ELSEVIER

Inorganica Chimica Acta 240 (1995) 567-574

Inorganica Chimica Acta

Reactions of the haloalcohols $HO(CH_2)_nCl$ ($n=2, 3$) with platinum(II)- alkynyl and -alkyne complexes. X-ray crystal structure of *trans*-$[Pt(Me)\{C(OCH_2CH_2Cl)(CH_2Ph)\}(PPh_3)_2][BF_4]$ ☆

Umberto Belluco [a], Roberta Bertani [a], Rino A. Michelin [a,*], Mirto Mozzon [a],
Franco Benetollo [b], Gabriella Bombieri [c], Robert J. Angelici [d,*]

[a] *Istituto di Chimica Industriale and Centro di Studio per la Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione del CNR, Facoltà di Ingegneria, Università di Padova, Via F. Marzolo 9, 35131 Padua, Italy*
[b] *Istituto di Chimica e Tecnologie Inorganiche dei Materiali Avanzati del CNR, Corso Stati Uniti 4, 35100 Padua, Italy*
[c] *Istituto di Chimica Farmaceutica, Università di Milano, Viale Duca degli Abbruzzi, 20131 Milan, Italy*
[d] *Department of Chemistry, Iowa State University, Ames, IA 50011, USA*

Received 18 April 1995; revised 21 July 1995

Abstract

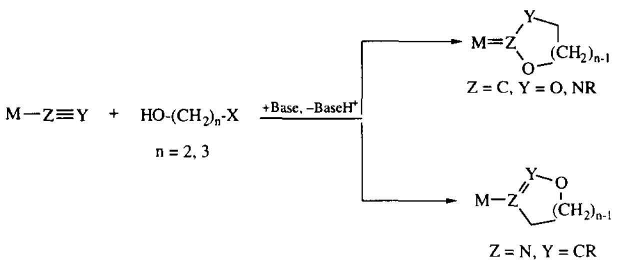
The chloro complexes *trans*-$[Pt(Me)(Cl)(PPh_3)_2]$, after treatment with $AgBF_4$, react with 1-alkynes HC≡C–R in the presence of NEt_3 to afford the corresponding acetylide derivatives *trans*-$[Pt(Me)(C{\equiv}C{-}R)(PPh_3)_2]$ (R = *p*-tolyl (**1**), Ph (**2**), $C(CH_3)_3$ (**3**)). These complexes, with the exception of the t-butylacetylide complex, react with the chloroalcohols $HO(CH_2)_nCl$ ($n=2, 3$) in the presence of 1 equiv. of HBF_4 to afford the alkyl(chloroalkoxy)carbene complexes *trans*-$[Pt(Me)\{C[O(CH_2)_nCl](CH_2R)\}(PPh_3)_2][BF_4]$ (R = *p*-tolyl, $n=2$ (**4**), $n=3$ (**5**); R = Ph, $n=2$ (**6**)). A similar reaction of the bis(acetylide) complex *trans*-$[Pt(C{\equiv}C{-}Ph)_2(PMe_2Ph)_2]$ with 2 equiv. HBF_4 and 3-chloro-1-propanol affords *trans*-$[Pt(C{\equiv}CPh)\{C(OCH_2CH_2CH_2Cl)(CH_2Ph)\}(PMe_2Ph)_2][BF_4]$ (**7**). The alkyl(chloroalkoxy)-carbene complex *trans*-$[Pt(Me)\{C(OCH_2CH_2Cl)(CH_2Ph)\}(PPh_3)_2][BF_4]$ (**8**) is formed by reaction of *trans*-$[Pt(Me)(Cl)(PPh_3)_2]$, after treatment with $AgBF_4$ in $HOCH_2CH_2Cl$, with phenylacetylene in the presence of 1 equiv. of n-BuLi. The reaction of the dimer $[Pt(Cl)(\mu\text{-}Cl)(PMe_2Ph)]_2$ with *p*-tolylacetylene and 3-chloro-1-propanol yields *cis*-$[PtCl_2\{C(OCH_2CH_2CH_2Cl)(CH_2C_6H_4\text{-}p\text{-}Me)\}(PMe_2Ph)]$ (**9**). The X-ray molecular structure of (**8**) has been determined. It crystallizes in the orthorhombic system, space group $Pna2_1$, with $a=11.785(2)$, $b=29.418(4)$, $c=15.409(3)$ Å, $V=4889(1)$ Å^3 and $Z=4$. The carbene ligand is perpendicular to the Pt(II) coordination plane; the Pt–C(carbene) bond distance is 2.01(1) Å and the short C(carbene)–O bond distance of 1.30(1) Å suggests extensive electronic delocalization within the Pt–C(carbene)–O moiety.

Keywords: Crystal structures; Platinum complexes; Alkynyl complexes; Carbene complexes

1. Introduction

The haloalcohols $HO{-}(CH_2)_n{-}X$ ($n=2, 3$; X = Cl, Br) have been successfully used in reactions of transition metal complexes with unsaturated ligands such as CO [1], RNC [2] and RCN [3] to form cyclic carbene, 2-oxazoline and 1,3-oxazine complexes, as outlined in Scheme 1.

Transition-metal complexes with 1-alkyne and alkynyl ligands, have been shown [4] to react with alcohols to afford alkoxy(alkyl)carbene derivatives by a mechanism which is consistent with the intermediate formation of cationic metal–vinylidene complexes. Platinum(II) is no exception and



Scheme 1.

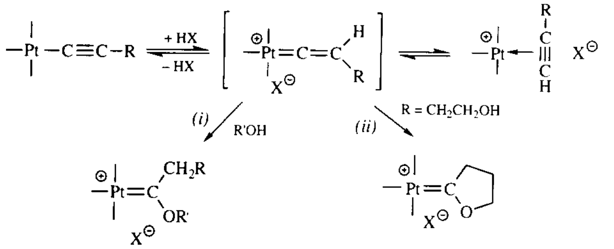
Scheme 2 illustrates some of these reactions (route (*i*)). Route (*ii*) is based on the use of alkynols, which, upon coordination to the metal center, undergo intramolecular nucleophilic attack of the alcohol functionality at the inter-

---

☆ In honor of Professor Fred Basolo.

* Corresponding authors.

SSDI 0020-1693(95)04584-V



Scheme 2.

mediate metal-coordinated vinylidene carbon atom to produce cyclic oxocarbene complexes [5].

In view of the reaction chemistry described in Schemes 1 and 2 and of the noted similarity of the vinylidene unit to the isoelectronic carbonyl ligand [6], we thought it was of interest to explore the reactions of the haloalcohols HO–$(CH_2)_n$–Cl ($n=2$, 3) with Pt(II)–(η^2)alkyne and Pt(II)–(η^1)alkynyl complexes with the aim to synthesize cyclic oxocarbenes, which might be formed by initial attack of the oxygen atom of the alcohol or the alkoxide (when in the presence of a base) at the α-carbon atom of the vinylidene intermediate and subsequent intramolecular ring closure at the nucleophilic β-carbon atom by Cl^- displacement. The results of this study are reported herein.

2. Experimental

2.1. General procedures

All reactions were carried out under an N_2 atmosphere. All the solvents were of reagent grade and used without further purification. IR spectra were taken on a Perkin-Elmer 983 spectrophotometer (abbrev.: 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: $CDCl_3$, δ 7.23; CD_2Cl_2, δ 5.32. The $^{13}C\{^1H\}$ NMR shifts are given relative to the solvent resonance: $CDCl_3$, δ 77.0; CD_2Cl_2 δ 53.8. $^{31}P\{^1H\}$ NMR spectra were run on a Varian FT 80-A spectrometer; 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 (abbrev.: s = singlet, t = triplet, qt = quintet, dq = doublet of quartets, m = multiplet, br = broad). 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.

2.2. Starting complexes

The complexes *trans*-[Pt(Me)Cl$(PPh_3)_2$] [7], *trans*-[Pt(C≡CPh)$_2$(PMe$_2$Ph)$_2$] [8] and [Pt(Cl)(μ-Cl)(PMe$_2$Ph)]$_2$ [9] were prepared according to literature procedures.

2.3. Synthesis of the complexes

2.3.1. *Trans-[Pt(Me){C≡C(C$_6$H$_4$-p-Me)}(PPh$_3$)$_2$] (1)*

A suspension of *trans*-[Pt(Me)Cl$(PPh_3)_2$] (600 mg, 0.78 mmol) in acetone (100 ml) was treated with a solution of 0.262 M $AgBF_4$ (3 ml, 0.78 mmol) in acetone at r.t. and the reaction mixture was stirred for 1 h. It was then filtered to remove solid AgCl and treated with triethylamine (0.16 ml, 1.17 mmol) and *p*-tolylacetylene (0.3 ml, 2.34 mmol). The reaction mixture was stirred overnight and during this time the colour of the suspension turned brown. After filtration, the solid was treated with CH_2Cl_2 (50 ml). The resulting solution was filtered and then reduced to a small volume (20 ml). Addition of n-pentane (30 ml) gave the product as a white solid, which was filtered off and dried under vacuum. Yield: 610 mg (92%). M.p. 190–192 °C (decomp.). *Anal.* Calc. for $C_{46}H_{40}P_2Pt \cdot CH_2Cl_2$: C, 60.39; H, 4.53. Found: C, 60.65; H, 4.52%. IR (nujol mull): ν(C≡C) 2101 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.47 (t, ^2J(HPt) 53.5, ^3J(HP) 6.5, 3H, CH_3); 2.10 (s, 3H, CH_3(C_6H_4-*p*-Me)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 24.98 (s, ^1J(PPt) 2993).

2.3.2. *Trans-[Pt(Me){C≡CPh}(PPh$_3$)$_2$] (2)*

This compound was prepared as described for **1** starting from *trans*-[Pt(Me)Cl$(PPh_3)_2$] (300 mg, 0.39 mmol), a solution of 0.262 M $AgBF_4$ (1.5 ml, 0.39 mmol) in acetone, triethylamine (80 μl, 0.58 mmol) and phenylacetylene (130 μl, 1.17 mmol) in acetone (50 ml). Yield: 210 mg (64.4%). M.p. 185–188 °C (decomp.). *Anal.* Calc. for $C_{45}H_{38}P_2Pt \cdot CH_2Cl_2$: C, 62.48; H, 4.55. Found: C, 62.51; H, 4.69%. IR (nujol mull): ν(C≡C) 2103 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.46 (t, ^2J(HPt) 53.1, ^3J(HP) 6.4, 3H, CH_3); $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.61 (s, ^1J(PPt) 2969).

2.3.3. *Trans-[Pt(Me){C≡C–C(CH$_3$)$_3$}(PPh$_3$)$_2$] (3)*

This compound was prepared as described for **1** starting from *trans*-[Pt(Me)Cl$(PPh_3)_2$] (352 mg, 0.46 mmol), a solution of 0.262 M $AgBF_4$ (1.97 ml, 0.46 mmol) in acetone, triethylamine (96 μl, 0.69 mmol) and 3,3-dimethyl-1-butyne (169 μl, 1.37 mmol) in acetone (50 ml). Yield: 296 mg (79%). M.p. 186–188 °C (decomp.). *Anal.* Calc. for $C_{43}H_{42}P_2Pt \cdot CH_2Cl_2$: C, 58.67; H, 4.92. Found: C, 58.70; H, 4.87%. IR (nujol mull): ν(C≡C) 2103 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ −0.62 (t, ^2J(HPt) 55.1, ^3J(HP) 6.1, 3H, CH_3); 0.46 (s, 9H, C$(CH_3)_3$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 26.42 (s, ^1J(PPt) 3021).

2.3.4. *Trans-[Pt(Me){C(OCH$_2$CH$_2$Cl)(CH$_2$C$_6$H$_4$-p-Me)}(PPh$_3$)$_2$][BF$_4$] (4)*

To a solution of **1** (150 mg, 0.18 mmol) in benzene (10 ml) at 0 °C was added a solution of 54% HBF_4 (14 μl, 0.19 mmol) in diethylether and then 2-chloroethanol (0.2 ml, 2.98 mmol). The colourless solution was allowed to reach r.t. and stirring was continued overnight, during which time a white solid precipitate was obtained. The reaction mixture was filtered off, the solid product washed with n-pentane (3 × 10 ml) and dried under vacuum. Yield: 112.2 mg (61.2%). M.p. 169–172 °C (decomp.). *Anal.* Calc. for $C_{48}H_{46}OClP_2BF_4Pt$: C, 56.62; H, 4.56. Found: C, 56.91; H, 4.51%. IR (nujol mull): ν(C–O) 1280 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ −0.13 (t, ^3J(HP) 8.6, ^2J(HPt) 44.8, 3H, CH_3); 2.31 (s, 3H, $CH_3(C_6H_4$-*p*-Me)); 3.35 (s, 2H, $CH_2(C_6H_4$-*p*-Me)); 3.41 (t, ^3J(HH) 5.0, 2H, CH_2Cl); 4.82 (t, ^3J(HH) 5.0, ^4J(HPt) 19.2, 2H, OCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 321.6 (t, ^2J(CP) 4.4, ^1J(CPt) 813, $C_{(carbene)}$); 83.3 (s, ^3J(CPt) 58.3, OCH_2); 62.2 (s, ^2J(CPt) 66.1, $CH_2(C_6H_4$-*p*-Me)); 40.4 (s, CH_2Cl); −1.45 (s, ^1J(CPt) 381, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 23.41 (s, ^1J(PPt) 2906).

2.3.5. *Trans-[Pt(Me){C(OCH$_2$CH$_2$CH$_2$Cl)(CH$_2$C$_6$H$_4$-p-Me)}(PPh$_3$)$_2$][BF$_4$] (5)*

This compound was prepared as described for **4** starting from **1** (170 mg, 0.20 mmol), a solution of 54% HBF_4 (16 μl, 0.22 mmol) in diethylether and 3-chloro-1-propanol (0.2 ml, 2.39 mmol) in benzene (10 ml). Yield: 125 mg (60.6%). M.p. 185–188 °C (decomp.). *Anal.* Calc. for $C_{49}H_{48}OClP_2BF_4Pt$: C, 57.02; H, 4.69. Found: C, 57.18; H, 4.69%. IR (nujol mull): ν(C–O) 1294 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −0.12 (t, ^2J(HPt) 45.2, ^3J(HP) 8.5, 3H, CH_3); 2.30 (s, 3H, CH_3); 3.29 (t, ^3J(HH) 5.9, 2H, CH_2Cl); 1.83 (qt, 2H, –CH_2–), 3.38 (s, 2H, $CH_2(C_6H_4$-*p*-Me)); 4.69 (t, ^3J(HH) 6.0, ^4J(HPt) 19.9, 2H, OCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 320.3 (t, ^2J(CP) 6.1, ^1J(CPt) 803, $C_{(carbene)}$); 80.79 (s, ^3J(CPt) 59.6, OCH_2); 61.75 (s, ^2J(CPt) 67.0, $CH_2(C_6H_4$-*p*-Me)); 30.51 (s, CH_2); 40.77 (s, CH_2Cl); 21.11 (s, CH_3); −1.81 (t, ^2J(CP) 6.2, ^1J(CPt) 370, CH_3). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 23.76 (s, ^1J(PPt) 2894).

2.3.6. *Trans-[Pt(Me){C(OCH$_2$CH$_2$CH$_2$Cl)(CH$_2$Ph)}(PPh$_3$)$_2$][BF$_4$] (6)*

This compound was prepared as described for **4** starting from **2** (200 mg, 0.24 mmol), a solution of 54% HBF_4 (19 μl, 0.26 mmol) in diethylether and 3-chloro-1-propanol (0.2 ml, 2.39 mmol) in benzene (20 ml). Yield: 186 mg (76.1%). M.p. 180–182 °C (decomp.). *Anal.* Calc. for $C_{48}H_{46}OClP_2BF_4Pt$: C, 56.62; H, 4.55. Found: C, 56.75; H, 4.64%. IR (nujol mull): ν(C–O) 1276 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −0.11 (t, ^2J(HPt) 45.2, ^3J(PH) 8.5, 3H, CH_3); 1.83 (qt, ^3J(HH) 6.4, 2H, CH_2); 3.26 (t, ^3J(HH) 5.9, 2H, CH_2Cl); 3.45 (s-br, 2H, CH_2Ph); 4.88 (t, ^3J(HH) 5.9, ^4J(HPt) 19.9, 2H, OCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 319.6 (t, ^2J(CP) 6.1, ^1J(CPt) 793, $C_{(carbene)}$); 80.9 (s, ^3J(CPt) 60.2, OCH_2); 62.2 (s, ^2J(CPt) 67.6, CH_2Ph); 40.71 (s, CH_2Cl); 30.50 (s, CH_2); −1.81 (t, ^2J(CP) 5.8, ^1J(CPt) 369, CH_3). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 23.77 (s, ^1J(PPt) 2806).

2.3.7. *Trans-[PtC≡CPh){C(OCH$_2$CH$_2$CH$_2$Cl)(CH$_2$Ph)}(PMe$_2$Ph)$_2$][BF$_4$] (7)*

This compound was prepared as described for **4** starting from *trans*-[Pt(C≡CPh)$_2$(PMe$_2$Ph)$_2$] (80 mg, 0.12 mmol), a solution of 54% HBF_4 (19 μl, 0.26 mmol) in diethylether and 3-chloro-1-propanol (0.4 ml, 4.78 mmol) in benzene (10 ml). Yield: 65.2 mg (63.5%). M.p. 162–165 °C (decomp.). *Anal.* Calc. for $C_{35}H_{40}OClP_2BF_4Pt$: C, 49.11; H, 4.71. Found: C, 49.29; H, 4.86%. IR (nujol mull): ν(C≡C) 2119 (s) cm^{-1}; ν(C–O) 1290 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 5.03 (t, ^3J(HH) 6.0, ^4J(HPt) 21.4, 2H, OCH_2); 3.64 (s, 2H, CH_2Ph); 3.56 (t, ^3J(HH) 6.1, 2H, CH_2Cl); 2.29 (qt, ^3J(HH) 6.1, 2H, –CH_2–); 1.97 (dq, ^4J(HH) 4.2, ^2J(HP) 3.92, ^3J(HPt) 34.4, 12H, PMe). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ −13.18 (s, ^1J(PPt) 2310).

2.3.8. *Trans-[Pt(Me){C(OCH$_2$CH$_2$Cl)(CH$_2$Ph)}(PPh$_3$)$_2$][BF$_4$] (8)*

To a suspension of *trans*-[Pt(Me)Cl(PPh$_3$)$_2$] (300 mg, 0.39 mmol) in 2-chloroethanol (20 ml) was added phenylacetylene (64 μl, 0.58 mmol) and then a solution of 0.95 M $AgBF_4$ (0.41 ml, 0.39 mmol) in acetone at r.t. The reaction mixture turned violet and then a solution of 1.6 M n-BuLi (0.26 ml, 0.43 mmol) in n-hexane was added. The colour of the suspension turned yellow and stirring was continued for 15 min. It was then taken to dryness and the solid residue was treated with CH_2Cl_2 (100 ml). After filtration, the resulting solution was reduced to a small volume (20 ml). Addition of Et_2O (30 ml) gave the product as a white solid, which was filtered off, washed with benzene (3×10 ml), n-pentane (3×10 ml) and dried under vacuum. Yield: 209 mg (53.3%). M.p. 168–170 °C (decomp.). *Anal.* Calc. for $C_{47}H_{44}OClP_2BF_4Pt$: C, 56.22; H, 4.42. Found: C, 56.92; H, 4.80%. IR (nujol mull): ν(C–O) 1270 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ −0.21 (t, ^2J(HPt) 45.3, ^3J(HP) 8.6, 3H, CH_3); 3.35 (s-br, 2H, CH_2Ph); 3.41 (s, ^3J(HH) 4.8, 2H, CH_2Cl); 4.85 (t, ^4J(HPt) 16.9, ^3J(HH) 4.8, 2H, OCH_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ $C_{(carbene)}$: too low intensity to be observed; 83.33 (s, ^3J(CPt) 58.5, OCH_2); 62.18 (s, ^2J(CPt) 67.4, CH_2Ph); 40.40 (s, CH_2Cl); −1.49 (s, ^1J(CPt) 374, CH_3). ^{31}P{^{1}H}NMR (CD_2Cl_2): δ 23.79 (s, ^1J(PPt) 2902).

2.3.9. *Cis-[PtCl$_2${C(OCH$_2$CH$_2$CH$_2$Cl)(CH$_2$C$_6$H$_4$-p-Me)}(PMe$_2$Ph)] (9)*

To a yellow suspension of [Pt(Cl)(μ-Cl)(PMe$_2$Ph)]$_2$ (164 mg, 0.20 mmol) in benzene (20 ml) at r.t. was added *p*-tolylacetylene (77 μl, 0.61 mmol) and then 3-chloro-1-propanol (1 ml, 11.95 mmol). The solution obtained was stirred for 10 h, during which time the colour changed from yellow to brown. Addition of n-pentane (20 ml) gave a light brown solid which was filtered off. This solid was vigorously stirred in benzene (5 ml) for 10 min and then filtered. The white solid obtained was washed with n-pentane (3×10 ml) and dried under vacuum. Yield: 150 mg (60%). M.p. 164–167 °C (decomp.). *Anal.* Calc. for $C_{20}H_{26}OCl_3PPt$: C, 39.07; H, 4.26. Found: C, 39.09; H, 4.27%. IR (nujol mull): ν(PtCl) 284, 310 (m) cm^{-1}; ν(C–O) 1286 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.64 (d, ^2J(HP) 11.6, ^3J(HPt) 44.8, 3H, PMe); 1.63 (d, ^2J(HP) 11.5, ^3J(HPt) 46.4, 3H, PMe); 3.88 and 3.53 (AB pattern, ^2J(HH) 17.8, 2H, $CH_2(C_6H_4$-*p*-Me)); 2.25 (m, 2H, CH_2); 2.16 (s, 3H, CH_3); 3.40 (m, 2H, CH_2Cl);

5.04 (m, 1H, OCH_2); 5.60 (m, 1H, OCH_2). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 275.6 (d, ^2J(CP) 12.2, ^1J(CPt) 1202, $C_{(carbene)}$); 82.27 (s, ^3J(CPt) 81.5, OCH_2); 61.57 (s, ^2J(CPt) 106.3, $CH_2(C_6H_4$-p-Me)); 40.98 (s, CH_2Cl); 31.20 (s, CH_2); 21.16 (s, PMe); 14.52 (s, ^2J(PtC) 82.5, PMe). $^{31}P\{^1H\}$NMR (CD_2Cl_2): δ −18.12 (s, ^1J(PPt) 3756).

2.4. X-ray structure determination of trans-[Pt(Me){C(OCH₂CH₂Cl)(CH₂Ph)}(PPh₃)₂][BF₄] (8)

Crystal data: $Mr = 1004.2$, orthorhombic, space group $Pna2_1$, $a = 11.785(2)$, $b = 29.418(4)$, $c = 15.409(3)$ Å; $V = 4889(1)$ Å^3, $Z = 4$, $D_x = 1.364$ g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 3.04 mm^{-1}, $F(000) = 2000$, $T = 295$ K. A prismatic (white) crystal of dimensions $0.30 \times 0.16 \times 0.42$ mm was lodged in a Lindemann glass capillary and centered on a four-circle Philips PW1100 (Febo System) diffractometer with graphite-monochromated (Mo Kα) radiation $\lambda = 0.71069$ Å). The orientation matrix and preliminary unit-cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying the orientation angles χ and Φ over a range of 120°, with $6 \leq \theta \leq 9°$. For the determination of precise lattice parameters, 30 strong reflections with $9 \leq \theta \leq 11°$ were considered. Integrated intensities for hkl reflections ($h = 0 \rightarrow 14$, $k = 0 \rightarrow 16$, $l = 0 \rightarrow 13$ were measured in the interval $\theta = 3$–$27°$), using $\theta/2\theta$ scans. Three standard reflections, −2,5,1; 2,5,1; 1,6,1 were collected every 200 reflections. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz-polarization effects and for absorption as described by North et al. [10]. No correction was made for extinction.

The structure was solved by heavy atoms methods [11]. Refinement was carried out by full-matrix least-squares; the function minimized was $\Sigma w(F_o{}^2 - F_c{}^2)^2$, with weighting scheme $w = 1/[\sigma^2(F_o{}^2) + (0.0531P)^2 + 25.14P]$, where $P = \max(F_o{}^2 + 2F_c{}^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were placed in calculated positions with fixed, isotropic thermal parameters (1.2 U_{eq} of the parent carbon atom). Conventional $R = 0.0414$, based on F values of 4216 reflections having $F_o{}^2 \geq 3\sigma(F_o)^2$ and $S = 1.291$, (wR on $F^2 = 0.110$). The absolute configuration of the space group was assigned on the basis of Flack parameter [12]. Structure refinement was carried out with SHELXL-93 [13] using the scattering factors inclosed therein; the drawing was produced using ORTEP II [14]. Final atomic coordinates are given in Table 1; selected bond lengths and angles are given in Table 2.

Table 1

Fractional atomic coordinates and equivalent thermal parameters ($Å^2 \times 10^3$) for non-H atoms for *trans*-[Pt(Me){C(OCH_2CH_2Cl)(CH_2Ph)}($(PPh_3)_2$][BF_4] (**8**)

Atom	x	y	z	U_{eq}
Pt	0.51284(3)	0.12172(1)	0.1502	31.6(1)
P(1)	0.4962(3)	0.1233(1)	0.3004(2)	32.5(9)
P(2)	0.5487(3)	0.1350(1)	0.0038(2)	35.6(9)
Cl	0.4901(5)	−0.0709(2)	0.1752(4)	95(2)
C(1)	0.635(1)	0.1791(4)	0.168(1)	53(5)
C(2)	0.402(1)	0.0677(4)	0.1302(7)	41(4)
C(3)	0.263(1)	0.0676(5)	0.114(1)	50(4)
O	0.4398(7)	0.0259(3)	0.1246(5)	42(3)
C(4)	0.570(1)	0.0140(4)	0.139(1)	51(6)
C(5)	0.583(1)	−0.0339(5)	0.113(1)	60(6)
C(6)	0.194(1)	0.1094(4)	0.144(1)	40(4)
C(7)	0.122(1)	0.1079(5)	0.218(1)	52(5)
C(8)	0.054(1)	0.1463(6)	0.242(1)	69(6)
C(9)	0.062(1)	0.1850(5)	0.194(1)	65(5)
C(10)	0.133(2)	0.1866(6)	0.122(1)	62(6)
C(11)	0.197(1)	0.1497(5)	0.095(1)	55(5)
C(12)	0.526(1)	0.1943(5)	−0.0265(9)	44(4)
C(13)	0.436(1)	0.2198(5)	0.016(1)	59(5)
C(14)	0.411(2)	0.2634(5)	−0.010(1)	69(6)
C(15)	0.469(2)	0.2827(7)	−0.075(1)	95(9)
C(16)	0.568(3)	0.2590(7)	−0.119(2)	97(9)
C(17)	0.592(2)	0.2137(6)	−0.093(1)	66(7)
C(18)	0.701(1)	0.1163(4)	−0.0331(9)	36(4)
C(19)	0.726(1)	0.1112(4)	−0.121(1)	50(5)
C(20)	0.842(2)	0.0965(5)	−0.146(1)	70(6)
C(21)	0.930(1)	0.0855(6)	−0.089(1)	68(7)
C(22)	0.905(1)	0.0899(6)	−0.004(2)	79(7)
C(23)	0.791(1)	0.1063(5)	0.028(1)	48(5)
C(24)	0.444(1)	0.1045(4)	−0.0705(8)	35(3)
C(25)	0.348(1)	0.1258(5)	−0.115(1)	51(5)
C(26)	0.262(1)	0.1011(6)	−0.160(1)	67(7)
C(27)	0.273(2)	0.0536(7)	−0.161(1)	76(7)
C(28)	0.366(1)	0.0322(5)	−0.1197(9)	52(5)
C(29)	0.452(1)	0.0576(5)	−0.0766(9)	50(4)
C(30)	0.633(1)	0.1025(4)	0.3580(8)	39(4)
C(31)	0.735(1)	0.0878(4)	0.3102(9)	40(4)
C(33)	0.839(1)	0.0654(7)	0.443(1)	66(6)
C(32)	0.838(1)	0.0687(5)	0.354(1)	58(5)
C(34)	0.734(2)	0.0799(7)	0.489(1)	75(6)
C(35)	0.633(1)	0.0975(5)	0.4486(9)	49(5)
C(36)	0.465(1)	0.1807(4)	0.338(1)	45(5)
C(37)	0.536(2)	0.2020(6)	0.401(1)	66(6)
C(38)	0.499(2)	0.2470(7)	0.428(2)	88(9)
C(39)	0.393(3)	0.2663(8)	0.388(2)	98(9)
C(40)	0.325(2)	0.2450(6)	0.326(1)	75(7)
C(41)	0.362(1)	0.2027(5)	0.302(1)	54(5)
C(42)	0.372(1)	0.0910(4)	0.3525(7)	37(3)
C(43)	0.366(1)	0.0434(5)	0.336(1)	52(5)
C(44)	0.272(2)	0.0189(5)	0.376(1)	67(6)
C(45)	0.189(1)	0.0364(6)	0.430(1)	74(7)
C(46)	0.200(1)	0.0832(6)	0.453(1)	62(5)
C(47)	0.292(1)	0.1093(5)	0.412(1)	55(6)
B	1.036(2)	0.0179(7)	0.656(2)	78(7)
F(1)	0.967(2)	0.0053(7)	0.595(1)	114(7)
F(2)	0.982(1)	0.0096(7)	0.739(1)	121(7)
F(3)	1.1426(9)	−0.0094(5)	0.661(1)	125(5)
F(4)	1.075(1)	0.0604(4)	0.655(2)	163(7)

3. Results and discussion

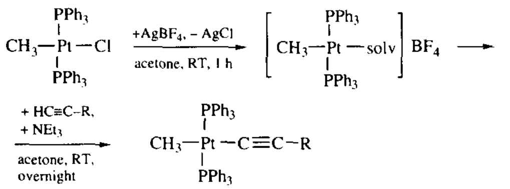
3.1. Synthesis of the complexes

The synthesis of the acetylide complexes **1–3** has been achieved in a similar way previously reported for some Pt(II) and Ni(II) derivatives [15], which consists in treating the chloro complexes *trans*-[Pt(Me)Cl($(PPh_3)_2$] with 1 equiv. of $AgBF_4$ in acetone at r.t., followed, after filtration of AgCl,

Table 2
Selected bond distances (Å) and angles (°) for *trans*-[Pt(Me){C(OCH$_2$CH$_2$Cl)(CH$_2$Ph)}(PPh$_3$)$_2$][BF$_4$] (**8**)

Pt–P(1)	2.322(4)	Pt–P(2)	2.322(4)
Pt–C(1)	2.16(1)	Pt–C(2)	2.01(1)
P(1)–C(30)	1.83(1)	P(1)–C(36)	1.82(1)
P(1)–C(42)	1.82(1)	P(2)–C(12)	1.82(1)
P(2)–C(18)	1.82(1)	P(2)–C(24)	1.84(1)
Cl–C(5)	1.77(2)	C(2)–C(3)	1.52(2)
C(2)–O	1.30(1)	C(3)–C(6)	1.51(2)
O–C(4)	1.46(1)	C(4)–C(5)	1.47(2)
C(6)–C(7)	1.38(2)	C(6)–C(11)	1.41(2)
C(7)–C(8)	1.40(2)	C(8)–C(9)	1.36(2)
C(9)–C(10)	1.34(2)	C(10)–C(11)	1.35(2)
B–F(1)	1.25(3)	B–F(2)	1.43(4)
B–F(3)	1.40(2)	B–F(4)	1.32(2)
C(1)–Pt–C(2)	178.3(5)	P(2)–Pt–C(2)	94.7(3)
P(2)–Pt–C(1)	83.8(4)	P(1)–Pt–C(2)	97.1(3)
P(1)–Pt–C(1)	84.4(5)	P(1)–Pt–P(2)	167.9(1)
Pt–P(1)–C(42)	119.0(4)	Pt–P(1)–C(36)	110.5(5)
Pt–P(1)–C(30)	114.5(4)	C(36)–P(1)–C(42)	101.9(6)
C(30)–P(1)–C(42)	101.7(5)	C(30)–P(1)–C(36)	107.9(6)
Pt–P(2)–C(24)	114.8(4)	Pt–P(2)–C(18)	113.7(4)
Pt–P(2)–C(12)	112.9(4)	C(18)–P(2)–C(24)	102.2(6)
C(12)–P(2)–C(24)	103.1(6)	C(12)–P(2)–C(18)	109.1(6)
Pt–C(2)–O	125.1(9)	Pt–C(2)–C(3)	127.8(8)
C(3)–C(2)–O	107(1)	C(2)–C(3)–C(6)	116(1)
C(2)–O–C(4)	121(1)	O–C(4)–C(5)	107(1)
Cl–C(5)–C(4)	113(1)	F(3)–B–F(4)	106(2)
F(2)–B–F(4)	107(2)	F(2)–B–F(3)	101(2)
F(1)–B–F(4)	118(2)	F(1)–B–F(3)	111(2)
F(1)–B–F(2)	112(3)		

by the addition of 3 equiv. of the corresponding 1-alkyne in the presence of a slight excess of NEt$_3$ (Eq. (1)):

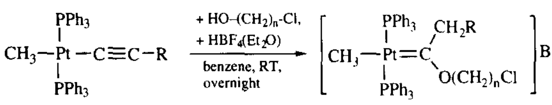


R = p-tolyl (**1**), Ph (**2**), C(CH$_3$)$_3$ (**3**)

(1)

The yields of the acetylide derivatives ranged between 64–92%. The complexes **1–3** are white, air stable, crystalline solids. Their IR spectra show ν(C≡C) around 2100 cm^{-1} as a strong absorption, while the ^{31}P{^{1}H} NMR spectra confirm their *trans* geometry (a singlet with ^{195}Pt satellites for the phosphines). This geometry is also supported by ^{1}H NMR spectra which also show the CH$_3$ ligand as a triplet resonance, flanked by ^{195}Pt satellites, due to coupling to two magnetically equivalent PPh$_3$ ligands (see Section 2).

Complexes **1** and **2** were treated with 1.1 equiv. of an ethereal solution of HBF$_4$ at 0 °C in C$_6$H$_6$ and to the reaction mixture was then added an excess of the haloalcohol HO–(CH$_2$)$_n$–Cl ($n = 2, 3$) to afford the corresponding haloalkoxy carbene complexes **4–6** as summarized in Eq. (2):



(2)

R = p-tolyl, n = 2, (**4**)
R = p-tolyl, n = 3, (**5**)
R = Ph, n = 3, (**6**)

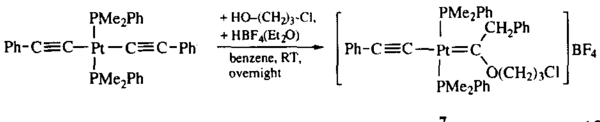
Complex **3**, under experimental conditions and reaction times similar to those reported in Eq. (2), gave a poorly soluble material which, on the basis of spectroscopic data, did not give evidence of the carbene ligand.

Complexes **4–6** show in their ^{1}H NMR spectra the CH$_2$R protons in the range 3.35–3.45 ppm as singlets. The –OCH$_2$– protons appear as triplets in the range 4.69–4.88 ppm due to coupling with the adjacent methylene protons, flanked by ^{195}Pt satellites (^4J(HPt) ~19 Hz). The –CH$_2$Cl protons appear also as triplets in the range 3.26–3.41 ppm, due to coupling with the OCH$_2$ protons. All the above signals have been assigned on the basis of homonuclear decoupling experiments. The triplet resonance of the 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 **4–6** (as well as the other carbene complexes **7–9**) a strong absorption at ~1280 cm^{-1} is assigned to ν_{str}(C–O) of the carbene ligand, also in analogy with this type of assignment for other alkoxy(alkyl)carbene complexes of Pt(II) [5a,16].

The ^{13}C{^{1}H} NMR spectra of **4–6** show the carbene carbon at ~320 ppm as a triplet due to coupling with the two PPh$_3$ ligands, flanked by ^{195}Pt satellites (^1J(PtC) 790–810 Hz). The –CH$_2$R and –OCH$_2$– carbons appear as singlets at ~60 and 80 ppm, respectively, flanked by ^{195}Pt satellites.

Similarly, the reaction of the bis(acetylide) complex *trans*-[Pt(C≡CPh)$_2$(PMe$_2$Ph)$_2$] with 2.2 equiv. of a 54% ethereal solution of HBF$_4$ at r.t. in C$_6$H$_6$ in the presence of an excess of HO–(CH$_2$)$_3$–Cl afforded in 63% yield the cationic complex **7**, in which only one acetylide ligand has been converted to the corresponding alkyl(alkoxy)carbene (Eq. (3)) as was also found for the similar reaction of *trans*-[Pt(C≡CCF$_3$)$_2$(PMe$_2$Ph)$_2$] with MeOH, in which, however, only 1 equiv. of HPF$_6$ was used [17]:



7

(3)

The *trans* geometry of **7** is confirmed by the singlet resonance of the PMe$_2$Ph ligands in the ^{31}P NMR spectrum. The ^{1}H NMR data of the carbene ligand are similar to those described above for **4–6**.

The reactions of Pt(II) complexes with 1-alkynes and haloalcohols were also investigated. Thus, the (alkyl)-alkoxycarbene complex **8** was obtained in 53% yield by reaction of *trans*-[Pt(Me)Cl(PPh$_3$)$_2$] with AgBF$_4$ in the pres-

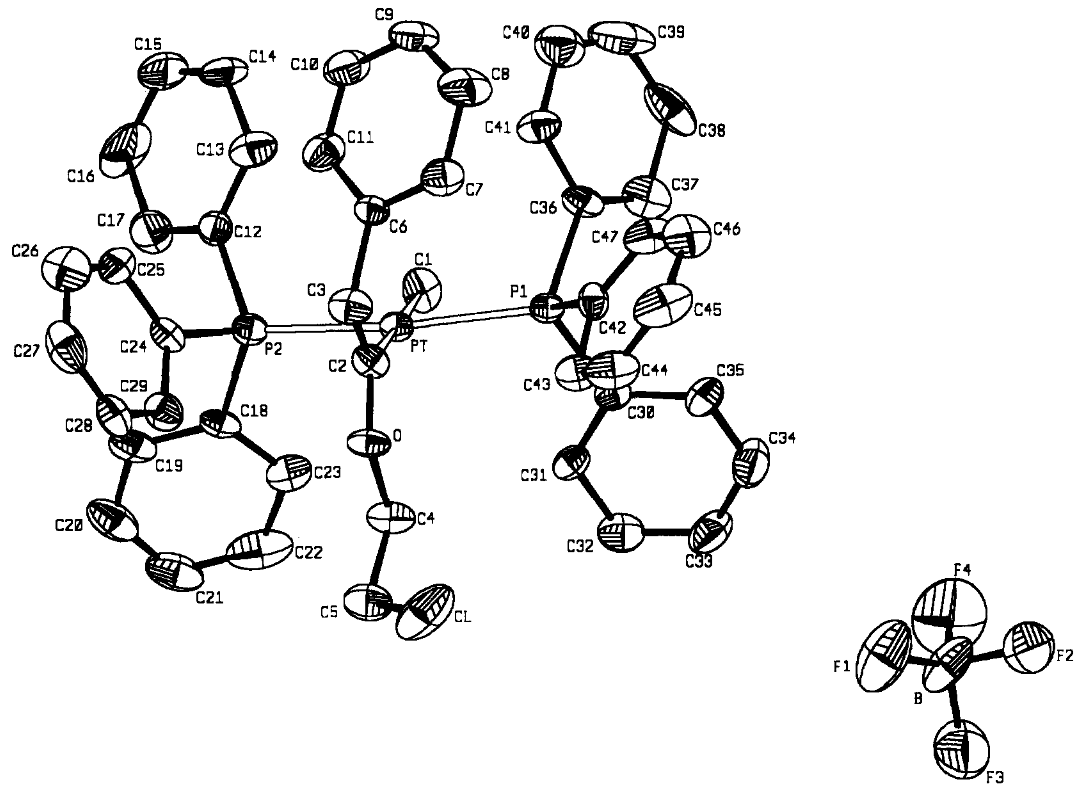
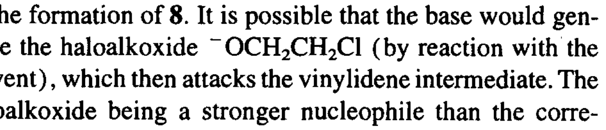


Fig. 1. Perspective view for *trans*-[Pt(Me){C(OCH$_2$CH$_2$Cl)(CH$_2$Ph)}(PPh$_3$)$_2$][BF$_4$] (**8**) with the atomic numbering scheme.

ence of 1.5 equiv. of phenylacetylene and 1.1 equiv. of n-BuLi in 2-chloroethanol as solvent according to Eq. (4):

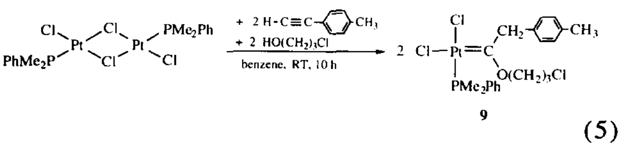


$$\mathrm{CH_3{-}Pt(PPh_3)_2{-}Cl} \xrightarrow[\text{2-chloroethanol, RT, 15 min}]{+\mathrm{AgBF_4}, -\mathrm{AgCl};\ +\mathrm{PhC{\equiv}CH}, +\text{n-BuLi}} \left[\mathrm{CH_3{-}Pt(PPh_3)_2{=}C(CH_2Ph)(O(CH_2)_2Cl)}\right]\mathrm{BF_4} \quad (4)$$

8

Spectroscopic data of **8** are in agreement with those found for **4–6** (see Section 2). It is observed that reaction (4) carried out under the same experimental conditions and reaction times, but in the absence of n-BuLi, did not give evidence of the formation of **8**. It is possible that the base would generate the haloalkoxide $^-$OCH$_2$CH$_2$Cl (by reaction with the solvent), which then attacks the vinylidene intermediate. The haloalkoxide being a stronger nucleophile than the corresponding alcohol, the formation of **8** occurs in much shorter reaction times compared with the other reactions (2), (3) and (5), which were carried out without a base.

The reaction of the dimer [Pt(Cl)(μ-Cl)(PMe$_2$Ph)]$_2$ in C$_6$H$_6$ at r.t. with a 3-fold excess of *p*-tolylacetylene in the presence of an excess of 3-chloro-1-propanol gave in 60% yield the neutral (alkyl)alkoxycarbene derivative **9** (Eq. (5)):



9

(5)

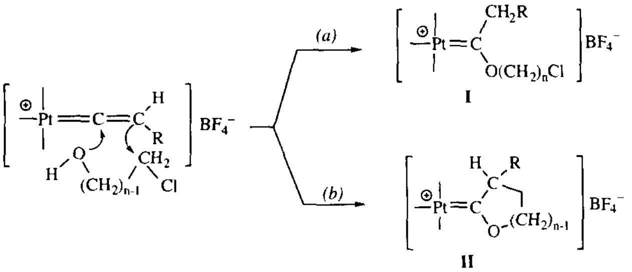
The ^{1}H NMR spectrum of **9** shows some differences from those found for **4–7**. The CH$_2$-*p*-tolyl protons give rise to an AB pattern at 3.88 and 3.53 ppm, as previously observed for the similar carbene complexes *cis*-[PtCl$_2${C(OR′)-(CH$_2$R)}(PMe$_2$Ph)] (R′ = Me, Et, n-Pr; R = Ph, Me, Et) [18]. The –OCH$_2$– protons appear as two distinct multiplets at 5.04 and 5.60 ppm, while the –CH$_2$Cl protons appear as a complex multiplet at 3.40 ppm. The P–Me protons are non equivalent, each Me group giving rise to a doublet flanked by ^{195}Pt satellites. The ^{13}C{^{1}H} NMR spectrum shows the carbene carbon at 275 ppm (^1J(CPt) 1202 Hz), at higher field compared to those for **4–6** and **8**, which have a methyl group *trans* to the carbene ligand.

3.2. X-ray structure of 8

The crystal structure is composed of *trans*-[Pt(Me)-{C(OCH$_2$CH$_2$Cl)(CH$_2$Ph)}(PPh$_3$)$_2$]$^+$ cations and [BF$_4$]$^-$ anions as shown in the ORTEP view in Fig. 1, which also shows the atom numbering scheme. The coordination geometry around Pt(II) is *trans* square planar; individual deviations of the Pt, C(1), C(2) and P(2) atoms from their least-squares plane do not exceed ±0.03 Å. The orientation of the carbene ligand around the Pt–C(2) bond is such as to make the plane through the C(3), C(2), O and Pt atoms perpendicular to the Pt coordination sphere, the dihedral angle being 90.3(4)°; the carbene plane is skewed with respect to the phenyl bonded to the C(3) carbon atom (dihedral angle 66.9(4)°). The latter phenyl group is sandwiched between two phenyls of the *trans* oriented PPh_3 ligands and is rather parallel to the $C(12) \rightarrow C(17)$ phenyl group (dihedral angle 8.4(4)°), while it is perpendicular to the other phenyl group $C(36) \rightarrow C(41)$ (dihedral angle 100.9(4)°). The coordination geometry around the carbene carbon C(2) is characterized by a rather planar arrangement of the bonded atoms (deviations from the least-squares plane range from −0.018 to 0.007(8) Å). The bond angles at the C(2) deviate significantly from 120°, the C(3)–C(2)–O angle being 107(1)°, which is comparable with the C–C–O angle of 111.6(8)° in *cis*-$[PtCl_2\{C(OEt)(CH_2Ph)\}(PMe_2Ph)]$ [18], while the Pt–C(2)–C(3) and Pt–C(2)–O bond angles are 127.8(8) and 125.1(9)°, respectively. The C(2)–C(3), C(3)–C(6), O–C(4), C(4)–C(5) and C(5)–Cl bond distances have values characteristic of single bonds. The C(2)–O bond distance of 1.30(1) Å is comparable to the corresponding bond distance of 1.283(11) Å found in *cis*-$[PtCl_2\{C(OEt)(CH_2Ph)\}(PMe_2Ph)]$ [18], which has been considered as having a partial double bond character responsible for the stabilization of the carbene ligand. With the exception of the terminal phenyl group and the chlorine atom, the ligand conformation is *trans* planar as shown by the values of the torsion angles C(3)–C(2)–O–C(4) (−179(1)°) and C(2)–O–C(4)–C(5) (−170(1)°), while O–C(4)–C(5)–Cl is −61(1)°, the terminal chlorine being *gauche* with respect to the oxygen atom of the ligand. The Pt–C(2) bond length of 2.01(1) Å may be compared with those found for cationic alkyl(alkoxy)carbenes such as *trans*-$[Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2][PF_6]$ ($Pt–C_{(carbene)}$ 2.13(1) Å) [19a] and *trans*-$[Pt(Me)\{\overline{COCH_2CH_2CH_2}\}(PMe_2Ph)_2][PF_6]$ ($Pt–C_{(carbene)}$ 2.00(2) Å) [19b]. It is however longer than that reported for the neutral carbene complex *cis*-$[PtCl_2\{C(OEt)(CH_2Ph)\}(PMe_2Ph)]$ ($Pt–C_{(carbene)}$ 1.920(9) Å) [18], where the carbene ligand is *trans* to chloride. The Pt–P bond distances of 2.322(4) and 2.321(4) Å are similar to those found in *trans*-$[PtBr\{\overline{CN(C_6H_4\text{-}p\text{-}Me)CH_2CH_2O}\}(PPh_3)_2][BF_4]$ (Pt–P 2.322(2) and 2.332(2) Å) [2a]. The P(1)–Pt–P(2) angle is distorted from linearity (167.9(2)°), being bent in the direction of the methyl group in order to avoid the steric bulk of the carbene ligand. In the parent compound *trans*-$[Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2][PF_6]$ [19a], where the {C(OMe)Me} ligand has a smaller steric bulk, the corresponding P(1)–Pt–P(2) angle is 173.1(4)°. The C(2)–Pt–C(1) bond angle is rather linear (178.1(5)), while in *trans*-$[Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2][PF_6]$ the {C(OMe)MePt} unit exhibits two angles (173.2(5) and 165.3(5)°) for the two alternative positions of the carbene ligand. The $Pt–C_{(methyl)}$ bond distance of 2.156(11) Å is in agreement with that found in *trans*-$[Pt(Me)\{C(OMe)Me\}(PMe_2Ph)_2][PF_6]$ ($Pt–C_{(methyl)}$ 2.13(1) Å) [19a].

4. Conclusions

The results reported above indicate that the reactions of the chloroalcohols $HO–(CH_2)_n–Cl$ ($n = 2, 3$) with Pt(II)-acetylides or Pt(II) complexes with 1-alkynes proceed analogously to those previously reported for normal alcohols ROH, yielding chloroalkoxy(alkyl)carbene complexes of type **I**, likely via vinylidene intermediates (Scheme 3, route (*a*)).



Scheme 3.

No experimental or spectroscopic evidence has been found for the formation of the cyclic carbene products **II** (route (*b*)), even when the reactions were carried out in the presence of a base, thus indicating that the reactions of alkynes proceed differently from those with carbonyl, isocyanide and nitrile ligands, where cyclic products were observed and suggesting that protonation of the β-vinylidene atom carbon is favoured over ring closure at the $-CH_2Cl$ moiety.

Alternative synthetic strategies to cyclic carbenes of type **II** from acetylenes promoted by transition metal centers are in progress.

5. Supplementary material

Observed and calculated structure factors for **8**, atomic coordinates of H atoms and anisotropic thermal parameters are available from F.B. on request.

Acknowledgements

R.A.M. thanks MURST and CNR for support of this work. R.A.M. and R.J.A. appreciate partial support of this project by a NATO Collaborative Research Grant (CRG 931224). We thank also Miss Barbara Violetto for her contribution to the experimental work.

References

[1] (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.

[2] (a) R.A. Michelin, L. Zanotto, D. Braga, P. Sabatino and R.J. Angelici, *Inorg. Chem., 27* (1988) 85; (b) *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.

[3] (a) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetollo and R.J. Angelici, *Organometallics, 10* (1991) 1751; (b) *J. Chem. Soc., Dalton. Trans.*, (1993) 959; (c) R.A. Michelin, U. Belluco, M.

Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, *Inorg. Chim. Acta, 220* (1994) 21; (d) R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetollo, G. Bombieri and R.J. Angelici, *Organometallics, 13* (1994) 1341.

[4] M.I. Bruce and A.G. Swincer, *Adv. Organomet. Chem., 22* (1983) 59, and Refs. therein.

[5] (a) M.H. Chisholm and H.C. Clark, *Inorg. Chem., 10* (1971) 1711; (b) K.H. Dötz, W. Sturm and H.G. Alt, *Organometallics, 6* (1987) 1424, and Refs. therein; (c) N. Ruiz, D. Péron and P.H. Dixneuf, *Organometallics, 14* (1995) 1095, and Refs. therein.

[6] H. Werner, *Angew. Chem., Int. Ed. Engl., 29* (1990) 1077.

[7] H.C. Clark and L.E. Manzer, *J. Organomet. Chem., 59* (1973) 411.

[8] H.D. Empsall, B.L. Shaw and A.J. Stringer, *J. Organomet. Chem., 94* (1975) 131.

[9] A.C. Smithies, P. Schimdt and M. Orchin, *Inorg. Synth., 12* (1970) 240.

[10] A.C.T. North, D.C. Philips and F.S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.

[11] G.M. Sheldrick, SHELX-86, in G.M. Sheldrick, C. Kruger and R. Goddard (eds.), *Crystallographic Computing 3,* Oxford University Press, London, 1985.

[12] H.D. Flack, *Acta Crystallogr., Sect. A, 39* (1983) 876.

[13] (a) G.M. Sheldrick, *Acta Crystallogr., Sect. A, 46* (1990) 467; (b) G.M. Sheldrick, Z. Dauter, K.S. Wilson, H. Hope and L.C. Sieker, *Acta Crystallogr., Sect. D, 49* (1993) 18.

[14] C.K. Johnson, ORTEP II, *Rep. ORNL-5138,* Oak Ridge National Laboratory, TN, USA, 1976.

[15] (a) F.R. Hartley, in J. Wilkinson and F.G.A. Stone (eds.), *Comprehensive Organometallic Chemistry,* Vol VI, Pergamon, Oxford, 1982, Ch. 39, p. 704, and Refs. therein; (b) M.H. Chisholm and H.C. Clark, *Inorg. Chem., 10* (1971) 2557; (c) K. Oguro, M. Wada and R. Okawara, *J. Organomet. Chem., 159* (1978) 417.

[16] M.H. Chisholm, H.C. Clark, W.S. Johns, J.E.H. Ward and K. Yasufuku, *Inorg. Chem., 14* (1975) 900.

[17] R.A. Bell, M.H. Chisholm, D.A. Couch and L.A. Rankel, *Inorg. Chem., 16* (1977) 677.

[18] G.K. Anderson, R.J. Cross, L. Manojlovic-Muir, K.W. Muir and R.A. Wales, *J. Chem. Soc., Dalton Trans.,* (1979) 684.

[19] (a) R.F. Stepaniak and N.C. Payne, *J. Organomet. Chem., 7* (1973) 213; (b) *72* (1974) 453.