentane. The solid was filtered off, washed with pentane and dried under vacuum. Yield: 45 mg (67%). M.p. 187–189°C dec. *Anal.* Calc. for $C_{48}H_{45}ClOP_2Pt$: C, 61.97; H, 4.88. Found: C, 60.92; H, 4.75%. IR (Nujol mull): ν(OH) 3535 (m), ν(C–O) 1265 cm^{-1}. ^1H NMR (δ, $CDCl_3$): *Z* isomer: −0.56 [t, 3H, CH_3, ^2J(HPt) 46.9, ^3J(HP) 6.4], 2.24 [s, 3H, CH_3(*p*-tolyl)], 5.45 [s, 1H, =CH(*p*-tolyl), ^3J(HPt) 47.0], 3.1 [m, 4H, OCH_2CH_2Cl]. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 26.55 [s, ^1J(PPt) 3244]; *E* isomer (~10%): δ 2.16 [s, 3H, CH_3(*p*-tolyl)], 4.91 [s, 1H, =CH(*p*-tolyl) ppm, ^3J(HPt) 24.1 Hz], 3.72 and 2.55 [m, 4H, OCH_2CH_2Cl]). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 22.78 [s, ^1J(PPt) 3124].

2.3.6. *Deprotonation of 1, 2 and 3*

The reaction of **1** with NEt_3 was followed by ^1H and $^{31}P\{^1H\}$ NMR at room temperature. In an NMR tube under nitrogen containing **1** (30 mg, 0.028 mmol) in $CDCl_3$ (0.5 ml) was added NEt_3 (4.2 μl, 0.030 mmol). The ^1H and ^{31}P NMR spectra showed immediately the following resonances.

which were attributed to the vinyl derivative *trans*-[Pt(Me){C(OCH$_2$CH$_2$Br)=CH(*p*-tolyl)}(PPh$_3$)$_2$]; *Z* isomer: −0.55 [t, 3H, CH$_3$, ^2J(HPt) 50.2, ^3J(HP) 6.4], 5.45 [s, 1H, =CH, ^3J(HPt) 44.8], 2.26 [s, 3H, CH$_3$(*p*-tolyl)], 3.00 and 2.87 [m, 4H, OCH$_2$CH$_2$Br]. ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 26.9 [s, ^1J(PPt) 3243]. The signals corresponding to the *E* isomer could not be assigned.

The reaction of **2** with NEt$_3$ was also followed by ^{1}H and ^{31}P{^{1}H} NMR at room temperature. In an NMR tube under nitrogen containing **2** (30 mg, 0.027 mmol) in CDCl$_3$ (0.5 ml) was added NEt$_3$ (42 μl, 0.030 mmol). The ^{1}H and ^{31}P NMR spectra showed immediately the following resonances, which were assigned to the vinyl derivative *trans*-[Pt(Me){C(OCH$_2$CH$_2$I)=CH(*p*-tolyl)}(PPh$_3$)$_2$]; *Z* isomer: δ −0.51 [t, 3H, CH$_3$, ^2J(HPt) 46.9, ^3J(HP) 6.4], 5.55 [s, 1H, =CH, ^3J(HPt) 45.3], 2.29 [s, 3H, CH$_3$(*p*-tolyl)], 3.02 and 2.63 [m, 4H, OCH$_2$CH$_2$I]. ^{31}P{^{1}H} NMR (δ, CDCl$_3$): 26.95 [s, ^1J(PPt) 3246]; *E* isomer (~10%): the corresponding signals could not be safely assigned.

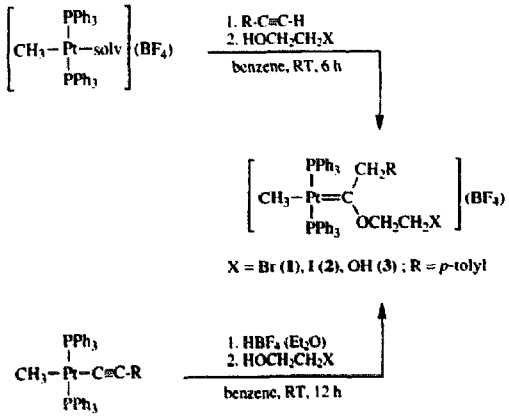
The reaction of **3** with n-BuLi was followed by ^{1}H and ^{31}P{^{1}H} NMR at room temperature. In an NMR tube under nitrogen containing **3** (49 mg, 0.049 mmol) in CDCl$_3$ (0.5 ml) was added n-BuLi (0.031 ml of a 1.6 M n-hexane solution). The ^{1}H and ^{31}P NMR spectra showed immediately the following resonances, which were attributed to the vinyl derivative *trans*-[Pt(Me){C(OCH$_2$CH$_2$OH)=CH(*p*-tolyl)}(PPh$_3$)$_2$]; Z isomer: δ −0.43 [t, 3H, CH$_3$, ^2J(HPt) 48.2, ^3J(HP) 6.4], 5.54 [s, 1H, =CH, ^3J(HPt) 45.2], 2.24 [s, 3H, CH$_3$(*p*-tolyl)], 2.97 [m, 4H, OCH$_2$CH$_2$O], 4.87 [t, 1H, OH, ^3J(HH) 7.0]. ^{31}P{^{1}H} NMR: 26.95 [s, ^1J(PPt) 3246]; *E* isomer (~15%): δ 5.05 [br, 1H, =CH(*p*-tolyl)], 2.41 [s, 3H, CH$_3$(*p*-tolyl)], 3.81 and 3.41 [m, 4H, OCH$_2$CH$_2$O]. ^{31}P{^{1}H} NMR: 24.58 [s, ^1J(PPt) 3156].

3. Results and discussion

3.1. Reactions of platinum(II)–alkyne and –alkynyl complexes with HOCH$_2$CH$_2$X (X = Br, I, OH)

The reactions of *trans*-[Pt(Me)(PPh$_3$)$_2$(solv)][BF$_4$] with a slight molar excess of *p*-tolylacetylene in benzene at room temperature for 6 h in the presence of an excess of HOCH$_2$CH$_2$X afford in good yield the corresponding (alkoxy)alkyl carbene complexes **1–3** as illustrated in Scheme 2.

Complexes **1–3** can be also prepared, but in lower yield, by reaction in benzene at room temperature for 12 h of *trans*-[Pt(Me)(C≡C-*p*-tolyl)(PPh$_3$)$_2$] with ~10-fold excess of HOCH$_2$CH$_2$X in the presence of a stoichiometric amount of the strong acid HBF$_4$. Both reactions are also accompanied with the formation as a by-product of the carbonyl derivative *trans*-[Pt(Me)(CO)(PPh$_3$)$_2$][BF$_4$], which is likely generated by C≡C bond breaking, promoted by Pt(II), of the alkynyl ligand in the presence of traces of H$_2$O (see further).

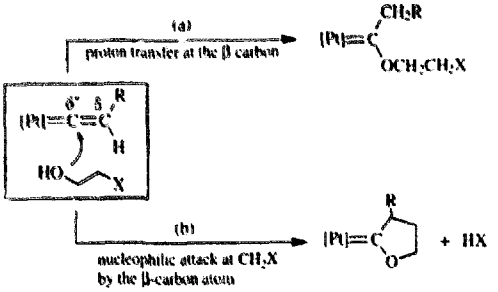


Scheme 2.

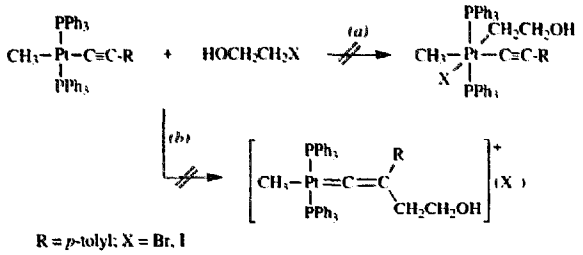
Complexes **1–3** show in their ^{1}H NMR spectra the CH$_2$R protons in the range 3.28–3.49 ppm as singlets. The –OCH$_2$– protons appear as triplets (except for **1** which is a multiplet) in the range 4.88–5.00 ppm due to coupling with the adjacent methylene protons. The –CH$_2$X protons appear also as triplets in the range 3.00–3.79 ppm, due to coupling with the OCH$_2$ protons. All the above signals have been assigned on the basis of homonuclear decoupling experiments and by comparison with the spectra reported for similar compounds derived by reaction of 2-chloroethanol [2]. The triplet resonance of the Pt(II)-coordinated CH$_3$ group in the ^{1}H NMR and the singlet resonance for the PPh$_3$ ligands in the ^{31}P NMR spectra confirm the *trans* geometry of these complexes.

In the nujol mull IR spectra of **1–3**, a medium absorption at ~1280 cm^{-1} is assigned to ν_{as}(C–O) of the carbene ligand, also in analogy with this type of assignment for other alkoxy(alkyl)carbene complexes of Pt(II) [2].

The formation of the (alkoxy)alkyl carbene complexes **1–3** is consistent with a mechanism involving the intermediacy of a vinylidene species (Scheme 3), which could be generated either by isomerization of the terminal alkyne promoted by an unsaturated metal species [10], in the present case *trans*-[Pt(Me)(PPh$_3$)$_2$(solv)][BF$_4$], or by protonation of the β-carbon of the acetylide by HBF$_4$ [1a,b]. Although never detected for Pt(II), a large number of vinylidene complexes has been isolated or characterized for several other transition metal centers [1a,b]. Theoretical and reactivity studies have shown that the α-carbon atom of the vinylidene is electrophilic, while an increased electron density is located



Scheme 3.



Scheme 4.

at the β-carbon atom [1]. This would explain in Scheme 3 (route (a)) the nucleophilic attack by the hydroxy function at the α-carbon atom followed by proton transfer at the nucleophilic β-carbon.

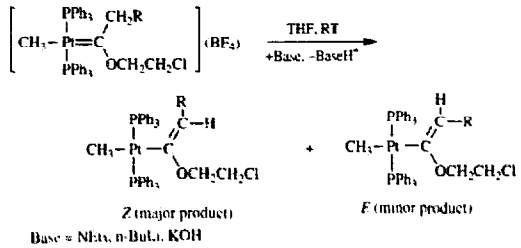
There was no evidence of the formation of cyclic oxycarbene complexes by ring closure of the nucleophilic vinylidene β-carbon atom on the CH_2X moiety (route (b)). These reactions could be facilitated in the case of the haloalcohols $HOCH_2CH_2X$ (X = Br, I), which have, on the basis of C–X bond distances [C–Cl (176.7 pm) < C–Br (193.7 pm) < C–I (213.5 pm)] and bond energy [C–Cl (351 kJ mol^{-1}) > C–Br (293 kJ mol^{-1}) > C–I (234 kJ mol^{-1})] considerations for alkyl halides in the gas phase [11], a more easily displaced X^- compared to Cl^- in 2-chloroethanol.

In the case of the reactions of the acetylide *trans*-[Pt(Me)(C≡C-*p*-tolyl)$(PPh_3)_2$] with $HOCH_2CH_2X$ (X = Br, I), carried out in the absence of HBF_4, there was also no evidence of side reaction pathways involving the CH_2–X group either at the metal center via an oxidative addition process to form Pt(IV) derivatives (Scheme 4, route (a)), which is known to occur for Pt(II) [12], or an electrophilic attack at the β-carbon atom of the acetylide to yield a vinylidene species (route (b)), as otherwise reported to occur for certain Ru–acetylide complexes with alkyl iodides [1a,b].

The lack of this type of reactivity by *trans*-[Pt(Me)(C≡C-*p*-tolyl)$(PPh_3)_2$] indicates a poor nucleophilic character for both the metal center and the β-carbon atom of the acetylide. This feature is further supported by the fact that also in the carbene complexes **1–3** the CH_2X moiety of the carbene ligand, although in a favorable position, does not interact with the Pt(II) center via an intramolecular oxidative addition.

The involvement of an electrophilic vinylidene intermediate in the synthesis of complexes **1–3** can also explain the parallel formation of small amounts (~5%) based on the integration ratios of the methyl resonances in the proton NMR spectra) of the carbonyl derivative *trans*-[Pt(Me)(CO)$(PPh_3)_2$][BF_4] [13]. In fact, this latter complex might be originated by attack of water on the intermediate vinylidene [Pt]=C=C(H)R to give an unstable hydroxycarbene species of the type [Pt]=C(OH)–CH_2(R) [14], which eventually rearranges to the carbonyl derivative, similarly to what was recently found by Bianchini et al. in the formation of the carbonyl complex *mer*-[(PNP)RuCl(CH_2Ph)(CO)] (PNP = $CH_3CH_2CH_2N(CH_2CH_2PPh_2)_2$) [15] from the reaction of 1-alkynes with water. Further studies of the Pt(II) systems are underway.

Complexes **1–3** are stable in the solid state and in solution but react with bases forming the corresponding vinyl derivatives. In the case of the chloroethoxy–carbene complex the vinyl product *trans*-[Pt(Me){C(OCH_2CH_2Cl)=CH-(*p*-tolyl)}$(PPh_3)_2$] was isolated (Eq. (2)).

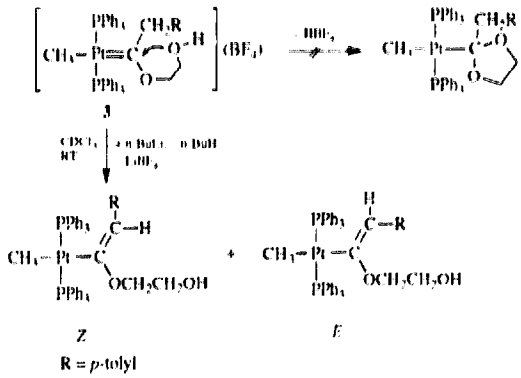


(2)

The product is obtained also by using KOH and n-BuLi as the bases. In all cases the formation of the =CH moiety is well evidenced in the ^{1}H NMR spectra which show the methine signal at about 5 ppm flanked by ^{195}Pt satellites (^3J(HPt) ~45 Hz for the *Z* isomer having the Pt and H groups *trans* to each other and ~24 Hz for the *E* isomer). It is noteworthy that both *E* and *Z* isomers are formed in different ratios [16]. The *Z* isomers are identified on the basis of the higher value of the ^3J(HPt) coupling constant with ^{195}Pt (see Section 2). The ^{1}H NMR spectra show that in 2 h the corresponding signals of the bromo- and iodo-vinyl derivatives *trans*-[Pt(Me){C(OCH_2CH_2Br)=CH(*p*-tolyl)}$(PPh_3)_2$] and *trans*-[Pt(Me){C(OCH_2CH_2I)=CH(*p*-tolyl)}$(PPh_3)_2$] disappear indicating rearrangement processes to still uncharacterized mixtures of products.

It is noteworthy that in the case of **3** no intramolecular reaction is observed of the free –OH group with the electrophilic carbene carbon, which would expect to form a five-membered dioxy heterocycle (Scheme 5).

Although this reaction could be facilitated by a base, it is observed that addition of one equivalent of n-BuLi selectively deprotonates the methylene group α to the carbene carbon rather than the hydroxyl proton with the formation of the neutral α-alkoxyalkenyl (vinyl ether) derivative (see Section 2).



Scheme 5.

Acknowledgements

R.A.M. thanks MURST and CNR (CNR/JNICT cooperation program) for financial support.

References

[1] (a) M.I. Bruce and A.G. Swincer, Adv. Organomet. Chem., 22 (1983) 59; (b) M.I. Bruce, Chem. Rev., 91 (1991) 197; (c) H.H. Chisholm and H.C. Clark, Acc. Chem. Res., 6 (1973) 202.

[2] U. Belluco, R. Bertani, R.A. Michelin, M. Mozzon, F. Benetollo, G. Bombieri and R.J. Angelici, Inorg. Chim. Acta, 240 (1995) 567.

[3] R.A. Michelin, M. Mozzon, B. Vialetto, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, Organometallics, 15 (1996) 4096.

[4] R.A. Michelin, M. Mozzon, B. Vialetto, R. Bertani, G. Bandoli and R.J. Angelici, Organometallics, 17 (1998) 1220.

[5] (a) R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino and R.J. Angelici, Inorg. Chem., 27 (1988) 85; (b) R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino and R.J. Angelici, Inorg. Chem., 27 (1988) 93; (c) R. Bertani, M. Mozzon and R.A. Michelin, Inorg. Chem., 27 (1988) 2809; (d) R. Bertani, M. Mozzon, F. Benetollo, G. Bombieri and R.A. Michelin, J. Chem. Soc., Dalton Trans., (1990) 1197; (e) R. Bertani, M. Mozzon, R.A. Michelin, F. Benetollo, G. Bombieri, T.J. Castilho and A.J.L. Pombeiro, Inorg. Chim. Acta, 189 (1991) 175; (f) U. Belluco, R.A. Michelin, R. Ros, R. Bertani, G. Facchin, M. Mozzon and L. Zanotto, Inorg. Chim. Acta, 198–200 (1992) 883, and Refs. therein.

[6] (a) H. Motschi and R.J. Angelici, Organometallics, 1 (1982) 343; (b) L. Zanotto, R. Bertani and R.A. Michelin, Inorg. Chem., 29 (1990) 3265.

[7] R.A. Michelin, M. Mozzon and R. Bertani, Coord. Chem. Rev., 147 (1996) 299.

[8] D.D. Perrin, W.L.F. Armarego and D.R.Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1980.

[9] H.C. Clark and L. E. Manzer, J. Organomet. Chem., 175 (1973) 411.

[10] (a) J. Silvestre and R. Hoffmann, Helv. Chim. Acta, 68 (1985) 1461; (b) H. Werner, Angew. Chem., Int. Ed. Engl., 29 (1990) 1077.

[11] R.D. Chambers and S.R. James, in J.F. Stoddart (Ed.), Comprehensive Organic Chemistry, Vol. 1, Pergamon, Oxford, 1979, Ch. 3, p. 525.

[12] (a) U. Belluco, Organometallic and Coordination Chemistry of Platinum, Academic Press, London, 1974; (b) J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1980.

[13] C. Eaborn, K.J. Odell and A. Pidcock, J. Chem. Soc., Dalton Trans., (1979) 134.

[14] W.E. Buhro, A. Wong, J.H. Merrfield, G.-Y. Lin, A.C. Constable and J.A. Gladysz, Organometallics, 2 (1983) 185.

[15] C. Bianchini, J.A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, J. Am. Chem. Soc., 118 (1996) 4585.

[16] G. Bandoli, P.A. Caputo, F.P. Intini, M.F. Sivo and G. Natile, J. Am. Chem. Soc., 119 (1997) 10370.